# Preparation of Diamidochloro(cyclopentadienyl)titanium Derivatives as Pre-Catalysts for Olefin Polymerization − X-ray Molecular Structure of [Ti($\eta^5$-$C_5H_5$){1,2-$C_6H_4(NCH_2CH_2CH_3)_2$}Cl] and [Ti{$\eta^5$-$C_5H_4(SiMe_3)$}-{1,2-$C_6H_4(NCH_2CH_2CH_3)_2$}Cl]

Vanessa Tabernero,[a] Tomás Cuenca,*[a] and Eberhardt Herdtweck[b]

*Dedicated to Professor José Vicente Soler on the occasion of his 60th birthday*

**Keywords:** Cyclopentadienyl ligands / N ligands / Olefin polymerization / Titanium

The synthesis of *N*,*N*′-alkyl 1,2-phenylenediamines 1,2-$C_6H_4(NHR)_2$ [R = $CH_2CH_2CH_3$ (*n*Pr), $CH_2$*t*Bu (Np)] was carried out in three steps by lithiation of the primary 1,2-phenylenediamine, reaction with the appropriate acyl chloride and reduction with $LiAlH_4$. The addition of *n*BuLi to a stirred solution of *N*,*N*′-alkyl diamines in cold hexane resulted in the immediate deposition of the corresponding lithium salts, which react with [$MCp^{R'}Cl_3$] to give the diamidochloro($\eta^5$-cyclopentadienyl)titanium and -zirconium complexes [$MCp^{R'}${1,2-$C_6H_4(NR)_2$}Cl] (**4**–**10**) [M = Ti, Zr; $Cp^{R'}$ = $\eta^5$-$C_5H_5$, $\eta^5$-$C_5(CH_3)_5$, $\eta^5$-$C_5H_4(SiMe_3)$; R = *n*Pr, Np]. The compound [Ti($\eta^5$-$C_5H_5$){1,2-$C_6H_4$(N*n*Pr)$_2$}Cl] (**3**) was obtained by treatment of [Ti($\eta^5$-$C_5H_5$)$Cl_3$] with 1,2-$C_6H_4$(NH*n*Pr)$_2$ in the presence of $NEt_3$ in toluene. All the reported compounds were characterized by the usual analytical and NMR spectroscopic methods. The molecular structures of **3** and **7** were determined by single-crystal X-ray crystallography. The compounds described here were further investigated as potential olefin polymerization catalysts.

## Introduction

The organometallic chemistry of group 4 transition metals is based largely on $\eta^5$-cyclopentadienyl (Cp) complexes, for example [$MCp_2R_2$] and [$MCpR_3$] derivatives, which doubtless figure among the best known organometallic systems.[1] Chelating diamido ligands are gaining increasing interest in early transition metal chemistry.[2] Bidentate ($N^-$,$N^-$) and tridentate ($N^-$,$N^-$,X; X = O,N) diamido ligands have been used as alternatives to $\eta^5$-cyclopentadienyl-based fragments, and non-$\eta^5$-cyclopentadienyl Group 4 metal complexes containing these ligands have been investigated as precursors for living α-olefin polymerization processes.[3] Descriptions of titanium and zirconium derivatives combining $\eta^5$-cyclopentadienyl and diamido groups are limited, but they show an interesting chemical reactivity.[4] The well-known amido($\eta^5$-cyclopentadienyl)[5] and the more recently reported diamido($\eta^5$-cyclopentadienyl)[6] derivatives are attracting increasing interest in the context of α-olefin polymerization processes. The vast majority of group 4 metallocene and related complexes used as olefin polymerization precatalysts typically have two or more abstractable or insertable alkyl (or halide) groups attached to the metal. Examples of precatalysts containing only one such group that can be actived for olefin polymerization are scarce.[5h,6,7] This paper expands this class of compounds by reporting monochlorotitanium and -zirconium complexes supported by Cp and chelating diamido ligands which are of potential interest in the context of single-site olefin polymerization catalysis.

We are interested in the synthesis and chemical behaviour of [MCp′(LL)X] derivatives (Cp′ = substituted or unsubstituted $\eta^5$-cyclopentadienyl ring; LL = chelating diamido and dialkoxo[7] ligands) and describe herein the synthesis and characterization of new chlorodiamido complexes of titanium and zirconium [$MCp^{R'}${1,2-$C_6H_4(NR)_2$}Cl] [M = Ti, Zr; $Cp^{R'}$ = $\eta^5$-$C_5H_5$, $\eta^5$-$C_5(CH_3)_5$, $\eta^5$-$C_5H_4(SiMe_3)$; R = *n*Pr, Np]. The X-ray molecular structures of [Ti($\eta^5$-$C_5H_5$){1,2-$C_6H_4$(N*n*Pr)$_2$}Cl] and [Ti{$\eta^5$-$C_5H_4(SiMe_3)$}{1,2-$C_6H_4$(N*n*Pr)$_2$}Cl] are also described. All synthesized complexes were tested as potential catalysts for ethylene and styrene polymerization after activation with MAO.

