Diamido Complexes of Titanium and Zirconium as Catalyst Precursors for Ethylene Polymerization

Khalil, Ahmad*+

Department of Chemistry, Mirpur University of Science and Technology (MUST), Mirpur 10250, (AJK) PAKISTAN

Alt, G. Helmut

Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 101251, D-95440 Bayreuth, GERMANY

ABSTRACT: *A series of 8 new complexes of titanium and zirconium with diamido ligands bearing an ethylene and propylene bridge between the two amido groups were synthesized and tested for ethylene polymerization. Titanium complexes bearing an ethylene bridge between the two amido groups showed higher activities than the derivatives with a propylene bridge. In the case of the zirconium complexes, the propylene bridged complexes were more active than the corresponding ethylene bridged. The introduction of bulky groups on the ligand structure resulted in an increase of the activity. DFT calculations were performed to determine the activation energy barriers for different reaction steps. The calculated activation energy for the insertion of ethylene into an M-CH$_3$ bond is in the range of 12.2-16.8 kcal/mol and the activation energy for the chain termination via β-H transfer reaction is 12.5-14.4 kcal/mol.*

KEYWORDS: *Diamido; Titanium; Zirconium; Ethylene polymerization; Experimental and DFT studies.*

INTRODUCTION

Post-metallocene olefin polymerization catalysts have been extensively explored during the last three decades largely due to their high performance in olefin polymerization and co-polymerization reactions [1-16]. Transition metal complexes of diiminopyridine [17-19], α-diimine [20-26], β-diimine [27,28], phenoxyimine [29-32] and chelating diamido ligands [33-43] are the most frequently studied post-metallocene catalysts. Chelating diamido complexes of group (IV) metals are precursors of a promising catalyst system for olefin polymerization [33-43]. A variety of Ti and zirconium complexes with diamide ligands based on naphthalene, phenylene,

ethylene and propylene backbones have been studied for olefin polymerization reactions. *Carone et al.* reported ethylene polymerization properties of titanium and zirconium diamido complexes with o-C$_6$H$_4$(NSiMe$_3$)$_2$ ligands [33]. The zirconium complex showed good activity for ethylene polymerization but the titanium complex was less reactive. Titanium complexes with N,N′-disilylated 1,8-diaminonaphthalene ligands reported by Park and coworkers showed good activities for ethylene polymerization [36]. A diamido catalyst of titanium, [RN(CH$_2$)$_3$NR]TiMe$_2$ (R = 2,6-*i*Pr$_2$C$_6$H$_3$)/MAO, reported by *Scollard et al.* produced 350000 kg of

poly(1-hexene)/mol of catalyst. However, its zirconium analogue produced only 150 kg of poly(1-hexene)/mol catalyst.h [34,39]. The titanium catalysts [ArN(CH$_2$)$_3$NAr]TiCl$_2$ (R = 2,6-iPr$_2$C$_6$H$_3$) and [ArNCH$_2$PhCH$_2$NAr]TiCl$_2$ (R = 2,6-iPr$_2$C$_6$H$_3$) in combination with trialkylaluminium and boron compounds as cocatalysts showed high activities for propylene polymerization [41,42] and ethylene/2-butene copolymerization reactions [43]. These diamido systems are of great interest because they can also act as precursors for living α-olefin polymerization catalysts [35]. Herein we are reporting a new diamine ligand system containing an aniline moiety and a tertiary butylamine moiety bridged with an ethylene or propylene group. The corresponding titanium and zirconium complexes were investigated for their ethylene polymerization potential after activation with methylaluminoxane (MAO).

EXPERIMENTAL SECTION
General aspects

All reactions were carried out using Schlenk line technique under an inert atmosphere of argon. Toluene and n-pentane were purified by distillation over Na/K alloy. Deuterated solvents (CDCl$_3$ and CD$_2$Cl$_2$) were purchased from Eurisotop and stored over molecular sieves (3Å). Argon (5.0) and ethylene (3.5) were purchased from Rieβner Company. Methylaluminoxane (10% in toluene) was purchased from Chemtura Europe Limited. All other starting materials were commercially available and used as received.

NMR spectroscopy

A Varian Inova (400 MHz) spectrometer was available to record the NMR spectra. All spectra were recorded at 298K. The chemical shifts of the residual proton signals of the solvent were used as references (δ = 7.24 ppm for chloroform and δ = 5.30 ppm for methylene chloride) for the ^{1}H-NMR spectra, while the chemical shift of the solvent was used as a reference (δ = 77.0 ppm for chloroform-d$_1$ and δ = 54.0 ppm for methylene, chloride-d$_2$) for the ^{13}C-NMR spectra.

GC/MS

A FOCUS Thermo gas chromatography coupled with a DSQ mass detector was available to record the GC/MS spectra. A 30m HP-5 fused silica column (internal diameter 0.32 mm, film 0.25 μm and flow 1 mL/min) was used and helium (4.6) was applied as the carrier gas. The following temperature program was used to record the measurements.

Starting temperature: 50°C, duration: 2 minutes;
Heating rate: 20°C/minute, duration: 12 minutes;
Final temperature: 290°C, duration: 27 minutes.

DSC analysis

DSC analyses were performed on a Mettler Toledo DSC/DTA 821e instrument. The polymer samples were prepared by enclosing 4-6mg of the polymers in standard aluminum pans. The samples were introduced into the autosampler of the instrument and the measurements were recorded using the following temperature program:

First heating phase: from 50°C to 160°C (10°C/minute);
Cooling phase: 160°C to 50°C (10°C/minute);
Second heating phase: from 50°C to 160°C (10°C/minute).

