(N.N'-Dimethyl-p-toluamidinato)trichlorotitanium: Synthesis, Structure, and Polymerization Catalysis

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Received November 15, 1994[®]

Summary: A reaction between N-(trimethylsilyl)-N,N'dimethyl-p-toluamidine and TiCl₄ in CH₂Cl₂ produces (N,N'-dimethyl-p-toluamidinato)trichlorotitanium, which is formulated as a dimer with two chloro bridges. The new complex is moderately active in the polymerization of both styrene and ethylene when activated with methylaluminoxane.

Amidinato-transition methyl compounds have recently aroused much interest and expectation since the amidinate ligand has been considered as an alternative to the well-known cyclopentadienyl ligand.¹ In fact, an extensive variety of metal complexes of this type has been reported in the past few years,^{1,2} including group 4 mono(benzamidinate) { $[\eta$ -C₆H₅C(NSiMe₃)₂]MCl₃}₂ (M = Ti, $Zr)^3$ and bis(benzamidinate) $[\eta$ -C₆H₅C(NSiMe₃)₂]₂- MCl_2 (M = Ti, Zr)⁴ complexes. More recently, the mixed-ligand compounds { $(\eta^5 - C_5 R_5)[\eta - C_6 H_5 C(NSiMe_3)_2]$ - MX_2 } (R = H, Me; M = Ti, Zr, Hf; X = Cl, alkyl)⁵ have been found to be active for the polymerization of ethylene and propylene. We have recently demonmono-[N,N'-bis(trimethylsilyl)benzstrated that amidinato]titanium complexes polymerize styrene with methylaluminoxane (MAO) as cocatalyst in a highly syndiospecific process,⁶ although the reaction rates are lower than those achieved with CpTiCl₃ or IndTiCl₃.⁷

Here we report the preparation of N-trimethylsilyl-N,N'-dimethyl-p-toluamidine (1) and (N,N'-dimethyl-ptoluamidinato)trichlorotitanium (2), together with the application of the latter as a precursor in the catalytic polymerization of styrene and ethylene.

Following the procedure described by Boeré,⁸ {p- $MeC_6H_4C(NMe)N[Me(SiMe_3)]$ (1) was obtained in 52%

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yield from a reaction of p-tolunitrile and lithium dimethylamide and subsequent reaction with chlorotrimethylsilane (Scheme 1). The ¹H NMR spectrum of 1 showed the aromatic protons of the tolyl group as an apparent doublet of doublets (δ 7.08 ppm) due to an AA'BB' splitting pattern characteristic in para unsymmetrically disubstituted benzenes.⁹ The two methyl groups attached to the nitrogens were recorded as a broad singlet (~ 16 Hz) at 2.88 ppm. The equivalence of these methyl groups is the consequence of the fluxional behavior of the trimethylsilyl group along the NCN-amidine framework and is in complete agreement with earlier findings for PhC(NMe)N[Me(SiMe₃)] and PhC(NSiMe₃)N(SiMe₃)₂.^{8b} Both the trimethylsilyl group and the methyl group of the *p*-tolyl fragment appeared as singlets at -0.22 and 2.36 ppm, respectively. Compared to analogous resonances for p-MeC₆H₄C(NSiMe₃)N- $(SiMe_3)_2$ (δ 0.09 and 2.37 ppm)^{8a} in the same deuterated solvent, almost the same chemical shift is observed for the methyl protons in the para position, but the SiMe₃ signal in 1 is shifted ca. 0.3 ppm to higher field. This shift is understandable considering that, in 1, two of the SiMe₃ groups linked to the nitrogens are replaced by stronger electron-donating groups.

A reaction between 1 and TiCl₄ in CH₂Cl₂ solution at room temperature produced $\{[p-MeC_6H_4C(NMe)_2]TiCl_2\}_2$ (2) in 69% yield (Scheme 1). The ¹H NMR spectrum of 2 showed the AA'BB' splitting pattern for the protons on the aromatic ring and a singlet for the methyl protons on the tolyl group. Interesting, in either chloroform d_1 , benzene- d_6 , or toluene- d_8 , the two methyls attached to the nitrogens were magnetically nonequivalent. This result was unexpected considering that, in $\{[\eta-PhC (NSiMe_3)_2]TiCl_3\}_2$, the protons of the SiMe₃ groups were found to be equivalent by ¹H NMR.³ An example of nonequivalent SiMe₃ groups in the same benzimidinate ligand has been reported for $[\eta$ -PhC(NSiMe₃)₂]₃UMe.^{2c} In this case, X-ray crystal structure and variabletemperature ¹H NMR (VT ¹H NMR) studies indicated that the geometry of this uranium molecule is responsible for such a behavior.

The compound $\{[\eta - PhC(NSiMe_3)_2]TiCl_3\}_2$ is known to exist as a dimer with two chloro bridges that complete a distorted octahedral environment around the titanium atoms.³ At each metal center, one nitrogen atom of the amidinato group is located in a cis position to the chloro bridges and the other trans to one chloro bridge, with two different titanium-nitrogen bond lengths (2.07 Å, cis; 1.99 Å, trans) in the solid state. By analogy with this structure, we propose 2 to be a dimeric molecule with the same cis and trans disposition of the nitrogens

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⁽⁹⁾ Günther, H. NMR Spectroscopy; John Wiley and Sons: New York, 1987.

Scheme 1



 $L = THF (3), PMe_3(4); Tol = p-MeC_6H_4$

Table 1. VT ¹H NMR Spectral Data for 2 in Toluene-d₈

	<i>T</i> (K)									
	263	298	313	333	363	373				
δ (<i>N</i> -Me) (trans)	2.72	2.76	2.79	2.82	2.87	2.89				
$\delta(N-Me)$ (cis)	1.91	1.98	2.03	2.09	2.17	2.20				
gap (ppm)	0.81	0.78	0.76	0.73	0.70	0.69				

of the *p*-toluamidinate ligand.¹⁰ In **2**, a stronger interaction of the nitrogens with titanium could be expected because of the more efficient electron-donating nature of the methyl substituents. Furthermore, these methyl groups are linked directly to nitrogen, whereas in $\{[\eta, \cdot]\}$ PhC(NSiMe₃)₂]TiCl₃₂ there is an additional bond through the silicon atom. Considering these arguments, the dimeric structure of 2 has to be rigid enough in solution to make the amidinato methyls nonequivalent in the ¹H NMR spectrum, differentiating the cis and trans positions relative to the chloro bridges.

In order to test the strength of such a conformation, a VT ¹H-NMR experiment was carried out in toluene d_8 (see Table 1). Increasing the temperature from -10to 100 °C failed to coalesce the two amidinato methyl signals. Instead, both resonances broadened and the chemical shift difference between them decreased significantly. It can be estimated that the two methyl resonances will collapse to a singlet at temperatures considerably above 100 °C. After this VT ¹H-NMR experiment and over the course of several days at 25 °C, the spectrum of this sample was unchanged, indicating a high thermal stability for 2.

As observed for $\{[\eta - PhC(NSiMe_3)_2]TiCl_3\}_2$, the dimer 2 is easily broken by using electron-donor solvents or ligands (Scheme 1).⁶ In an NMR-tube scale experiment, a solution of 2 in CDCl₃ was treated with an excess of THF (8:1) and the spectrum was recorded. The volatiles were then carefully removed, keeping the sample under vacuum overnight. The spectrum was again recorded by redissolving the solid in CDCl₃. The ¹H NMR spectrum of this solid was identical to the previous one, except that one molecule of THF was present per amidinate ligand, indicating the formation of $[\eta$ -MeC₆H₄C(NMe₂)₂]TiCl₃·THF (**3**).¹¹ The same experiment conducted with PMe₃ instead of THF led to the formation of the corresponding phosphine adduct $[\eta-MeC_6H_4C(NMe_3)_2]TiCl_3 PMe_3$ (4).¹²

Complex 2 was found to be active in the polymerization of both styrene and ethylene when activated with MAO, but 2/MAO does not polymerize propylene. Table 2 summarizes some representative results.¹³

Previously, we have shown that $\{[\eta-PhC(NSiMe_3)_2] TiCl_3$ (5)/MAO polymerized styrene under the above conditions with very high syndiotactic yield (SY = %s-PS); 94% of the product remained after extraction with refluxing 2-butanone.⁶ Instead, the syndiospecificity of 2/MAO was similar to that of CpTiCl₃/MAO, whereas the syndiospecificity of 5/MAO was comparable to IndTiCl₃/MAO.^{7a} The difference may be explained by

⁽¹⁰⁾ The stability provided by the Cl bridges to mono(benzamidinato)titanium complexes has already been demonstrated.⁶ For example, in contrast to the thermal stabilities of 2 and $\{[\eta-PhC(NSiMe_3)_2]\}$ - $TiCl_3$ ₂, [η -PhC(NSiMe_3)₂]TiMe_3 could not be isolated because it was readily converted to $[\eta$ -PhC(NSiMe₃)₂]₂TiMe₂, and $[\eta$ -PhC(NSiMe₃)₂]-Ti(O-Pr-i)₃ underwent thermolysis under mild conditions.

^{(11) &}lt;sup>1</sup>H NMR spectrum of [p-MeC₆H₄C(NMe)₂]TiCl₃'THF in CDCl₃: $\begin{array}{l} \delta_{\rm AA'} ~ 7.63~(2~{\rm H},~{\rm C_6H_4},~J_{\rm AB}+J_{\rm AB'}=8~{\rm H2});~ \delta_{\rm BB} ~ 7.30~(2~{\rm H},~{\rm C_6H_4},~J_{\rm AB}+J_{\rm AB'}=8~{\rm H2});~ 4.08~({\rm m},~4~{\rm H},~{\rm THF});~ 3.81~({\rm s},~3~{\rm H},~{\rm trans}~N{\rm -Me});~ 3.16~({\rm tr$ H, cis N-Me); 2.43 (s, 3 H, Me); 1.89 (m, 4 H, THF) (trans and cis refer

refer to the PMe₃ position).

⁽¹³⁾ The procedure used to polymerize styrene has been given in detail in ref 7a, and the procedure to polymerize ethylene is given in: (a) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. J. Am. Chem. Soc. **1991**, 113, 8570. (b) Tsai, W.-M.; Rausch, M. D.; Chien, J. C. W. Appl. Organomet. Chem. 1993, 7, 71.

Table 2. Olefin Polymerization by 2/MAO^a

run	monomer ^b	[Ti] (µM)	Al/Ti	yield (mg)	activityc	% s-PS ^d	$10^{-5} M_{\rm w}$
1	S	25	4000	53	5.0×10^{5}	77	
2	S	50	4000	59	3.6×10^{5}	68	
3	S	50	2000	77	4.7×10^{5}	84	
4	E	25	4000	40	5.7×10^{4}		0.96
5	E	50	4000	115	8.3×10^{4}		0.78
6	Е	50	2000	97	7.0×10^4		1.03

^{*a*} Polymerization conditions: volume = 50 mL of toluene, $T_p = 20$ °C, $t_p = 1.5$ h. ^{*b*} S = 43.49 mmol of styrene; E = ethylene at 15 psig ([C₂H₄] = 0.37 M). ^{*c*} For styrene, g of polymer/(mol of Tirmol of styrene+h); for ethylene, g of polymer/(mol of Tir[C₂H₄]+h). ^{*d*} % s-PS = (g of 2-butanone isoluble polymer/g of bulk polymer) × 100.

the smaller bulkiness of the N-methyl substituents in **2** compared to the N-trimethylsilyl substituents in **5**. Therefore, stereochemical control is greater in the latter than in the former, both in the conformational arrangement of the growing polymer chains and in the approaching fashion of the incoming monomer.

The two amidinate systems have very similar styrene polymerization activity, with 2/MAO slightly superior. This difference may be due to the better electron-donor character of the N-substituents in 2 and in agreement with the results observed with the effects of substituents in indenyl- and cyclopentadienyltrichlorotitanium complexes.¹⁴

In the polymerization of ethylene, **2**/MAO also showed a slightly higher activity (*i.e.* 7.0×10^4 g of PE/(mol of Ti·[C₂H₄]·h)) than **5**/MAO (5.5×10^4). These activities are nevertheless low as compared to high-activity ethylene polymerization catalysts systems such as Cp₂ZrCl₂/ MAO.¹⁵

Experimental Section

Reactions were carried out under an argon atmosphere using standard Schlenk techniques. Methylaluminoxane (MAO) was purchased from Akzo, and all other reagents were from Aldrich. Toluene, diethyl ether, and tetrahydrofuran (THF) were distilled with Na/K alloy under argon, whereas CH_2Cl_2 and styrene were distilled from CaH_2 . ¹H NMR spectra were recorded on a Varian XL-200 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

Synthesis of N-(Trimethylsilyl)-N,N'-dimethyl-p-toluamidine (1). Utilizing a literature procedure,⁸ a large scale stepwise reaction of p-tolunitrile (35.14 g, 0.30 mol) with lithium dimethylamide (15.31 g, 0.30 mol) was carried out in diethyl ether (250 mL) at room temperature. Replacement of the solvent by toluene, subsequent reaction with chlorotrimethylsilane (88.1 mL, 0.30 mol), and workup of the reaction mixture afforded 1 as a yellow oil. Fractional high vacuum distillation of this crude product (85 °C, 2×10^{-3} /mmHg) allowed the isolation of pure 1 (36.37 g, 52%) as a low-melting, colorless crystalline solid, mp 28 °C.

Anal. Calcd for $C_{13}H_{22}N_2Si$: C, 66.61; H, 9.46; N, 11.95. Found: C, 66.81; H, 9.59; N, 11.88. ¹H NMR (CDCl₃): $\delta_{AA'}$, 7.14 (2 H, C₆H₄, $J_{AB} + J_{AB'} = 8$ Hz); $\delta_{BB'}$ 7.03 (2 H, C₆H₄, $J_{AB} + J_{A'B} = 8$ Hz); 2.88 (br s, 16 Hz, 6 H, NMe); 2.36 (s, 3 H, Me); -0.22 (s, 9 H, SiMe₃).

Synthesis of (N,N'-Dimethyl-p-toluamidinato)trichlorotitanium (2). Slow addition of 1 (5.58 g, 23.8 mmol) to a solution of TiCl₄ (4.52 g, 23.8 mmol) in CH_2Cl_2 (30 mL) at room temperature, followed by stirring for 1 h and removal of the solvent, led to the dimer 2. Compound 2 was obtained as a fine yellow-orange powder and was recrystallized from CH_2 - Cl_2 , affording it analytically pure as a moisture-sensitive orange powder (5.21 g, 69%).

Anal. Calcd for $C_{10}H_{13}N_2Cl_3Ti$: C, 38.07; H, 4.15; N, 8.88. Found: C, 37.97; H, 4.28; N, 8.39. ¹H NMR (CDCl₃): $\delta_{AA'}$ 7.51 (2H, C₆H₄, J_{AB} + J_{AB'} = 8 Hz); $\delta_{BB'}$ 7.31 (2 H, C₆H₄, J_{AB} + J_{A'B} = 8 Hz); 3.60 (s, 3 H, trans *N*-Me); 3.23 (s, 3 H, cis *N*-Me); 2.43 (s, 3 H, Me). ¹H NMR (benzene-d₆): $\delta_{AA'}$ 7.09 (2 H, C₆H₄, J_{AA'} + J_{AB'} = 8 Hz); $\delta_{BB'}$ 6.76 (2 H, C₆H₄, J_{AA'} + J_{A'B} = 8 Hz); 2.70 (s, 3 H, trans *N*-Me); 1.93 (s, 3 H, cis *N*-Me); 1.88 (s, 3 H, Me). ¹H NMR (toluene-d₈): $\delta_{AA'}$ 7.10 (2 H, C₆H₄, J_{AB} + J_{AB'} = 8 Hz); $\delta_{BB'}$ 6.76 (2 H, C₆H₄, J_{AB} + J_{AB'} = 8 Hz); $\delta_{BB'}$ 6.76 (2 H, C₆H₄, J_{AB} + J_{AB'} = 8 Hz); $\delta_{BB'}$ 6.76 (2 H, C₆H₄, J_{AB} + J_{AB'} = 8 Hz); $\delta_{BB'}$ 6.76 (2 H, C₆H₄, J_{AB} + J_{AB'} = 8 Hz); 2.76 (s, 3 H, trans *N*-Me); 1.98 (s, 3 H, cis *N*-Me); 1.96 (s, 3 H, Me) (trans and cis refer to the chloro bridges).

Acknowledgment. J.C.F. is indebted to the MEC (Spain) for a postdoctoral fellowship.

OM940869O

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