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[a] Departamento de Química Inorgánica, Universidad de Alcalá,
Campus Universitario, 28871 Alcalá de Henares, Spain
Fax: + 34-91-8854683
E-mail: tomas.cuenca@uah.es
[b] Anorganisch-chemisches Institut, Technische Universität München,
Lichtenbergstrasse 4, 85747 Garching bei München, Germany

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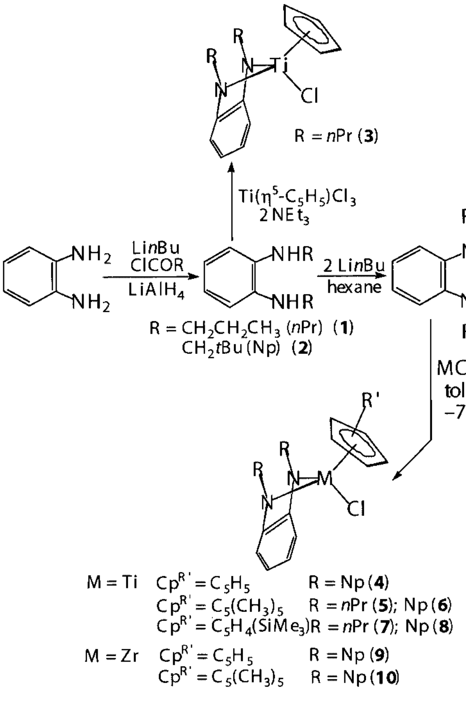
## Results and Discussion

The *N*,*N'*-alkyl-1,2-phenylenediamines 1,2-$C_6H_4(NHR)_2$ [R = *n*Pr (**1**), Np (**2**)] were synthesized in good yield from 1,2-diaminobenzene by successive *N*,*N'*-dilithiation, reaction with propionyl or trimethylacetyl chloride to give the corresponding diamide derivative, and reduction with $LiAlH_4$.[8] The propylamine was obtained as a brown oil and the neopentylamine as an orange solid. The synthesis of *N*,*N'*-bis(neopentyl)-1,2-phenylenediamine has been described previously and it has been used in the synthesis of 1,2-phenylenediaminotin(II) complexes through a transamination process.[9] The amines were spectroscopically and analytically characterized. As it was obtained as an oil, compound **1** could not be recrystallized or subjected to elemental analysis. The phenyl protons and the substituents on the nitrogen atoms exhibit a characteristic set of $^1H$ and $^{13}C\{^1H\}$ NMR resonances[10] (see Exp. Sect.).

The titanium and zirconium chelating diamido derivatives were synthesized by the usual approach based on the metathetical reaction of the dilithium salts of 1,2-phenylenediamines with the appropriate metal halide. Treatment of **1** and **2**, at −78 °C, successively with *n*BuLi in hexane and the appropriate titanium or zirconium compound [$MCp^{R'}Cl_3$] in toluene gave the corresponding mono-cyclopentadienyl chlorodiamido titanium and zirconium complexes [$MCp^{R'}\{1,2\text{-}C_6H_4(NR)_2\}Cl$] (**4−10**) [M = Ti, Zr; $Cp^{R'}$ = $\eta^5$-$C_5H_5$, $\eta^5$-$C_5(CH_3)_5$, $\eta^5$-$C_5H_4(SiMe_3)$; R = *n*Pr, Np] (Scheme 1). Similar attempts to obtain *N*,*N'*-dipropyl-1,2-phenylenediamidozirconium derivatives were unsuccessful, which may be attributed to the larger size of zirconium compared with titanium, favouring β-elimination decomposition pathways. The compound [Ti($\eta^5$-$C_5H_5$){1,2-$C_6H_4(NnPr)_2$}Cl] (**3**) was synthesized by reaction of [Ti($\eta^5$-$C_5H_5$)$Cl_3$] with 1,2-$C_6H_4(NHnPr)_2$ in the presence of $NEt_3$ in toluene. Group 4 metal phenylenediamido complexes of the non-cyclopentadienyl type[2d,9] $M(NN)X_2$ and monocyclopentadienyl[4c] type MCp''(NN)X have recently been reported.



Scheme 1

Complexes **3−10** were obtained as black or red-brown solids, soluble in aromatic hydrocarbons, dichloromethane, chloroform, diethyl ether and alkanes (hexane and pentane). Their purification was difficult, as they are highly soluble in alkanes and polar solvents. They are both air and moisture sensitive in solution and in the solid state, although they can be stored unaltered for weeks under an inert atmosphere. The complexes were characterized by the usual analytical and spectroscopic methods. The elemental analysis values found for **8** were inaccurate due to the presence of a small amount of LiCl in the mixture, which could not be removed.

