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Efficient synthesis and structural characterization of a post-metallocene α -olefin polymerization catalyst

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Abstract

We describe the fast one-pot synthesis of a chelating diamido dichloride titanium compound through sequential addition of the protonated ligand and triethylamine to $TiCl_4$. The bisamido complex has been structurally characterized. A monoamido intermediate has been isolated.

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1. Introduction

In the continuously evolving field of Ziegler-Natta olefin polymerization, the development of new homogeneous catalysts where the metallocene cyclopentadienyl ligands are replaced by other functional groups, the so-called "post-metallocene catalysts", has attracted considerable attention over the recent years [1,2]. Among the explored families, group 4 amido derivatives have been most particularly interesting. The potential of these compounds started to be recognized in the mid 1990s [3-5]. McConville and Schrock both made an impact in the field of postmetallocene catalysts by disclosing amido-based systems displaying outstanding performances in terms of activity and living character for the polymerization of terminal olefins [6-10]. More precisely, McConville showed that titanium derivatives 1^{R} and 2^{R} bearing a bulky, chelating bisamide ligand with a C₃ bridge could polymerize 1-hexene with high activity and in a living fashion (Scheme 1)

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[8]. Further studies using this family of catalysts for polymerization and copolymerization have been undertaken by Soga and co-workers, demonstrating the high potential of such catalysts in the manufacturing of $poly(\alpha$ -olefins) [11–13]. Chiral versions of these precatalysts have been developed by Mair in view of their application in isoselective 1-hexene polymerization [14]. Thus, the development of a simple, rapid synthesis of this type of catalyst precursor is of interest. We describe here the synthesis and structural characterization of such a species following a simple and fast procedure, which involves the diamine ligand precursor, TiCl₄ and NEt₃.

2. Results and discussion

The synthesis of $1^{\mathbb{R}}$ complexes reported by McConville and co-workers comprises two steps. The ligand precursor $(L^{\mathbb{R}})H_2$ is first deprotonated with MeLi and silylated into $[L^{\mathbb{R}}](SiMe_3)_2$. This moisture sensitive diamine is isolated and reacted with TiCl₄ in refluxing xylenes for 12 h to afford $1^{\mathbb{R}}$ with concomitant release of SiMe₃Cl (Scheme 2). The overall reported yield is 75%, with a cumulative reaction time of more than 24 h.



Scheme 1. Titanium bisamide precatalysts developed by McConville for α -olefin polymerization.



Scheme 2. Synthesis of complexes 1^R reported by McConville.

We considered in following a more direct route which would not involve the isolation of an intermediate compound. Thus, direct reaction of the $[L^{Me}]H_2$ ligand precursor and TiCl₄ was performed, and followed by triethylamine addition (Scheme 3). Filtration of the reaction mixture and recrystallization after stripping-off the volatiles afforded 1^{Me} as a red crystalline solid in a 84% yield.

Single crystals were grown from a toluene/pentane solution and were subjected to X-ray diffraction studies. The



Scheme 3. New access route to complex 1^{Me}.



Fig. 1. Molecular structure of $1^{\mbox{Me}}$ at 50% probability level with hydrogen atoms being omitted for clarity.

Table 1	
Crystal data and structure refinement details of $[TiCl_2 (N_2C_{19}H_{24})]$	
Empirical formula	C ₁₉ H ₂₄ N ₂ Cl ₂ Ti
Formula weight	399.20
Temperature (K)	100.0(3)
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	14.624(3)
b (Å)	7.696(2)
<i>c</i> (Å)	17.724(4)
α (°)	90.00
β (°)	105.168(3)
γ (°)	90.00
Volume ($Å^3$)	1925.2(7)
Ζ	4
D_{calc} (Mg/m ³)	1.377
Absorption coefficient (mm ⁻¹)	0.725
<i>F</i> (000)	832
Crystal dimensions (mm)	0.35 imes 0.25 imes 0.19
θ range for data collection (°)	2.38-25.99
Index ranges	$-18 \leqslant h \leqslant 18$
	$-9 \leqslant k \leqslant 9$
	$-21 \leq l \leq 21$
Reflections collected	11605
Independent reflections (R_{int})	3568 (0.057)
Data/restraints/parameters	3568/0/289
Goodness-of-fit on F^2	1.070
Final R indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0429, wR_2 = 0.0883$
R indices (all data)	$R_1 = 0.0731, wR_2 = 0.0961$
Largest difference in peak and hole ($e \text{ Å}^{-3}$)	0.351 and -0.361

ORTEP representation of the solid-state structure of 1^{Me} is displayed in Fig. 1. Table 1 gathers crystal data and structure refinement details.