Nitrogen was used as a cooling medium. Melting enthalpies and melting points were taken from the second heating phase. The values were calibrated using indium as a standard (m.p. 429.78K, H$_m$ = 28.45J/g).

Computational details

DFT calculations were carried out with Gaussian 09 [44] using B3LYP functional [45-47]. All geometries were optimized using the 6-31G* basis set for H, C and N atoms. Titanium and zirconium atoms were described with the Stuttgart RSC 1997 ECP basis set. Transition states were optimized using the Berny algorithm [48]. The optimized geometries were verified by vibrational frequency analysis.

General description of ethylene polymerization experiments

For the catalytic ethylene polymerization, complexes **5-12** were activated with MAO (M:Al=1:1000). The activated complexes were suspended in 250mL n-pentane and transferred to a 1-liter Büchi reactor. An ethylene pressure of 10 bar was applied for 1 hour. After disconnecting the ethylene flow, the system was cooled to room temperature. The pressure was released and the obtained polymer was filtered over a frit, washed with dilute hydrochloric acid, water and finally with acetone and dried under vacuum.

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General synthesis procedure for the diamine compounds (1-4)

A mixture of 20mmol of a dibromoalkane compound, 10mmol of the appropriate aniline, 10mmol of potassium carbonate and DMF (10mL), was heated at 100-105°C for 5 hours. After cooling to room temperature, distilled water (100mL) was added and the mixture was extracted with diethyl ether (2×100mL). The ether phase was dried over sodium sulphate, the solvent was removed by rotary evaporation and the residue was distilled to give the N-substituted bromoalkyl aniline derivative in 60-70% yield. An amount of 5mmol of the appropriate N-substituted bromoalkyl aniline derivative, 5mmol of potassium carbonate and an excess of tertiary butylamine were refluxed in 100mL THF for 6-8 hours. After cooling to room temperature, 50mL of distilled water and 100mL of diethyl ether were added. The organic phase was separated and dried over sodium sulphate. The solvent was removed and the residue was distilled to give the required diamine compound as an oil in 70-80% yield.

1: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.09-7.04 m (1H), 6.98-6.94 m (1H), 6.89 dd (J = 7.4 Hz, 1H), 3.28 sep (1H, CH), 2.99 t (J = 5.7 Hz, 2H, CH$_2$), 2.79 t (J = 5.7 Hz, 2H, CH$_2$), 2.31 s (3 H, CH$_3$), 1.22 d (J = 6.9 Hz, 6H, CH$_3$), 1.12 s (9H, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 145.2, 140.6, 130.5 (C$_q$), 128.4, 123.6, 122.2 (CH), 50.6 (CH$_2$), 50.2 (C$_q$), 42.8 (CH$_2$), 29.2 (CH$_3$), 27.5 (CH), 24.0 (CH$_3$), 18.9 (CH$_3$) ppm.

MS: 248 [M$^+$] (12), 163 (100), 146 (40), 86 (60).

2: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.08-6.98 m (3H), 3.32 septet (2H, CH), 2.93 t (2H, CH$_2$), 2.79 t (2H, CH$_2$), 1.21 d (J = 6.8 Hz, 12H, CH$_3$), 1.11 s (9H, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 143.9, 142.1 (C$_q$), 123.4, 123.3 (CH), 52.5 (CH$_2$), 50.2 (C$_q$), 42.7 (CH$_2$), 29.2 (CH$_3$), 27.6 (CH), 24.2 (CH$_3$) ppm.

MS: 276 [M$^+$] (6), 191 (100), 86 (70).

3: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 6.99-6.95 m (2H), 6.79 dd (J = 7.4 Hz , 1H), 3.04 t (J = 6.6 Hz, 2H, CH$_2$), 2.69 t (J = 6.6 Hz, 2H, CH$_2$), 2.28 s (6H, CH$_3$), 1.79-1.69 m (2H, CH$_2$), 1.10 s (9H, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 146.3, 129.2 (C$_q$), 128.6, 121.6 (CH), 50.1 (C$_q$), 47.3, 40.9, 32.1 (CH$_2$), 29 (CH$_3$), 18.6 (CH$_3$) ppm.

MS: 234 [M$^+$] (38), 148 (65), 134 (100).

4: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = 7.09-6.98 m (3H), 3.28 septet (2H, CH(CH$_3$)$_2$), 2.92 t (2H, CH$_2$), 2.72 t (J = 6.6 Hz, 2H, CH$_2$), 1.83-1.73 m (2H, CH$_2$), 1.22 d (J = 6.8 Hz, 12H, CH$_3$), 1.09 s (9H, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 143.6, 142.5 (C$_q$), 123.6, 123.5 (CH), 51.1 (CH$_2$), 50.2 (C$_q$), 41.3 (CH$_2$), 31.9 (CH$_2$), 29.0 (CH$_3$), 27.6 (CH), 24.3 (CH$_3$) ppm.

MS: 290 [M$^+$] (20), 204 (40), 190 (45), 174 (75), 146 (50).

General synthesis procedure for the diamido complexes of titanium and zirconium (5-12)

n-Butyllithium (2mmol, 1.6M in hexanes) was added to 1mmol of the appropriate diamine compound dissolved in 50mL diethyl ether at -78°C, and the reaction mixture was stirred for 2 hours at room temperature. Then it was transferred to a metal salt suspension (1mmol) in 50mL diethyl ether at -78°C and the reaction mixture was stirred for 24 hours at room temperature. Diethyl ether was removed and toluene (100mL) was added. The mixture was filtered and the volume of the filtrate was reduced. The complex was precipitated by adding pentane. The residue was filtered, washed with pentane and dried under vacuum to obtain the desired complex in 40% yield.