Most importantly in this type of complexes, the diamido ligand can adopt different coordination modes[4e,11] and has two possible conformations (*supine* or*prone*)[12] relative to the cyclopentadienyl ring. The $^1H$ NMR spectra ($C_6D_6$ and $CDCl_3$, room temperature) show the presence of only one species, ruling out a mixture of the two rotamers (*supine-prone* automerization) observed in solutions of similar monocyclopentadienyl diene complexes.[4d,4e] The spectra show the expected resonances for the cyclopentadienyl rings: one singlet for the $C_5H_5$ and the $C_5Me_5$ protons and two sets of pseudo triplets for the $C_5H_4(SiMe_3)$ ring protons, corresponding to an AA'BB' spin system. The $^1H$ NMR resonances of the cyclopentadienyl protons appear as signals at $\delta$ = 6.20−6.30 ppm for Cp, $\delta$ = 6.40−6.73 ppm for $CpSiMe_3$ and $\delta$ = 1.65−1.75 ppm for $C_5Me_5$. Such shifts suggest that the cyclopentadienyl protons are not influenced by phenylene magnetic anisotropy[13] and lead us to propose that the phenylenediamido ligand adopts a *supine* conformation.[4c] The methyl protons of the $SiMe_3$ group exhibit one singlet ($\delta$ = 0.25−0.26 ppm). The spectra for compounds **3** and **7** show sets of multiplet, multiplet and triplet for the N-$CH_2$-$CH_2$-$CH_3$ fragment protons, respectively, while two multiplets for the N−$CH_2$ protons are observed in the spectrum of the pentamethylcyclopentadienyl derivative **5**. These data indicate the diastereotopic nature of the methylene protons bonded to the nitrogen atom. In the spectra of compounds **4**, **6**, and **8−10** in $C_6D_6$, the neopentyl groups show a singlet for the methyl protons and a doublet of doublets corresponding to the diastereotopic methylene protons. Similar spectroscopic features indicate that the neopentyl-group signals in the spectra of compounds **4**, **6**, **8** and **9** in $CDCl_3$ exhibit a diastereotopic behaviour for the N−$CH_2$ protons, while the spectrum of **10** in $CDCl_3$ shows only one singlet assignable to these protons. Characteristic low-field chemical shift trends are observed for the N−$CH_2$ protons on going from free diamine ($\delta$ = 2.6 ppm for **1** and $\delta$ = 2.8 ppm for **2**) to an amido coordination mode to the Lewis acid titanium atom in complexes **3−10** ($\delta$ = 4−3.5 ppm). The phenyl protons appear as two multiplets in the usual range.

In the $^{13}C$ NMR spectra of the free diamines **1** and **2** the signals of the imine C-atoms are observed at $\delta$ = 138 and 138.9 ppm, respectively. The corresponding resonances for the titanium and zirconium complexes are found at higher field, at around $\delta$ = 125 ppm and $\delta$ = 137 ppm for the neopentyl and propyl derivatives, respectively. These spectroscopic data are in agreement with $C_s$ symmetry, consistent with the presence of a mirror plane containing the Ti and Cl atoms and bisecting the N−Ti−N angle of the chelate diamido ligand.

A nuclear Overhauser enhancement (NOE) study of the complexes[12c,12d] containing the Cp ligand confirms this proposal. Irradiation of the Cp signal of the propyl derivative **3** results in a significant NOE enhancement of the $CH_2$ signals, while irradiation of the Cp signal of the neopentyl derivative **4** results in significant NOE enhancements in the *t*Bu and the $CH_2$ signals. Irradiation of the Cp signals of **3** and **4** does not cause NOE enhancements in the phenyl signals. These observations suggest that the propyl and neopentyl groups are in close proximity to the Cp ring, with the diamido ligand adopting a *supine* conformation, consistent with the disposition found in the solid state from the X-ray structural analysis of **3** and **7**.

### Crystal Structure of [Ti($\eta^5$-$C_5H_5$){1,2-$C_6H_4$(N*n*Pr)$_2$}Cl] (3) and [Ti{$\eta^5$-$C_5H_4$($SiMe_3$)}{1,2-$C_6H_4$(N*n*Pr)$_2$}Cl] (7)

In order to establish the solid-state molecular geometry for compounds of this type, X-ray crystal-structure analyses of **3** and **7** were carried out. Single crystals of **3** and **7** obtained by slow recrystallization from hexane solution were of good enough quality to be analyzed by X-ray diffraction. The crystal structure of **3** is shown in Figure 1 and Table 1 summarizes selected bond lengths and angles.