The solid-state structure of 1^{Me} is similar to that of the dimethyl derivative 2^{Me} described by McConville [6]. The metal adopts a distorted tetrahedral configuration. The chelating diamido ligand adopts a boat-type configuration. As a consequence of the aryl groups' orientation, the methyl groups shield the metal above and below the N-Ti-N plane. As expected from amido functions, the nitrogens are planar. The Ti1-N1 and Ti1-N2 bond distances of 1.849(2) and 1.854(2) Å, respectively, are typical of titanium amido bonds [6,14,15]. The Ti1-Cl1 and Ti-Cl2 distances (2.2548(10)) and 2.2755(9)Å, respectively) are unremarkable. The N1-Ti-N2 chelating angle of $100.68(11)^{\circ}$ is sharper than that of the dimethyl derivative 2^{Me} of 102.6(3)° [6]. The same angle is also wider than in the dichloride derivative of the more bulky bisisopropylaryl ligand $1^{i\mathbf{Pr}}$ (99.2(2)°) [6]. Accordingly, the Cl–Ti–Cl angle in 1^{Me} (107.02(4)°) is slightly narrower than that of the isopropylaryl complex $\mathbf{1}^{i\mathbf{Pr}}$ (107.77(9)°).

In our procedure, the triethylamine is used to trap the HCl released during the formation of the Ti–N bond, as it could protonate a ligand's nitrogen and prevent complete reaction. The direct reaction between titanium tetrachloride and diols generating chelating alkoxide complexes has been reported by Schaverien [16]. However, in this case, in contrast to what we observe for the amido derivative **1**^{Me}, the use of a base to capture the released HCl gas is



Scheme 4. Formation, proposed structure and reactivity of 3^{Me}.

not only unnecessary, but also detrimental to the course of the reaction, since the formation of the alkoxide does not occur when NEt_3 is used.

Reaction between $[L^{Me}]H_2$ and titanium tetrachloride in toluene affords a brown precipitate, which was separated by filtration and characterized by NMR, IR, Raman and elemental analysis. Both proton and carbon NMR indicate the presence of a non-symmetric [L] framework. Furthermore, the presence of a TiN(Ar)CH₂ moiety is evidenced by characteristic ¹H and ¹³C signals (triplet centered at 4.35 ppm, and singlet at 57.48 ppm, respectively). In addition, a broad ¹H NMR signal centered at 7.80 ppm (2H), along with a deshielded NCH₂ multiplet (3.73 ppm, compared to 3.12 ppm for $[L]H_2$) are indicative of an anilinium fragment, ArNH₂-CH₂, which is further confirmed by the presence of a ¹³C NMR signal at 50.62 ppm. The infrared spectrum comprises a broad peak at 3150 cm^{-1} , assigned to v_{N-H} in anilinium (R)(Ar)NH₂⁺. This is consistent with the formulation of 3^{Me} as a monoamido compound resulting from a single Ti-amido bond formation and where the thus released HCl would be trapped by the second nitrogen atom into an anilinium group (see Scheme 4). Closely related [TiCl₃(NRR')] compounds have been prepared by Bürger and Neese, from TiCl₄ and the corresponding silylated amine with the release of SiMe₃Cl [17]. Based on the low-frequency region spectrum, the authors proposed a polynuclear structure for such compounds. Indeed, the Raman spectrum of 3^{Me} comprises features similar to those of these monoamido species: a strong intensity line at 302 cm⁻¹ (terminal Ti–Cl) and several low intensity signals at 267 and 240 (br) cm⁻¹ (bridging TiCl). This tends to indicate that 3^{Me} exists as polynuclear entities. The rather low wavenumber of the N-H vibration (3150 cm^{-1}) may be indicative of some degree of hydrogen bonding, the intra- or intermolecular nature being undetermined without X-ray structure diffraction data [18,19].

The addition of excess triethylamine to a suspension of 3^{Me} affords quantitatively (NMR) the bisamido derivative 1^{Me} : the formation of the second titanium amido function results from trapping of two equivalents of HCl by NEt₃. ¹H NMR studies confirm the formation of NEt₃HCl. Noteworthy, this method could not be successfully extended to the more sterically crowded (L^{iPr})H₂ derivative, which did not react under analogous reaction conditions.

In conclusion, we have shown that the synthesis of a postmetallocene catalyst precursor can be carried out following a very simple procedure under mild conditions in a much shorter time than with the reported procedure. The reaction has been shown to proceed via a monoamido complex.

3. Experimental

3.1. General procedures

All experiments were carried out under an argon atmosphere in a M-Braun glove box or by using standard Schlenk techniques. TiCl₄ was purchased from Strem Chemicals. Solvents were dried under nitrogen using conventional reagents, degassed by freeze-pump-thaw cycles and stored in the glove box over 3 A molecular sieves. 1,3-Bis(2,6-dimethylanilino)propane $((L^{Me})H_2)$ was prepared according to the published procedures [6]. NMR analyses were run on a Bruker Avance 300 (¹H: 300 MHz, ¹³C: 75 MHz) at room temperature and referenced to SiMe₄. Elemental analyses were carried out at the Service d'Analyse, LSEO, University of Dijon, France, ORTEP drawings were generated by ORTEP-3 1.074 [20]. Infrared spectra were acquired on a Nicolet Protégé 460 equipped with a Harrick cell. Micro-Raman spectra were recorded at room temperature using the 531.95 nm second harmonic line of a Nd:YAG laser. A 50X microscope objective was used to focus the excitation beam (13.6 µm spot) and collect the scattered light at the same time. The scattered light was collected through a confocal hole (150 µm) by a nitrogencooled CCD (Labram Infinity, Jobin Yvon). The Raman spectra of the materials were collected under inert conditions by means of a home-made sealed cell loaded under Ar and equipped with a quartz window.

3.1.1. $[Ti(L)Cl_2]$ (1^{Me})

A solution of $(L)H_2$ (0.500 g, 1.85 mmol) in 25 mL of toluene was added to a solution of $TiCl_4$ (0.370 mg, 1.95 mmol) in 25 mL of toluene cooled at -78 °C. The reaction mixture immediately turned red-brown, and a brown precipitate formed. The cooling bath was removed once the addition was complete, and after 15 min, 2 mL NEt₃ (14.3 mmol) were slowly added under vigorous stirring. Once the reaction mixture had reached room-temperature, the dark red supernatant was separated by cannula transfer. The residual precipitate was washed with toluene $(2 \times 10 \text{ mL})$. The volume of the combined toluene fractions was reduced under vacuum. After cooling to -25 °C, a first crop of (0.450 g) dark red crystalline 1^{Me} was obtained. A second batch (0.171 g) was obtained after further concentration and cooling of the residual mother liquor (combined yield 84%). Spectroscopic data matched those reported in the literature [6]. Raman (cm^{-1}) : 843 (s), 716 (m), 579 (s), 525 (m), 355 (m), 278 (w).

3.1.2. X-ray structure of 1^{Me}

A red irregular crystal of the studied complex was mounted on a Bruker Smart-Apex II-CCD automatic diffractometer equipped with a CCD detector, and used for data collection. X-ray intensity data were collected with graphite-monochromated Mo K α radiation ($\lambda =$ 0.71073 Å) at the temperature of 100.0(3) K, with the ω scan mode. The full Ewald sphere reflections were collected up to $2\theta = 52^{\circ}$. The unit cell parameters were determined from least-squares refinement of the setting angles of 259 strong reflections. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization, and numerical absorption corrections were applied. The structure was solved by direct methods [21-23]. All the non-hydrogen atoms were refined anisotropically using full-matrix leastsquares on F^2 . The hydrogen atoms were found from difference Fourier synthesis and refined with individual isotropic temperature factors equal to 1.2 (or 1.5 for methyl groups) times the value of the equivalent temperature factor of the parent atom. SHELXTL chain of programs was used for all the calculations [24]. Atomic scattering factors were those incorporated in the computer programs.

3.1.3. $[Ti(LH_2)Cl_4]$ 3^{Me}

To a solution of 34 mg of TiCl₄ (1.8×10^{-4} mol) in toluene (2 mL) was added dropwise at -20 °C a solution of $50 \text{ mg} (L)\text{H}_2 (1.77 \times 10^{-4} \text{ mol})$ in toluene (2 mL). A brown precipitate formed immediately, which was separated by filtration and washed with pentane $(2 \times 2 \text{ mL})$ to afford 75 mg of a brown solid (89% yield). ¹H NMR (CDCl₃): 7.87 (s, br, 2H, NH₂), 7.37 (m, 1H, CH Ar), 7.21 (m, 5H, CH Ar), 4.35 (t, ${}^{2}J_{H-H} = 7.5$ Hz, 2H, Ti–N–CH₂), 3.73 (m, 2H, ArNH₂-CH₂), 2.46 (s, 6H, ArMe), 2.37 (m, 2H, CH₂CH₂CH₂), 2.27 (s, 6H, ArMe). ¹³C NMR (CDCl₃): 143.61, 132.68, 130.88, 130.79, 130.59, 130.12, 129.89, 129.56 (C Ar), 57.48 (TiNCH₂), 50.62 (ArNH₂-CH₂), 25.14 (CH₂CH₂CH₂), 18.92 (ArMe), 17.48 (ArMe). IR (diffuse reflectance, cm⁻¹): 3150 (w), 3058 (w), 2988 (w), 2968 (w), 2925 (w), 1573 (s), 1468 (m), 1383 (m), 1314 (w), 1262.33 (w), 1193 (w), 1169 (m), 1122 (w), 1094 (m), 1030 (m), 993 (m), 944 (m), 911 (m), 902 (m), 844 (m), 826 (m), 783 (s), 744 (m), 708 (m), 677 (m), 666 (m), 653 (m), 615 (m), 600 (m), 575 (m), 562 (m). Raman (cm⁻¹): 953 (m), 904 (s), 850 (s), 761 (w), 715 (s), 676 (w), 616 (s), 538 (s), 524 (m), 514 (m, br), 302 (s), 267 (w), 242 (br, w). Anal. Calc for C₁₉H₂₆Cl₄N₂Ti: C, 48.34; H, 5.55; N, 5.93. Found: C, 45.95; H, 5.36; N, 5.80%.

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Appendix A. Supplementary material

CCDC 666363 contains the supplementary crystallographic data for 1^{Me} . These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.02.034.

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