5: ^{1}H-NMR: (400 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.33-7.05 m (3H), 4.02 (br, 2H, CH$_2$), 3.73 (br, 2H, CH$_2$), 3.57 septet (CH), 2.69 s (3H, CH$_3$), 1.36 s (9H, CH$_3$), 1.25 d (J = 6.6 Hz, 6 H, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, CD$_2$Cl$_2$, 298 K): δ = 144.0, 132.9, 131.7 (C$_q$), 130.7, 130.6, 126.7 (CH), 58.3 (CH$_2$), 49.8 (C$_q$), 38.4 (CH$_2$), 28.7 (CH), 26.1, 25.3, 20.1 (CH$_3$) ppm.

6: ^{1}H-NMR: (400 MHz, CDCl$_3$, 298 K): δ = .28-7.24 m (1H), 7.17-7.13 m (2H), 4.34-3.14 m (6H), 1.52 s (9H, CH$_3$), 1.47 d (3H, CH$_3$), 1.22 d (3H, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, CDCl$_3$, 298 K): δ = 159.7, 138.7 (C$_q$), 128.5, 124.2 (CH), 64.1 (CH$_2$), 58.9 (C$_q$), 44.6 (CH$_2$), 28.7 (CH$_3$), 28.3 (CH), 24.1 (CH$_3$) ppm.

7: ^{1}H-NMR: (400 MHz, CD$_2$Cl$_2$, 298 K): δ = 6.96-6.93 m (2H), 6.80 dd (1H), 3.17-3.03 m (4H, CH$_2$), 2.40-2.33 m (2H, CH$_2$), 2.27 s (6H, CH$_3$), 1.46 s (9H, CH$_3$) ppm.

^{13}C-NMR: (100 MHz, CD$_2$Cl$_2$, 298 K): δ = 133.9, 132.9 (C$_q$), 130.7, 130.0 (CH), 58.0, 50.1 (CH$_2$), 39.5 (C$_q$), 26.2 (CH$_3$), 23.7 (CH$_2$), 19.4 (CH$_3$) ppm.

8: ^{1}H-NMR: (400 MHz, CD_2Cl_2, 298 K): δ = 7.22-7.02 m (3H), 3.22 septet (2H, CH), 2.99-2.88 m (4H, CH_2), 2.44-2.36 m (2H, CH_2), 1.50 s (CH_3), 1.20 d (CH_3) ppm.

^{13}C-NMR: (100 MHz, CD_2Cl_2, 298 K): δ = 143.7, 143.1 (C_q), 124.1, 123.2 (CH), 57.9 (CH_2), 51.4 (C_q), 42.5 (CH_2), 28.2 (CH), 26.7, 24.8 (CH_3) ppm.

9: ^{1}H-NMR: (400 MHz, $CDCl_3$, 298 K): δ = 7.06-6.89 m (3H), 3.56-3.09 m (1H, CH, 2H, CH_2), 2.28 s (3H, CH_3), 1.43 s (9H, CH_3), 1.16 d (6H, CH_3) ppm.

^{13}C-NMR: (100 MHz, $CDCl_3$, 298 K): δ = 143.7, 141.8, 131.6 (C_q), 128.6, 123.7, 123.4 (CH), 58.1 (C_q), 45.7, 43.1 (CH_2), 27.6 (CH), 26.2, 24.1, 19.6 (CH_3) ppm.

10: ^{1}H-NMR: (400 MHz, $CDCl_3$, 298 K): δ = 7.10-7.00 m (3H), 3.52-3.00 m (6H (2H, CH + 4H, CH_2)), 1.44 s (9H, CH_3), 1.18 d (12H, CH_3) ppm.

^{13}C-NMR: (100 MHz, $CDCl_3$, 298 K): δ = 143.0, 142.4 (C_q), 124.3, 123.6 (CH), 57.2 (Cq), 47.5, 43.0 (CH_2), 27.9 (CH), 26.0, 24.4 (CH_3) ppm.

11: ^{1}H-NMR: (400 MHz, $CDCl_3$, 298 K): δ = 7.12-7.07 m (1H), 7.05-6.98 m (2H), 3.32-2.85 m (6H, CH_2), 2.66 s (5H, CH_3), 1.47s (9H, CH_3) ppm.

^{13}C-NMR: (100 MHz, $CDCl_3$, 298 K): δ = 134.7, 132.3 (C_q), 130.0, 128.7 (CH), 57.2, 49.3 (CH_2), 39.0 (C_q), 25.8 (CH_3), 23.5 (CH_2), 19.3 (CH_3) ppm.

12: ^{1}H-NMR: (400 MHz, CD_2Cl_2, 298 K): δ = 7.45-7.15 m (3H), 3.68-2.96 m (8H (2H, CH + 6H, CH_2)), 1.47 s (9H, CH_3), 1.29 d (12H, CH_3) ppm.

^{13}C-NMR: (100 MHz, CD_2Cl_2, 298 K): δ = 143.5, 129.9 (C_q), 130.9, 126.4 (CH), 58.5 (CH_2), 52.8 (C_q), 39.8 (CH_2), 28.9 (CH), 26.3, 25.4 (CH_3), 24.2 (CH_2) ppm.

RESULTS AND DISCUSSION
Synthesis of diamine compounds 1-4

To synthesize the diamine compounds, an excess of the desired dibromoalkane was heated at 100-105°C with the desired aniline in DMF in the presence of potassium carbonate. The resulting mixture was distilled to give the N-substituted bromoalkyl aniline derivative. These N-substituted bromoalkyl aniline derivatives were refluxed in THF with tertiary butylamine in the presence of potassium carbonate to give the required diamine compounds (Scheme 1).