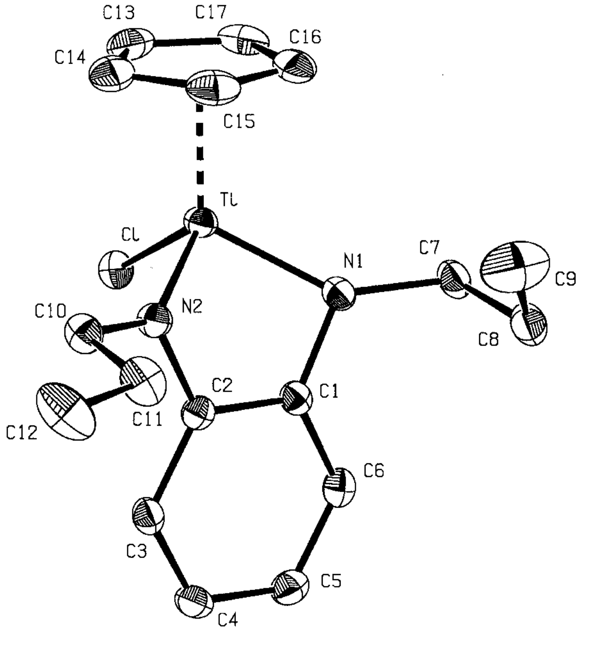


Figure 1. ORTEP representation of [Ti($\eta^5$-$C_5H_5$){1,2-$C_6H_4$($NCH_2CH_2CH_3$)2}Cl] (**3**) in the solid state; thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity

Table 1. Selected interatomic distances (Å) and angles (deg) for complexes **3** and **7**

| | **3** | **7** |
|---|---|---|
| Ti−Cl | 2.3270(5) | 2.3101(5) |
| Ti−N1 | 1.9018(14) | 1.9034(13) |
| Ti−N2 | 1.9014(13) | 1.9048(12) |
| Ti−C13 | 2.358(2) | 2.379(2) |
| Ti−C14 | 2.354(2) | 2.353(2) |
| Ti−C15 | 2.350(2) | 2.364(2) |
| Ti−C16 | 2.351(2) | 2.371(2) |
| Ti−C17 | 2.355(2) | 2.366(2) |
| Ti−Cg[a] | 2.029 | 2.038 |
| N1−C1 | 1.396(2) | 1.396(2) |
| N1−C7 | 1.461(2) | 1.461(2) |
| N2−C2 | 1.399(2) | 1.398(2) |
| N2−C10 | 1.456(2) | 1.464(2) |
| Cl−Ti−N1 | 104.46(4) | 105.64(4) |
| Cl−Ti−N2 | 108.22(4) | 104.51(4) |
| Cl−Ti−Cg | 117.64 | 119.77 |
| N1−Ti−N2 | 89.69(5) | 89.48(5) |
| N1−Ti−Cg | 117.46 | 116.34 |
| N2−Ti−Cg | 115.52 | 116.44 |
| Ti−N1−C1 | 95.24(9) | 97.05(9) |
| Ti−N1−C7 | 144.13(10) | 142.14(10) |
| C1−N1−C7 | 119.01(13) | 119.42(12) |
| Ti−N2−C2 | 95.37(10) | 96.63(9) |
| Ti−N2−C10 | 144.51(11) | 141.55(11) |
| C2−N2−C10 | 118.96(13) | 119.59(12) |

[a] Cg denotes the centroid of the Cp ligand.

The compound is monomeric with a tetrahedral coordination geometry around the titanium atom which coordinated by an $\eta^5$-cyclopentadienyl ring, a chloride ligand and the two nitrogen atoms of the symmetrically chelated diamido ligand. The structure contains a non-crystallographic plane of symmetry containing the cyclopentadienyl and phenylene ring centroids, the metal centre and the chlorine atom. As expected from the NMR spectroscopic data (solution studies), the phenylenediamido ligand adopts a *supine* conformation in the solid state, which minimizes the steric interaction with the Cp ring, although a *prone* conformation of the amido ligand in analogous monocyclopentadienyl diazadiene group 4 and 5 metal complexes has also been observed.[4d,4e] The nature of the alkyl substituents in the nitrogen atom seems to have a dramatic effect on the conformation geometry that the diene ligands adopt in half-sandwich complexes. In the literature, the *supine* conformation preferred for the *n*Pr substituents and the *prone* conformation preferred for the *t*Bu substituents have been found.[12d,14] Unfortunately, we were not successful in preparing crystals of the Np derivatives suitable for X-ray diffraction studies, although we propose that, as in compound **3**, a *supine* conformation can also be expected for Np derivatives in the solid state.

