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Note

# 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.

*Keywords:* Titanium; Amido ligand; Olefin polymerization; X-ray structure

## 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 post-metallocene 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 $\mathbf{1^R}$ and $\mathbf{2^R}$ bearing a bulky, chelating bisamide ligand with a $C_3$ bridge could polymerize 1-hexene with high activity and in a living fashion (Scheme 1) [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(α-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, $TiCl_4$ and $NEt_3$.

## 2. Results and discussion

The synthesis of $\mathbf{1^R}$ complexes reported by McConville and co-workers comprises two steps. The ligand precursor $(L^R)H_2$ is first deprotonated with MeLi and silylated into $[L^R](SiMe_3)_2$. This moisture sensitive diamine is isolated and reacted with $TiCl_4$ in refluxing xylenes for 12 h to afford $\mathbf{1^R}$ with concomitant release of $SiMe_3Cl$ (Scheme 2). The overall reported yield is 75%, with a cumulative reaction time of more than 24 h.

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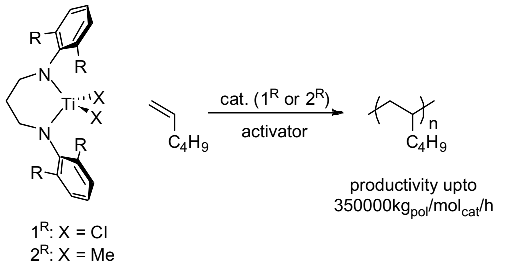
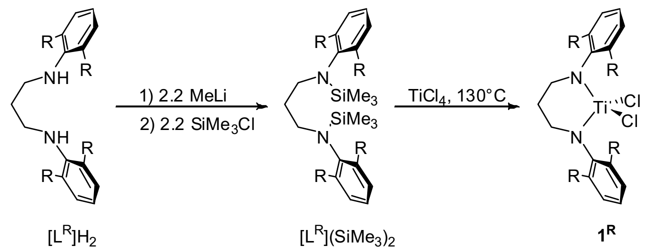


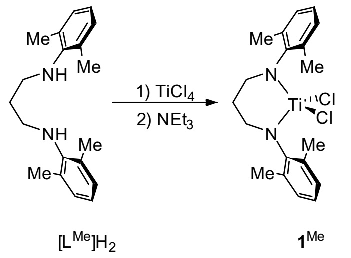
Scheme 1. Titanium bisamide precatalysts developed by McConville for α-olefin polymerization.



Scheme 2. Synthesis of complexes $1^{\mathbf{R}}$ 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 $TiCl_4$ was performed, and followed by triethylamine addition (Scheme 3). Filtration of the reaction mixture and recrystallization after stripping-off the volatiles afforded $\mathbf{1}^{\mathbf{Me}}$ 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 ORTEP representation of the solid-state structure of $\mathbf{1}^{\mathbf{Me}}$ is displayed in Fig. 1. Table 1 gathers crystal data and structure refinement details.



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

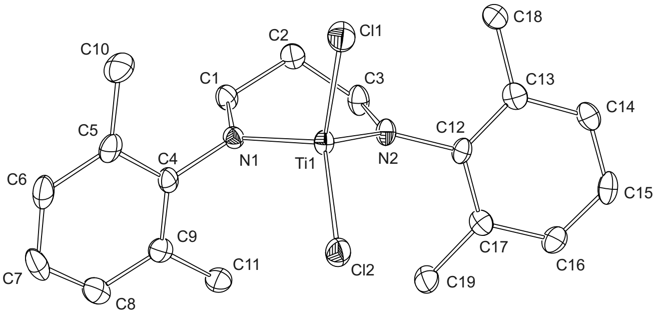


Fig. 1. Molecular structure of $1^{\mathbf{Me}}$ at 50% probability level with hydrogen atoms being omitted for clarity.

Table 1
Crystal data and structure refinement details of $[TiCl_2\ (N_2C_{19}H_{24})]$

| | |
|---|---|
| Empirical formula | $C_{19}H_{24}N_2Cl_2Ti$ |
| 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) |
| $c$ (Å) | 17.724(4) |
| $\alpha$ (°) | 90.00 |
| $\beta$ (°) | 105.168(3) |
| $\gamma$ (°) | 90.00 |
| Volume (Å$^3$) | 1925.2(7) |
| $Z$ | 4 |
| $D_{calc}$ (Mg/m$^3$) | 1.377 |
| Absorption coefficient (mm$^{-1}$) | 0.725 |
| $F$(000) | 832 |
| Crystal dimensions (mm) | 0.35 × 0.25 × 0.19 |
| $\theta$ range for data collection (°) | 2.38–25.99 |
| Index ranges | $-18 \leqslant h \leqslant 18$ |
| | $-9 \leqslant k \leqslant 9$ |
| | $-21 \leqslant l \leqslant 21$ |
| 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 $[I > 2\sigma(I)]$ | $R_1 = 0.0429$, $wR_2 = 0.0883$ |
| $R$ indices (all data) | $R_1 = 0.0731$, $wR_2 = 0.0961$ |
| Largest difference in peak and hole (e Å$^{-3}$) | 0.351 and −0.361 |

The solid-state structure of $\mathbf{1}^{\mathbf{Me}}$ is similar to that of the dimethyl derivative $\mathbf{2}^{\mathbf{Me}}$ 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)° is sharper than that of the dimethyl derivative $\mathbf{2}^{\mathbf{Me}}$ of 102.6(3)° [6]. The same angle is also wider than in the dichloride derivative of the more bulky bisisopropylaryl ligand $\mathbf{1}^{\boldsymbol{i}\mathbf{Pr}}$ (99.2(2)°) [6]. Accordingly, the Cl–Ti–Cl angle in $\mathbf{1}^{\mathbf{Me}}$ (107.02(4)°) is slightly narrower than of the isopropylaryl complex $\mathbf{1}^{\boldsymbol{i}\mathbf{Pr}}$ (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 $\mathbf{1}^{\mathbf{Me}}$, the use of a base to capture the released HCl gas is