Compounds **1**-**4** were characterized by GC/MS and ^{1}H- and ^{13}C-NMR spectroscopy. The ^{1}H-NMR spectrum of compound **2** (Fig. 1) shows a multiplet for the

aryl protons H5 and H6 at δ = 7.08-6.98 (m, 3H) ppm. A septet for the CH protons of the isopropyl groups (H7) appears at δ = 3.32 (septet, 2 H) ppm. Two triplets at δ = 2.93 t (2H) ppm and at δ = 2.79 t (2H) are assigned to the CH_2 protons H2 and H1. The signal for the methyl protons of the isopropyl groups (H8) can be located at δ = 1.21 (d, J = 6.8 Hz, 12H) ppm while the signal at δ = 1.11 (s, 9H) ppm is assigned to the tertiary butyl group (H10). The signals for the NH protons are not visible.

Synthesis of complexes

For the synthesis of diamido complexes, the corresponding diamine compounds were deprotonated with two equivalents of n-butyllithium followed by the addition of one equivalent of titanium tetrachloride or zirconium tetrachloride to synthesize the diamido complexes **5-12** (Scheme 2).
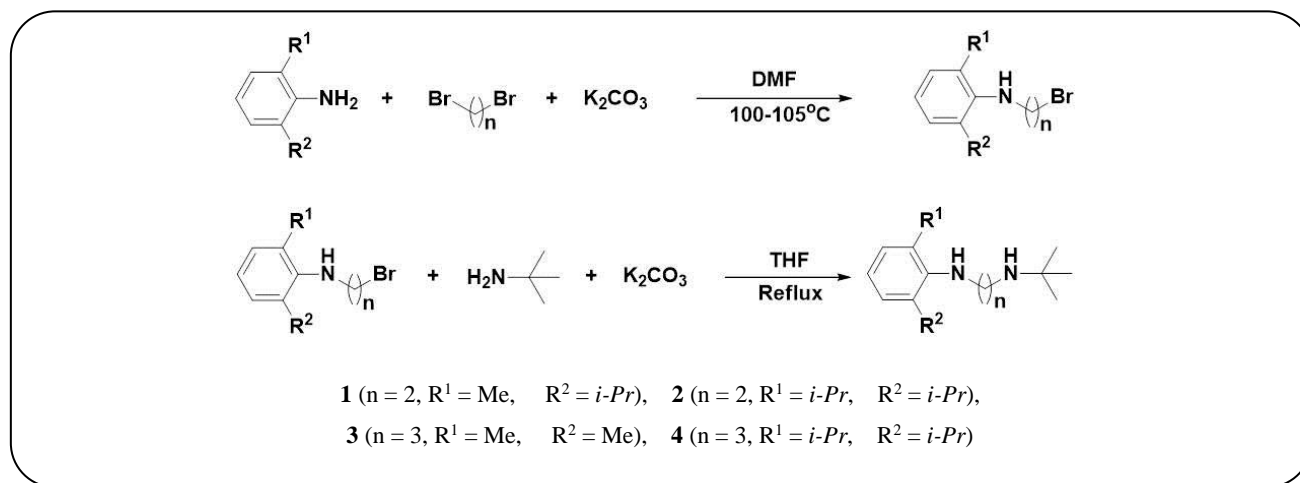
Complexes **5-12** were characterized by ^{1}H- and ^{13}C-NMR spectroscopy. In the ^{1}H-NMR spectrum of complex **6** (Fig. 2), the signals for the aryl protons H6 and H5 can be located at δ = 7.28-7.24 (m, 1H) and 7.17-7.13 (m, 2H) ppm. The signals at δ = 4.34-4.05 (m, 1H), 3.94-3.70 (m, 1H) and 3.61-3.14 (m, 4H) ppm are assigned to the CH protons of the isopropyl groups H7 and the CH_2 protons H1 and H2. At δ = 1.52 (s, 9H, CH_3) ppm the signal for the CH_3 protons of tertiary butyl group H10 shows up. The signals for the two isopropyl groups appear at δ = 1.47 (d, 3H, CH_3) and 1.22 (d, 3H, CH_3) ppm.

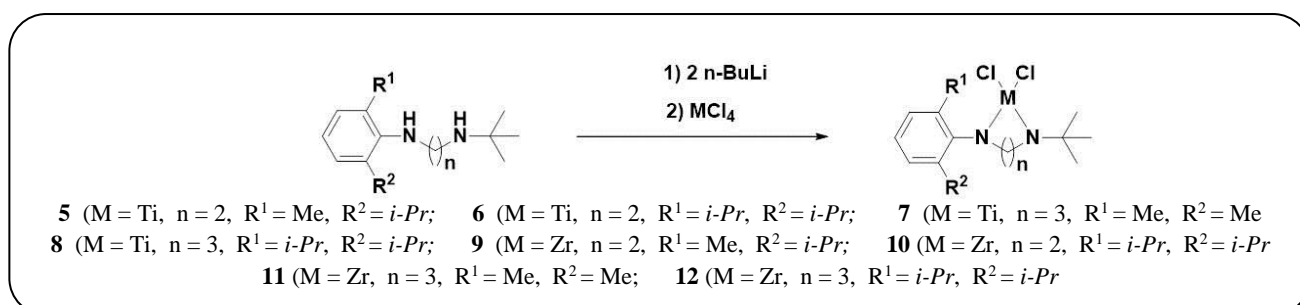### Optimized geometries of complexes 5-12

Density Functional Theory (DFT) studies were carried out to optimize the geometries of complexes **5-12.** The optimized geometries are given in Fig. 3. In the titanium complexes, the Ti-N bonds are in the range of 1.860-1.869Å, and the Ti-Cl bonds are in the range of 2.249-2.269Å. In the zirconium complexes, the Zr-N bonds are in the range of 2.028-2.038Å and the Zr-Cl bonds are in the range of 2.420-2.433Å.

Ethylene polymerization

The diamido complexes **5-12** were activated with MAO (M:Al=1:1000). The activated complexes were suspended in 250mL n-pentane and transferred to a 1 L autoclave. The homogeneous polymerization of ethylene was carried out at 60°C, with 10 bar pressure of ethylene, for 1 hour. The ethylene polymerization results and

Scheme 1. Synthesis of diamine compounds 1-4.

1 (n = 2, R^1 = Me, R^2 = *i-Pr*), **2** (n = 2, R^1 = *i-Pr*, R^2 = *i-Pr*),
3 (n = 3, R^1 = Me, R^2 = Me) **4** (n = 3, R^1 = *i-Pr*, R^2 = *i-Pr*)

Scheme 2: Synthesis of complexes 5-12.

5 (M = Ti, n = 2, R^1 = Me, R^2 = *i-Pr*; **6** (M = Ti, n = 2, R^1 = *i-Pr*, R^2 = *i-Pr*; **7** (M = Ti, n = 3, R^1 = Me, R^2 = Me
8 (M = Ti, n = 3, R^1 = *i-Pr*, R^2 = *i-Pr*; **9** (M = Zr, n = 2, R^1 = Me, R^2 = *i-Pr*; **10** (M = Zr, n = 2, R^1 = *i-Pr*, R^2 = *i-Pr*
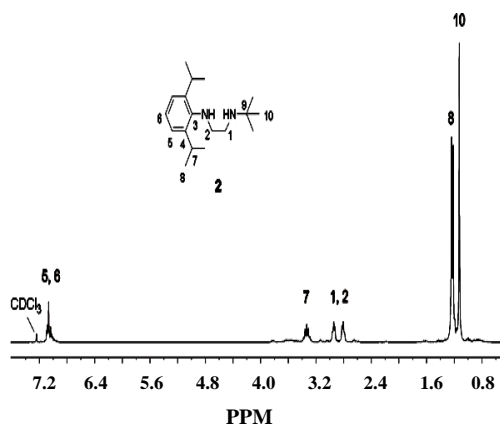**11** (M = Zr, n = 3, R^1 = Me, R^2 = Me; **12** (M = Zr, n = 3, R^1 = *i-Pr*, R^2 = *i-Pr*
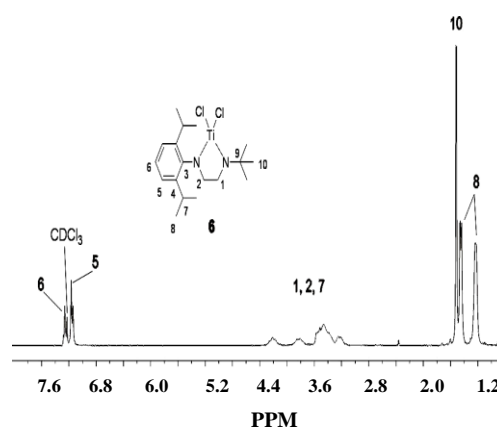

Fig. 1: ^{1}H-NMR spectrum of compound 2.

Fig. 2: ^{1}H-NMR spectrum of complex 6.

the DSC analysis data of the selected polymer samples is given in Table 1.

Complexes **5**-**12**/MAO systems show moderate activities towards ethylene polymerization. A comparison of the activities of titanium complexes **5** versus **6** and **7** versus **8** shows that complexes **6** and **8** bearing two bulky isopropyl groups on the aniline moiety give higher yields

of polyethylene as compared to **5** and **7** bearing methyl groups. A similar effect can be observed in analogous zirconium complexes **9**-**12**. The possible explanation for this effect can be derived from the fact that the presence of toluene substantially reduces the olefin polymerization activity of diamido catalysts by coordinating to the catalyst center [34,40]. The bulky alkyl groups present
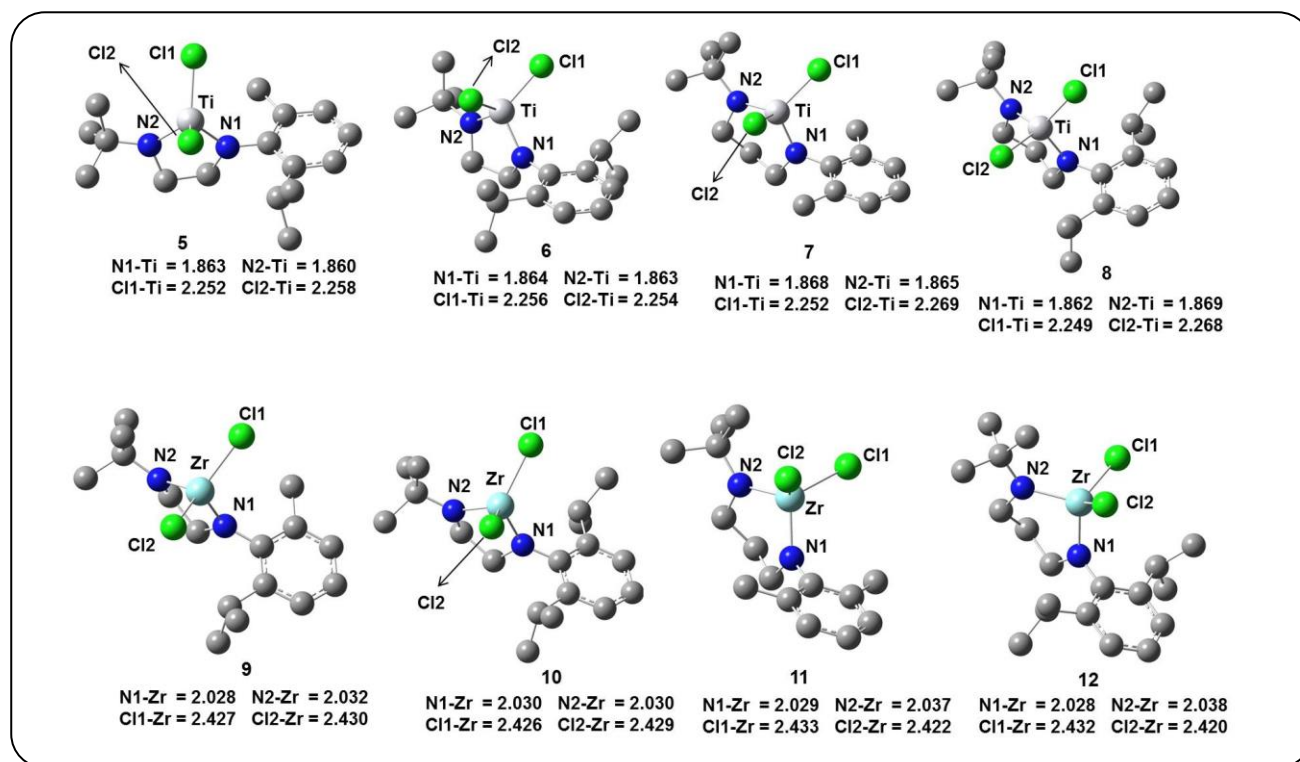
Fig. 3: Optimized geometries of complexes 5-12 (H atoms are removed for clarity, bond lengths are given in Å).

on the ligand's structure are expected to provide more protection to the catalyst center from approaching toluene molecules. Another prominent factor is the length of the chain bridging the two amido groups. Titanium complexes with ethylene bridged diamine ligands show higher activities than their zirconium analogues while zirconium complexes show higher activities with propylene bridged diamine ligands. The reason may be the formation of more stable complexes of the smaller titanium ion with ethylene bridged chelate while the comparatively bigger zirconium ion is expected to form more stable complexes with the larger propylene bridged chelates.
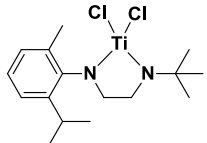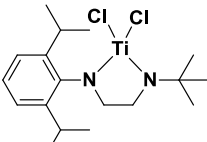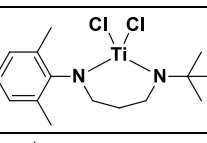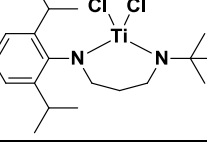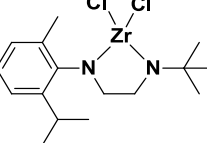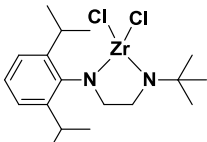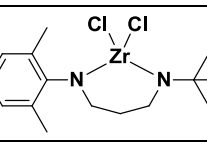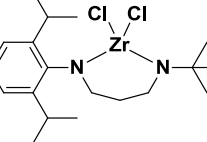
Differential Scanning Calorimetric (DSC) measurements of the polyethylene samples produced with diamido catalysts, **5**-**11** indicated that the catalysts produced high-density polyethylene with melting points > 135 °C and high degrees of crystallinity (Table 1). For example, the polyethylene sample produced by the zirconium diamido catalyst, **11** showed 138.67 °C melting temperature and 0.45 degrees of crystallinity.

Computational studies

The Cossee-Arlman mechanism has been widely accepted to interpret olefin polymerization by both metallocene and non-metallocene catalysts [49] and often applied in computational studies of olefin polymerizations [50-56]. Energy profile for Cossee-Arlman mechanistic studies of titanium complex **5** is given in Fig. 4. Methylaluminoxane activates complex **5** by extracting the two chloride ligands and alkylating with one methyl group to yield cationic complex **5Me⁺**. The cationic complex **5Me⁺** bearing one vacant coordination site is the actual olefin polymerization catalyst. Ethylene molecule coordinates at the vacant coordination site of complex **5Me⁺** to give complex **5Me⁺-C₂H₄** that is 4.7 kcal/mol more stable than the reactants. In **5Me⁺-C₂H₄** the C-C bond of coordinated ethylene (1.352Å) is longer than the C-C bond in the free ethylene molecule (1.331Å). The ethylene coordinated complex **5Me⁺-C₂H₄** undergoes ethylene insertion into M-CH₃ bond via a four centered transition state (**TS1**) to yield complex **5Pr⁺**. The activation energy for the ethylene insertion reaction is 12.2 kcal/mol and the propyl complex **5Pr⁺** is 4.5 kcal/mol more stable than the ethylene coordinated complex **5Me⁺-C₂H₄**. Coordination of another ethylene molecule with the complex **5Pr⁺** is followed by

Table 1: Polymerization and polymer data.

	Complex	Activity[a] (Kg PE/mol cat.h)	ΔH_m [J/mol]	T_m [°C]	Crystallinity (α)
5	*(Ti diamido complex structure)*	205	107.2	135.33	0.37
6	*(Ti diamido complex structure)*	263	-	-	-
7	*(Ti diamido complex structure)*	106	125.1	138.17	0.43
8	*(Ti diamido complex structure)*	190	114.1	139.83	0.39
9	*(Zr diamido complex structure)*	110	113.8	139.17	0.39
10	*(Zr diamido complex structure)*	116	128.1	137.83	0.44
11	*(Zr diamido complex structure)*	172	130.5	138.67	0.45
12	*(Zr diamido complex structure)*	209	-	-	-

a) Polymerization conditions: 250mL n-pentane, 65°C, 10 bar ethylene, 1h.
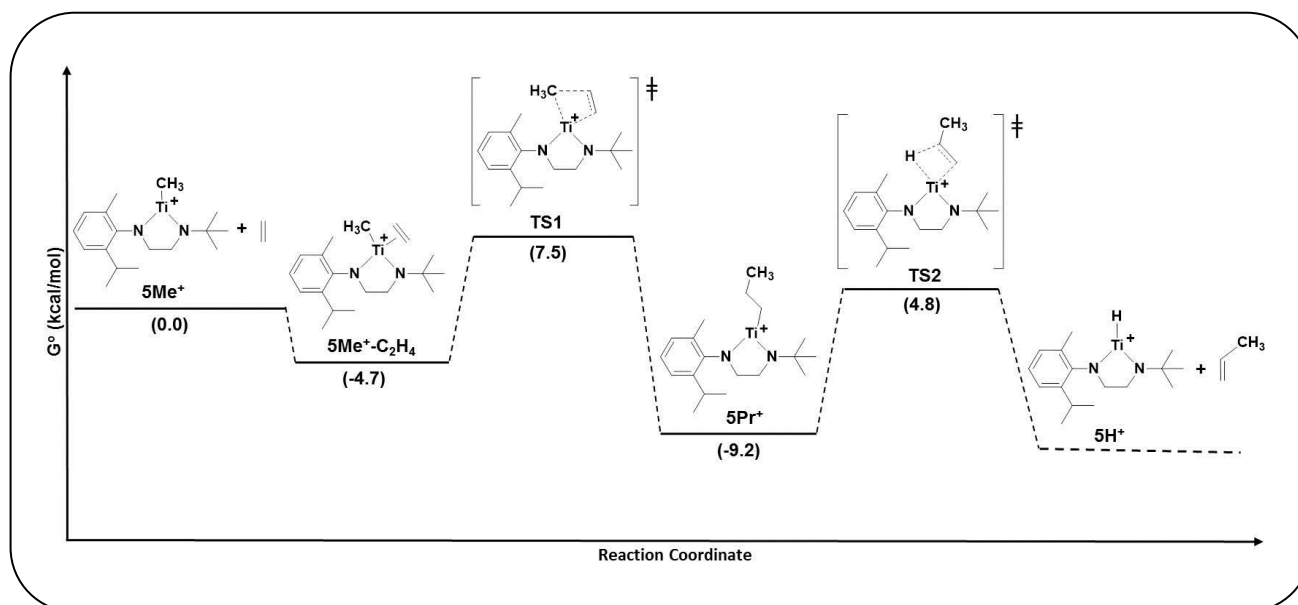
the ethylene insertion reaction. The catalytic cycle involving ethylene coordination and insertion goes on to produce alkyl chain. Finally, the produced alkyl chain is eliminated in the chain termination step. One of the widely accepted mechanisms for chain termination is the β-H transfer reaction [57]. The propyl complex **5Pr⁺** was selected as an example of the calculation of activation energy for the β-H transfer reaction. The calculated activation energy for the β-H transfer reaction (**TS2**) is 14.0 kcal/mol.

Mechanistic studies were performed on catalysts **7, 9** and **11**. The calculated Gibbs free energies for ethylene coordination, activation energies for ethylene insertion and β-H transfer reactions of catalysts **5, 7, 9** and **11** are given in Table 2. The lower activity of zirconium catalyst **9** compared with the analogous titanium catalyst **5** can be due to its high activation energies for ethylene insertion

Table 2: Gibbs free energies for ethylene coordination (ΔG_r) and activation energies for ethylene insertion (Ea-TS1)
and β-H transfer reaction (E_a-TS2) of catalysts 5, 7, 9 and 11.

Catalyst	ΔG_r (kcal/mol)	Ea-TS1 (kcal/mol)	E_a-TS2 (kcal/mol)	Experimental results (Kg PE/mol cat.h)
5	-4.7	12.2	14.0	205
7	-1.7	12.2	13.9	106
9	-5.7	16.8	14.4	110
11	-3.0	15.5	12.5	172

Fig. 4: Energy profile for different ethylene polymerization steps of 5Me+ (values within parenthesis represent Gibbs
free energy in kcal/mol).

and β-H transfer reactions. The titanium complex **7** shows lower activity than the zirconium catalyst **11** although its activation energy for ethylene insertion is lower than **11**. The reason can be the less favorable ethylene coordination reaction of catalyst **7** than **11**.

The optimized geometries of different stationary points along the ethylene polymerization pathway of catalyst **5** are shown in Fig. 5. In ethylene coordinated complex **5Me+-C₂H₄**, the C1-Ti and C2-Ti bond lengths are 2.513 and 2.598Å and the C1-C2 bond length is 1.352Å which is slightly longer than the C=C bond length in free ethylene (1.331Å). In the ethylene insertion transition state (**TS1**), the C1-C2 (1.407Å) and C3-Ti (2.115Å) bonds are longer than the corresponding C1-C2 and C3-Ti (2.065Å) bonds in **5Me+-C₂H₄**. In **TS2** C1-Ti (2.279Å) and C2-H1 (1.903Å) bonds are longer than

the corresponding C1-Ti (2.065Å) and C2-H1 (1.144Å) bonds in **5Pr+** whereas the C1-C2 bond is much shorter (1.338Å in TS2 vs 1.529Å in **5Pr+**).

CONCLUSIONS

Eight complexes of titanium and zirconium with ethylene and propylene bridged diamido ligands bearing an aniline and a tertiary butyl moiety were synthesized. These complexes were activated with methylaluminoxane and tested for ethylene polymerization. All complexes showed moderate activities for ethylene polymerization. The introduction of bulky isopropyl substituents on the aniline, moiety increased the catalytic activity of both titanium and zirconium catalysts. The titanium catalyst **8** possessing isopropyl substituents on the aniline moiety showed higher activity (190 kg PE/mol cat.h) than
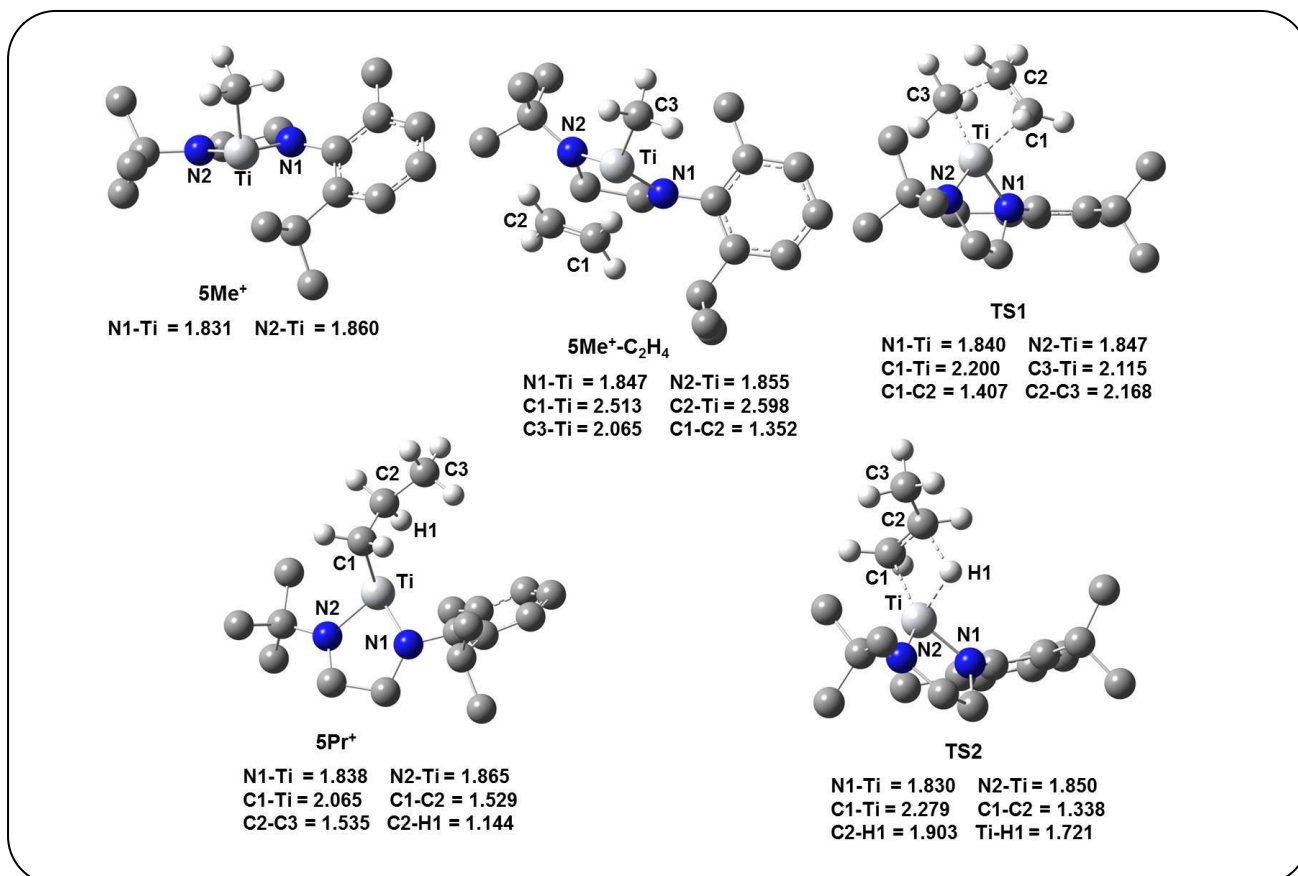
Fig. 5: Optimized geometries of 5Me⁺, 5Me⁺-C₂H₄, TS1, 5Pr⁺ and TS2 (bond lengths are given in Å).

catalyst **7** (106 kg PE/mol cat.h) with methyl substituents. Similarly, the zirconium catalyst **12** showed higher activity (209 kg PE/mol cat.h) than **11** (172 kg PE/mol cat.h). Another factor is the length of the chain bridging the two amido groups, the titanium complex **6** with an ethylene bridge showed higher activity (263 kg PE/mol cat.h) than **8** (190 kg PE/mol cat.h) with a propylene bridge. On the other hand, the zirconium complex **12** with a propylene bridge showed higher activity (209 kg PE/mol cat.h) than **10** (116 kg PE/mol cat.h) with an ethylene bridge. The DFT calculations for catalyst **5** indicated 12.2 kcal/mol activation energy for ethylene insertion into M-CH₃ bond and 14.0 kcal/mol for chain termination via β-H transfer reaction.

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