The titanium atom is located out of the plane defined by Cl and the nitrogen atoms [distance from Ti to N(1)−N(2)−Cl plane of 0.923(1) Å] which is almost parallel to the cyclopentadienyl ring with an interplanar angle of 4.6(1)°. The trigonal-planar geometry of the nitrogen atom, corresponding to $sp^2$ hybridization, is evidenced by the sums of the angles at N(1) (358.4°) and N(2) (358.8°) and the comparatively short Ti−N bond lengths of 1.9018(14) and 1.9014(13) Å, which point to a significant pπ-dπ interaction and are in agreement with reported values for related titanium amido[2d,2e,15] complexes. The N−Ti−N angle is 89.69(5)°. The Ti−C(1) and Ti−C(2) distances [2.4600(15) and 2.4635(15) Å] are long enough to allow donation of electron density from the C(1)−C(2) bond to the titanium atom. The phenylene ring shows a marked deformation. Thus, the C(1)−C(2) [1.427(2) Å] distance is significantly elongated with respect to the rest of the C−C distances in the ring (average 1.390 Å). These Ti−C and C(1)−C(2) bond lengths are longer and shorter, respectively, than similar distances reported for related diazadiene complexes[4d,4e] in which a π interaction between the double diene C−C bond and the metal centre is observed. The N−C bond lengths are 1.396(2) and 1.399(2) Å for N(1)−C(1) and N(2)−C(2), respectively, showing slight double-bond character,[16] while the N−C(Pr) bond lengths of 1.461(2) for N(1)−C(7) and 1.456(2) for N(2)−C(10) are consistent with single bonds.

The five-membered chelate ring is not planar and the phenylenediamido ligand is folded along the N(1)···N(2) vector with a fold angle, Θ, of 49.77(7)°. Similar folding has previously been interpreted in terms of $\kappa^4$-$\sigma^2$(N,N),π(C=C) bonding.[2e,4c,17] However, our results indicate this situation to be unlikely here.[9b]

The titanium-chlorine bond length is 2.3270(5) Å, slightly longer that those found for related monocyclopentadienyl- and dicyclopentadienyl-type chloride complexes.

The crystal structure of **7** is shown in Figure 2 and Table 1 summarizes selected bond lengths and angles. The structural parameters in the Ti-core of **7** are similar to those observed in compound **3**. The Cp ligand is oriented such that the $SiMe_3$ group is located in the plane bisecting the N−Ti−N angle and in a *trans* position with respect to the phenylene ligand.

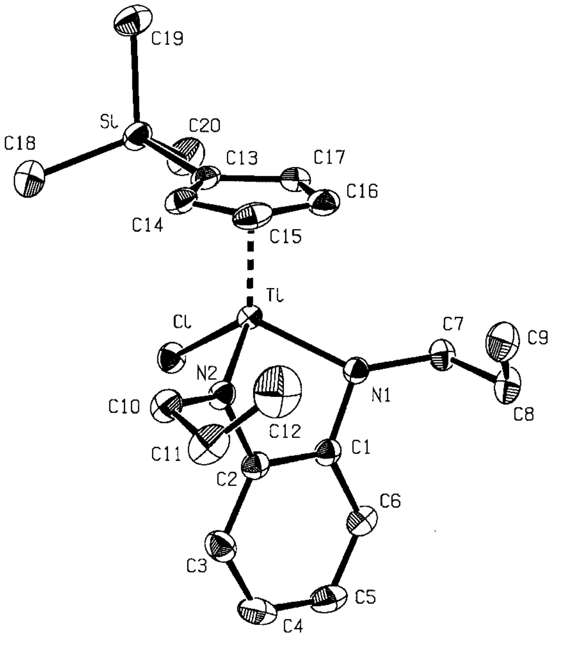
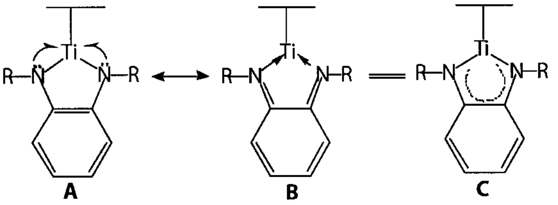


Figure 2. ORTEP representation of [Ti{$\eta^5$-$C_5H_4(SiMe_3)$}{1,2-$C_6H_4(NCH_2CH_2CH_3)_2$}Cl] (**7**) in the solid state; thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity

Various coordination modes[11] [from $\eta^1$-N to $\eta^4$-$N_2C_2$ ($\sigma^2$,π)] can be proposed for the diamido ligands, where the N substituents regulate the steric demands at the metal centre. The bonding of the phenylenediamido ligand in compounds **3−10** can be best described by a $\sigma^2$,*N*,*N* bond with a partial pπ-dπ nitrogen interaction (form **A** in Scheme 2) and electronic density delocalization through the N−C−C−N bond system (form **B** in Scheme 2) consistent with the resonance hybrid form **C**, and such a ligand can therefore produce more electronically saturated complexes, consistent with a dianionic moiety that can donate between four and six electrons to the metal centre. The phenylenediamido ligand can therefore be considered as a $\sigma^2$,π-enediamide group structure in which the π-component is mainly contributed by the two nitrogen lone pairs.[18]



Scheme 2

## Olefin Polymerization

Complexes **3−8** were studied as α-olefin polymerization pre-catalysts with methylalumoxane (MAO) as cocatalyst.

Ethylene polymerization was investigated using 50 mL total volume of toluene with 10−20 µmol of catalyst, with a Al/Ti molar ratio of 1000 at 25 °C and 1 atm pressure. The results are summarized in Table 2. Only traces of polymer or no polymerization were found when the reaction was carried out with propylene. Polymerization runs with the *n*Pr complexes resulted in moderate[19] activity (approx. 100 g of PE/mmol of Ti·atm·h) of PE with activity increasing in the order **7** < **5** < **3**. This result indicates that the activity is

Table 2. Polymerization of ethylene by [TiCp$^{R'}${1,2-$C_6H_4(NR)_2$}Cl]

| Entry | Catalyst[a] | Activity[b] | $\Delta H_m$ ($J\cdot g^{-1}$)[c] | $\alpha$ ($\Delta H_m/\Delta H^\circ_m$) | $T_m$ (°C)[c] |
|---|---|---|---|---|---|
| 1 | **3** | 150 | 72.85 | 25 | 134 |
| 2 | **4** | traces | − | − | − |
| 3 | **5** | 130 | 100.40 | 35 | 131 |
| 4 | **6** | 110 | 57.56 | 20 | 135 |
| 5 | **7** | 70 | 27.56 | 95 | 131 |
| 6 | **8** | 80 | 116.7 | 40 | 130 |

[a] Reaction conditions: temperature = 25 °C; pressure = 1 atm; 10−20 µmol of catalyst; molar ratio Al:Ti = 1000. [b] gPE/mmol Ti·atm·h. [c] Determined by DSC.

influenced greatly by the nature of the cyclopentadienyl substituents. A lower activity was observed for the Np derivatives. The activities of these chloro pre-catalyst systems are lower[20] than those found for the well-known non-cyclopentadienyl group 4 complexes containing chelating diamido ligands;[2c,2i,3a,3b,3d,20] rapid deactivation pathways[15d,21] of these chloro compounds after the reaction with MAO or TMA (present in MAO) could be a possible explanation for this behaviour.

The PE polymer samples obtained had melting points of 130−135 °C, characteristic of high density polyethylene, and remarkable differences in the $\Delta H$ enthalpy values. The degree of crystallinity ($a$) found for these PEs was lower than that expected for commercial HDPE, suggesting that chain branching occurs during the polymerization process.[22]

Styrene polymerization was studied using 35 mL total volume of toluene and 5 mL of monomer; the results are summarized in Table 3. For the *n*Pr derivatives, the activity for **3**/MAO was higher than for the system **7**/MAO; a lower activity was found for **5**/MAO (runs 1, 5 and 3, Table 3), indicating that the cyclopentadienyl ligands exert a strong influence on the activity of the catalyst and the order of activity is lower than that obtained for [CpTiCl$_3$] (used as a reference point) under similar conditions.[23] The polymers were precipitated in acidified MeOH, and syndiotactic polystyrene was obtained, as evidenced by NMR spectroscopic analysis and the melting point values.[24]

Table 3. Polymerization of styrene with [TiCp$^{R'}${1,2-C$_6$H$_4$(NR)$_2$}-Cl]

| Entry | Catalyst[a] | Activity[b] | $T_m$ (°C)[c] |
|---|---|---|---|
| 1 | **3** | 536 | 256 |
| 2 | **4** | 146 | 253 |
| 3 | **5** | 245 | 274 |
| 4 | **6** | 68 | 277 |
| 5 | **7** | 480 | 266 |
| 6 | **8** | 120 | 266 |

[a] Reaction conditions: temperature = 50 °C; molar ratio Al:Ti = 1000; solvent = toluene (35 mL); monomer = styrene (5 mL). [b] gPS/mmol Ti·h. [c] Determined by DSC.

It is a general observation that the complexes containing the *n*Pr amido ligand show higher polymerization activities than the Np derivatives, suggesting that the activity is highly influenced by the steric effect[25] at the titanium centre caused by *n*-propyl or neopentyl substituents at the nitrogen atom of the diamido ligand. Similar examples of the influence of bulky substituents on catalytic polymerization activity have been observed for related amidinate complexes.[26]

Attempts to copolymerize styrene/ethylene were unsuccessful and afforded a mixture of the two homopolymers.

The precatalyst complexes **3−8** have only one chloro ligand. We assume that initially the MAO cocatalyst reacts with these complexes by methyl−halide exchange to afford Ti−Me derivatives, followed by cleavage of one of the Ti−N bonds by the AlMe$_3$ component in the MAO cocatalyst to generate active cationic alkyl species in a Ziegler−Natta olefin polymerization model.[27]

## Conclusions

In this contribution we have described the synthesis and the characterization of new chloro mono(η$^5$-cyclopentadienyl)phenylenediamidotitanium and -zirconium complexes. X-ray diffraction studies confirm that compounds with *n*Pr substituted at the nitrogen atom adopt a *supine* conformation in the solid state which is maintained in solution, as deduced from the NMR spectroscopic data. The phenylenediamido ligand is bonded to the metal centre as a dianionic ligand showing a $\sigma^2,\pi$ structure in which the π-component is mainly contributed by the two nitrogen lone pairs. NMR spectroscopic studies indicate that in solution at room temperature only one species is present, with a *supine* conformation, and no *supine-prone* automerization (flipping of the titanium-diamido framework) is observed. The catalytic activity of these compounds for olefin polymerization, when activated with MAO, was tested and studied. The steric effect of the *n*-propyl or neopentyl substituents at the nitrogen atom of the diamido ligand, and the nature of the cyclopentadienyl ring, strongly influenced catalytic polymerization activity.

## Experimental Section

**General Considerations:** All manipulations were performed under argon using Schlenk and high-vacuum-line techniques or in a glove box model MO40-2. The solvents were purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent. Deuterated solvents were stored over activated 4-Å molecular sieves and degassed by several freeze-thaw cycles. 1,2-Diphenylamine, *n*BuLi, ClCOCH$_2$CH$_3$, ClCOC(CH$_3$)$_3$, LiAlH$_4$ and MgSO$_4$ (Aldrich) were purchased from commercial sources and used without further purification. NEt$_3$ (Aldrich) was distilled before use and stored over 4 Å molecular sieves. [Ti(η$^5$-C$_5$H$_5$)Cl$_3$],[28] [Ti(η$^5$-C$_5$Me$_5$)Cl$_3$],[29] [Ti(η$^5$-C$_5$H$_4$SiMe$_3$)Cl$_3$],[30] [Zr(η$^5$-C$_5$H$_5$)Cl$_3$]·DME[31] and [Zr(η$^5$-C$_5$Me$_5$)Cl$_3$][32] were prepared by known procedures.

Polymerization-grade ethylene was used as received. Reagent grade styrene (Aldrich) was distilled under reduced pressure from calcium hydride and stored in a refrigerator under argon. The polymerization solvent (toluene) was dried by refluxing over sodium-benzophenone and distilled before used in an inert atmosphere. MAO (Witco 10%) was used as a solution in toluene.

C, H and N microanalyses were performed on a Perkin−Elmer 2400 microanalyzer. The analytical data found for **8** deviated from expected values since LiCl could not be completely removed from the mixture. NMR spectra, measured at 25 °C were recorded on a Varian Unity FT-300 ($^1$H NMR at 300 MHz, $^{13}$C NMR at 75 MHz) spectrometer and chemical shifts were referenced to residual solvent protons.

**1,2-C$_6$H$_4$(NHCH$_2$CH$_2$CH$_3$)$_2$ (1):** *n*BuLi (100 mL of a 1.6 M solution, 160 mmol) was added dropwise to a solution of 1,2-phenylenediamine (8.6 g, 79.27 mmol) in 100 mL of THF at −78 °C. After stirring the reaction mixture for 12 hours, $ClCOCH_2CH_3$ (13.85 mL, 160 mmol) was added and the mixture stirred for an additional 4 h. The reaction mixture was slowly warmed to room temperature to give an orange solution and a white precipitate. After filtration, the solvent was reduced to half of its original volume under vacuum and a suspension of $LiAlH_4$ (10.0 g, 260 mmol) in 50 mL of diethyl ether was added dropwise. After stirring the solution for 12 h at 40 °C, excess $LiAlH_4$ was destroyed by addition of a saturated solution of $Na_2SO_4$. The solid precipitate was removed by filtration and the solution dried with $MgSO_4$. Removal of the solvent under vacuum gave a brown oil characterized as **1** (1.24 g, 8%). The compound was obtained as an oil that could not be recrystallized, preventing us from obtaining accurate elemental analysis data. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 6.96$ (m, 2 H, Ph), 6.72 (m, 2 H, Ph), 2.98 (broad, 2 H, NH), 2.78 (t, 4 H, $N-CH_2$), 1.34 (m, 4 H, $CH_2$), 0.78 (t, 6 H, $CH_3$) ppm. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.78$ (m, 2 H, Ph), 6.70 (m, 2 H, Ph), 3.24 (broad, 2 H, NH), 3.07 (t, 4 H, $N-CH_2$), 1.70 (m, 4 H, $CH_2$), 1.03 (t, 6 H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 138.0$ (*ipso*-Ph), 119.7−112.2 (Ph), 46.5 ($CH_2$), 23.2 ($CH_2$), 11.9 ($CH_3$) ppm.

**1,2-$C_6H_4(NHCH_2$*t*Bu)$_2$ (2):** The amine *o*-$C_6H_4(NHCH_2C$*t*Bu)$_2$ (**2**) was obtained as an orange solid (7.98 g, 32.15 mmol, 41%) following the procedure described for **1**, from *n*BuLi (100 mL, 160 mmol), 1,2-phenylenediamine (8.6 g, 79.0 mmol), $ClCOC(CH_3)_3$ (19.53 mL, 160 mmol) and $LiAlH_4$ (10.0 g, 260 mmol). $C_{16}H_{28}N_2$ (248.16): calcd. C 77.43, H 11.28, N 11.28; found C 76.72, H 11.53, N 11.34. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 7.00$ (m, 2 H, Ph), 6.74 (m, 2 H, Ph), 3.27 (broad, 2 H, NH), 2.67 (s, 4 H, $N-CH_2$), 0.88 (s, 18 H, *t*Bu) ppm. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.74$ (m, 2 H, Ph), 6.69 (m, 2 H, Ph), 3.30 (broad, 2 H, NH), 2.82 (s, 4 H, $N-CH_2$), 1.02 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 138.9$ (*ipso*-Ph), 119.9−113.0 (Ph), 56.6 ($CH_2$), 31.5 (*ipso*-*t*Bu), 27.9 (*t*Bu) ppm.

**[Ti($\eta^5$-$C_5H_5$){1,2-$C_6H_4(NCH_2CH_2CH_3)_2$}Cl] (3):** A toluene solution (30 mL) of *o*-$C_6H_4(NHPr)_2$ (0.84 g, 4.37 mmol) and $NEt_3$ (1.22 mL, 8.74 mmol) was added to a yellow solution of [Ti($\eta^5$-$C_5H_5$)$Cl_3$] (0.96 g, 4.37 mmol) in toluene (60 mL) at −78 °C. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature with stirring for 12 h. The solid formed was collected by filtration and the toluene removed under vacuum. The residue was extracted with pentane (2 × 30 mL). The filtrate was dried and the solid obtained recrystallized from cold pentane to give **3** as a black solid (1.16 g, 3.43 mmol, 78%). $C_{17}H_{23}ClN_2Ti$ (338.49): calcd. C 60.32, H 6.80, N 8.27; found C 60.02, H 6.72, N 8.03. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 7.36$ (m, 2 H, Ph), 6.97 (m, 2 H, Ph), 6.23 (s, 5 H, $C_5H_5$), 3.70 (t, 4 H, $CH_2$), 1.32 (m, 4 H, $CH_2$), 0.58 (t, 6 H, $CH_3$) ppm. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.48$ (m, 2 H, Ph), 7.11 (m, 2 H, Ph), 6.55 (s, 5 H, $C_5H_5$), 4.05 (t, 4 H, $CH_2$), 1.50 (m, 4 H, $CH_2$), 0.81 (t, 6 H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 137.8$ (*ipso*-Ph), 127.0, 116.1 (Ph), 114.8 ($C_5H_5$), 58.9 ($N-CH_2$), 24.6 ($CH_2$), 11.6 ($CH_3$) ppm.

**[Ti($\eta^5$-$C_5H_5$){1,2-$C_6H_4(NCH_2$*t*Bu)$_2$}Cl] (4):** *n*BuLi (4.50 mL of an 1.6 M solution, 7.26 mmol) was added dropwise to a stirred solution of *o*-$C_6H_4(NHCH_2$*t*Bu)$_2$ (0.90 g, 3.63 mmol) in 50 mL of hexane at −78 °C. After the addition was complete, the reaction mixture was stirred for 6 hours and then slowly warmed to room temperature; a white precipitate formed. This suspension was cooled to −78 °C and a solution of [Ti($\eta^5$-$C_5H_5$)$Cl_3$] (0.80 g, 3.63 mmol) in 50 mL of toluene was added. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. After filtration, the solvent was removed under vacuum to give a red-brown oil which was recrystallized from cold hexane. A red-brown solid was collected which was characterized as **4** (0.64 g, 1.66 mmol, 45%). $C_{21}H_{31}ClN_2Ti$ (394.58): calcd. C 63.92, H 7.86, N 7.10; found C 63.55, H 7.97, N 7.10. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 7.33$ (m, 2 H, Ph), 7.25 (m, 2 H, Ph), 6.31 (s, 5 H, $C_5H_5$), 3.88 (dd, 4 H, $CH_2$), 0.63 (s, 18 H, *t*Bu) ppm. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.48$ (m, 2 H, Ph), 7.41 (m, 2 H, Ph), 6.51 (s, 5 H, $C_5H_5$), 4.17 (dd, 4 H, $CH_2$), 0.75 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 127.8$, 119.2 (Ph), 122.3 (*ipso*-Ph), 115.1 ($C_5H_5$), 67.2 ($CH_2$), 35.7 (*ipso*-*t*Bu), 28.8 (*t*Bu) ppm.

**[Ti($\eta^5$-$C_5Me_5$){1,2-$C_6H_4(NCH_2CH_2CH_3)_2$}Cl] (5):** