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{[2-(Dimethylamino)ethyl]cyclopentadienyl}trichlorotitanium: A New type of Olefin Polymerization Catalyst

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Summary: ($C_5H_4CH_2CH_2NMe_2$)$TiCl_3$ (1) has been prepared in 96% yield as a highly moisture-sensitive solid which is readily hydrolyzed to a μ-oxo derivative (4). The ^1H NMR spectrum of ***1*** *is consistent with intramolecular coordination of the dimethylamino group to titanium. Compound* ***1*** *exhibits relatively low activity as a styrene polymerization catalyst but is remarkably active for both ethylene and propylene polymerizations.*

Group 4 metallocenes have dominated the homogeneous Ziegler−Natta polymerizations of ethylene and propylene.[1−6] Half-sandwich complexes are better known as precursors for styrene polymerization catalysts,[7] although they are also useful for other olefins.[8] There is a growing interest in the study of substituted-cyclopentadienyl−metal compounds that possess a terminal donor group in the side chain.[9] Intramolecular coordination has been established for complexes of this kind.[10−13] Coordination of this type could also be expected to affect both catalytic activity and selectivity.

We report here the synthesis[14] of {[2-(dimethylamino)ethyl]cyclopentadienyl}trichlorotitanium (**1**) and its application as a precursor in the catalytic polymerization of styrene, ethylene, and propylene.

The synthetic method for (C_5Me_5)$TiCl_3$[15] was adapted to synthesize ($C_5H_4CH_2CH_2NMe_2$)$TiCl_3$ (**1**; hereafter $Cp^N = C_5H_4CH_2CH_2NMe_2$). Treatment of the ligand (Cp^NH)[16] (32.24 g, 236 mmol) with *n*-BuLi (148.0 mL, 1.6 M in hexane) in THF (150 mL) at 0 °C and subsequent reaction with chlorotrimethylsilane (30.0 mL, 236 mmol) at 0 °C for 4 h followed by filtration of the precipitate, removal of the volatiles, and distillation at reduced pressure (51−52 °C, 5 × 10^{-3} mm Hg) afforded (Me_3Si)Cp^N (**3**) as a pale yellow liquid (44.12 g, 89%). The ^1H NMR spectrum of **3** showed three singlets in the ratio 1:1:18 corresponding to the trimethylsilyl group, together with different signals due to the dimethylamino group and ring protons on sp^3 and sp^2 carbons[18] in a mixture of at least three isomers.[19]

Reaction of **3** (8.90 g, 42.5 mmol) with $TiCl_4$ (8.06 g, 42.5 mmol) in either thoroughly dried toluene or CH_2Cl_2 (60 mL) at −78 °C, followed by removal of the

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[14] All reactions were carried out under an argon atmosphere using standard Schlenk techniques. All chemicals were purchased from Aldrich unless otherwise stated. Solvents were distilled over Na/K alloy or CaH_2 prior to use. ^1H NMR spectra were recorded on a Varian XL 200-MHz FT spectrometer. Chemical shifts are reported in δ units referenced to TMS. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

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[16] [2-(Dimethylamino)ethyl]cyclopentadiene (**2**) was synthesized by a modification of a literature procedure:[12a] 2-Chloro-1-(dimethylamino)ethane (43.04 g, 400 mmol) free of HCl[17] was added slowly to a stirred suspension of cyclopentadienyllithium in THF/hexane (1:1) (obtained from the reaction of *n*-BuLi (250 mL, 1.6 M in hexane) with freshly distilled cyclopentadiene (33.0 mL, 400 mmol) in THF (250 mL)) at 0 °C and the reaction mixture refluxed overnight. Filtration of the LiCl, removal of the solvents, and trap-to-trap distillation at reduced pressure afforded **2** as a colorless liquid (53.58 g, 98%). The physical and spectral data were identical with values given in the literature.[12a]

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[18] ^1H NMR of [(Me_3Si)($C_5H_4CH_2CH_2NMe_2$)] in $CDCl_3$ (δ): 6.70−6.05 (m, ring H on C_{sp^2}), 3.28 (br s, ring H on C_{sp^3}), 3.07−2.85 (m, ring H on C_{sp^3}) [4 H, C_5H_4]; 2.65−2.37 [m, 4 H, CH_2CH_2N]; 2.28 (s, major), 2.27 (s) [6 H, $N(CH_3)_2$]; 0.14 (s), 0.13 (s), −0.04 (s, major) [9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{12}H_{23}NSi$: C, 68.83; H, 11.07; N, 6.69. Found: C, 69.24; H, 11.54; N, 6.58.

[19] Abel, E. W.; Duster, M. D. *J. Organomet. Chem.* **1971**, *33*, 161.

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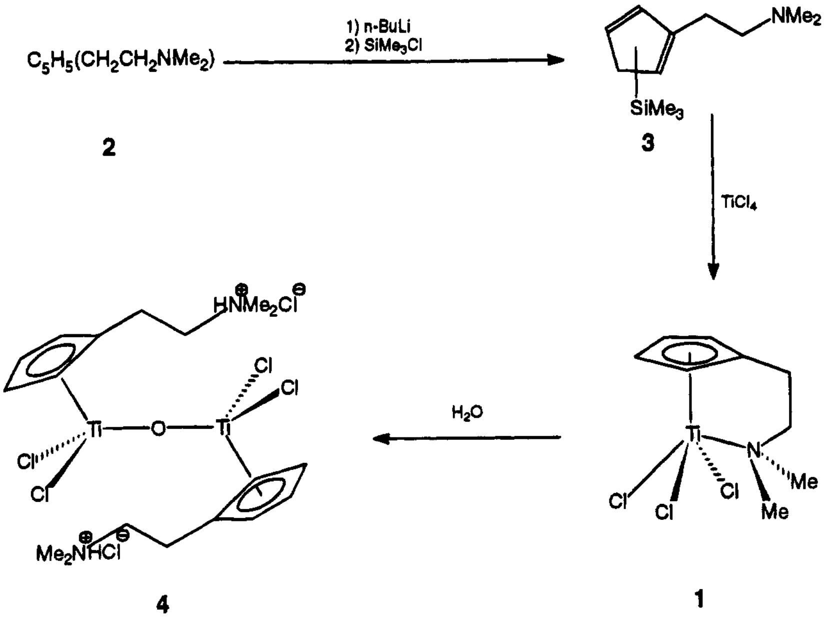
Scheme 1



solvent and washing with pentane (2 × 100 mL), led to the formation of Cp^NTiCl_3 (**1**; 11.84 g, 96%) as a yellow powder pure enough for synthetic purposes. An analytically pure sample was obtained by recrystallization from CH_2Cl_2 as a yellow-orange microcrystalline solid.[20] The ^1H NMR specturm of **1** showed a typical AA'BB' splitting pattern for the protons of the cyclopentadienyl ring, two triplets for the protons on the ethylenic side chain, and a singlet for the dimethylamino protons. An interesting feature in the spectrum of **1** in $CDCl_3$ is the downfield shift (*ca.* 0.4 ppm) observed for the signal of the methyl groups attached to nitrogen (δ 2.69) compared to analogous resonances for **2** (δ 2.27) or for **3** (δ 2.28) in the same deuterated solvent. Even more significant is the shift to lower field (*ca.* 0.7 ppm) of the signal for the methylene group linked to nitrogen in **1** (δ 3.26) relative to the comparable values in **2** (δ 2.53) and **3** (δ 2.51), together with a different splitting pattern for the ethylene group (two distinct triplets instead of a multiplet). These differences indicate an important change in the environment of the nitrogen atom in **1**. Similar observations have been made in cobalt[13c] and molybdenum[12a] compounds by comparing complexes with noncoordinated and intramolecularly coordinated dimethylamino groups to the metal center.[21] Therefore, we propose the same intramolecular coordination of the dimethylamino group in compound **1**.

Compound **1** is exceedingly sensitive to moisture. Exposure to air or reaction with 1/2 equiv of water leads to the hydrolysis product $[Cp^NTiCl_2(HCl)]_2(\mu\text{-}O)$ (**4**). For example, the reaction of **1** (1.00 g. 3.44 mmol) in CH_2Cl_2 (30 mL) with H_2O (31 μL, 1.72 mmol), first at −78 °C followed by slow warming to room temperature, results in the formatiom of the hydrochloride μ-oxo compound **4** in quantitative yield as a yellow powder. In its ^1H NMR spectrum,[24] the protons of the ammonium groups can be observed at low field as a broad signal (δ 12.35, ~45 Hz) due to the electric quadrupole moment of nitrogen.[25] In addition, the dimethylamino group signal is a doublet with J_{HN-CH} = 4 Hz, which is in the range expected for this coupling. It is also noteworthy that the protons representing the ethylene side chain in **4** occur as a broad singlet (~15 Hz) compared to the two triplets observed for **1**. This change is consistent with disruption of the intramolecular coordination of the dimethylamino group. When compound **1** was hydrolyzed with D_2O, the low-field broad singlet was not observed, and the signal due to the dimethylamino protons occurred as a singlet instead of a doublet.

Complexes containing half−sandwich dichlorotitanium fragments connected to each other via oxo bridges have been described elsewhere.[26] Most of them have been obtained by controlled hydrolysis of the corresponding trichloro compound, and in some cases an auxiliary amine has been used to remove the HCl byproduct.[27] In our case, the presence of the amino

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(20) ^1H NMR of $[(C_5H_4CH_2CH_2NMe_2)TiCl_3]$ (δ): in $CDCl_3$ 6.97 (t. 2 H, C_5H_4), 6.88 (t, 2 H, C_5H_4), 3.26 (t, 2 H, J = 6.5 Hz, CH_2N), 3.06 (t, 2 H, J = 6.5 Hz, CH_2), 2.69 (s, 6 H, $N(CH_3)_2$); in C_6D_6 6.33 (t, 2 H, C_5H_4), 6.12 (t, 2 H, C_5H_4), 2.29 (t, 2 H, J = 6.5 Hz, CH_2N), 2.00 (s, 6 H, $N(CH_3)_2$), 1.97 (t, 2 H, J = 6.5 Hz, CH_2). Anal. Calcd for $C_9H_{14}Cl_3NTi$: C, 37.21; H, 4.86; N, 4.82. Found: C, 36.68; H, 4.76; H, 4.70.

(21) These results indicate intramolecular coordination of the dimethylamino group to titanium in **1**. This conclusion is consistent with the X-ray molecular structure of $[(C_5H_4CH_2CH_2OMe)TiCl_3]$.[22] In the latter molecule, the methoxy group of the cyclopentadienyl ligand is coordinated to the titanium atom with a Ti−O bond length of 2.214 Å, which is the shortest distance around titanium. Further, the oxygen atom is located almost on the plane parallel to the cyclopentadienyl ring that contains the titanium atom (angle ring centroid−Ti−O = 99°). Considering the Fenske−Hall molecular orbital (FHMO) calculations performed on $CpTiCl_3$, it is clear that a Lewis acid−base interaction can be established between a lone pair of electrons on oxygen (or nitrogen in the case of **1**) and the e degenerate LUMO. These two vacant orbitals are comprised basically of metal d_{xy} and $d_{x^2-y^2}$ character, and they lie precisely parallel to the cyclopentadienyl ring.

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(24) ^1H NMR of $[(C_5H_4CH_2CH_2NMe_2{\cdot}HCl)TiCl_2]_2(\mu\text{-}O)$ in $CDCl_3$ (δ): 12.37 (br s, ~45 Hz, 2 H, N−H); 6.95−6.75 (2 m, 8 H, C_5H_4); 3.48 (br s, 8 H, CH_2CH_2N); 2.92 (d, 12 H, J = 4.4 Hz, $N(CH_3)_2$. Anal. Calcd for $C_{18}H_{30}N_2Cl_2Ti_2O$: C, 36.10; H, 5.05; N, 4.68. Found: C, 36.06; H, 5.12; N, 4.41.

(25) Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopy*; Sanunders: Philadelphia, 1979; p 134.

(26) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic Press: New York, 1974; p 43.

Table 1. Olefin Polymerization by Cp^NTiCl_3 Percursor[a]

run no.	monomer[b]			[Ti] (μM)	cocatalyst[c]			t_p (min)	yield (g)	activity[d] × 10^{-6}	$\bar{M}_w \times 10^{-5}$
		pressure (psig)	concn (M)			$[Ph_3C^+]/[Ti]$	[Al]/[Ti]				
1	E	15	0.37	25	MAO		2000	10	0.15	1.98	3.0
2	E	15	0.37	50	MAO		2000	10	0.56	3.62	2.4
3	E	15	0.37	50	MAO		4000	10	0.77	4.96	2.1
4	P	20	0.78	25	MAO		2000	90	0.79	0.54	3.2
5	P	20	0.78	50	MAO		2000	90	3.4	1.16	2.9
6	P	20	0.78	50	MAO		4000	30	1.85	1.90	4.5
7	P	20	0.78	100	MAO		2000	30	2.66	1.37	3.5
8	P	20	0.78	100	MAO		4000	30	2.97	1.53	3.4
9	P	20	0.78	100	Ph_3C^+/TIBA	0	20	30	0	0	0
10	P	20	0.78	100	Ph_3C^+/TIBA	0.5	20	7	0.13	0.56	3.5
11	P	20	0.78	100	Ph_3C^+/TIBA	1	20	7	2.19	4.82	4.5

[a] Polymerization conditions: volume, 50 mL of toluene; T_p = 20 °C. [b] E = ethylene, P = propylene. [c] TIBA = triisobutylaluminum, Ph_3C^+ = $[Ph_3C]^+[B(C_6F_5)_4]^-$. [d] g of polymer/(mol of Ti·[monomer]·h).

group in **1** presumably acts as a driving force to facilitate its hydrolysis, explaining its high moisture sensitivity relative even to $CpTiCl_3$.

It is now generally accepted that the reaction of methylaluminoxane (MAO) with a group 4 metallocene dichloride produces a catalytically active metallocenium species. For a half–sandwich case such as $CpTiCl_3$, the cation is likely the 10-electron $CpTi^+Me_xCl_{2-x}$ intermediate[28] with a coordination number of 3. In the case of **1**, the dimethylamino group raises the electron count to 12 and the coordination number to 4. Such a change has a marked effect on styrene polymerization. Cp^NTiCl_3 (**1**) when activated with MAO has a relatively low catalytic activity of 2.7 × 10^5 g of PS/(mol of Ti·mol of S·h) (S = styrene, PS = polystyrene); 88% of the PS has the syndiotactic structure (s-PS, insoluble in refluxing 2-butanone).[29] In comparison, under the same conditions, $CpTiCl_3$/MAO and $IndTiCl_3$/MAO have activities of 1.4 × 10^7 and 3.7 × 10^7 g of PS/(mol of Ti·mol of S·h) with 67 and 98% yields of s-PS.[7c] Therefore, the marked lowering in the catalytic reactivity of **1** toward styrene is most likely due to the coordination of the dimethylamino group, which destabilizes the complexation of styrene to titanium[30] and affects the stereoselectivity as well.

$CpTiCl_3$/MAO is virtually inactive as a catalyst precursor for ethylene or propylene polymerization.[31] Remarkably, however, **1** exhibits substantial activities for these monomers (Table 1).[32] It has an ethylene polymerization activity of 5 × 10^6 g of PE/(mol of Ti·$[C_2H_4]$·h), giving polyethylene (PE) with M_w (2–3) × 10^5. Even more impressive is the propylene polymerization behavior. The best results were obtained by in situ alkylation of **1** with triisobutylaluminum and generation of the cation from it with $[Ph_3C]^+[B(C_6F_5)_4]^-$.[2c,34] Not only is the propylene polymerization as high as in the ethylene case, but the polypropylene molecular weight is higher than that of the polyethylene. However, the process is without stereoselectivity, as indicated by the lack of melting transition in the polypropylene produced. The effects of the dimethylamino group are therefore very significant in terms of the catalytic reactivity of **1** compared to that of $CpTiCl_3$.

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(28) A metal-activated carbocationic olefin intermediate has also recently been proposed: Quyoum, R.; Wang, Q.; Tudoret, M.-J.; Baird, M. C.; Gillis, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 6435.

(29) (a) The procedure used to polymerize styrene has been given in detail in ref 7c. (b) Best result conditions: [Ti] = 50 μM; Al/Ti = 4000; T_p = 50 °C; t_p = 3 h. The Yield of PS was 90 mg.

(30) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Grassi, A. *Makromol. Chem.* **1991**, *192*, 223.

(31) Comparative studies: $A(CpTiCl_3/\text{ethylene})$ = 6.2 × 10^4 g of polymer/(mol of Ti·$[C_2H_4]$·h) under the same reaction conditions as in run 3 in Table 1; $A(CpTiCl_3/\text{propylene})$ = 0 using MAO or $[Ph_3C]^+[B(C_6F_5)_4]^-$ as cocatalyst under any conditions given in Table 1; $A(Cp_2TiCl_2/\text{ethylene})$ = 1.74 × 10^7 g of polymer/(mol of Ti·$[C_2H_4]$·h) under the same conditions as in run 3 in Table 1; $A(Cp_2TiCl_2/\text{propylene})$ = 2.6 × 10^4 g of polymer/(mol of Ti·$[C_3H_6]$·h) (conditions as in run 6 Table 1) and 1.6 × 10^5 (conditions as in run 11, Table 1).

(32) (a) The procedure used to polymerize ethylene and propylene has been given in detail in the literature.[33] (b) For the polymerization of propylene with the catalytic system $Cp^NTiCl_3/TIBA/[Ph_3C]^+[B(C_6F_5)_4]^-$, the order of addition to the monomer-saturated toluene was TIBA, Cp^NTiCl_3, stirring for 5 min, and finally $[Ph_3C]^+[B(C_6F_5)_4]^-$.[34]

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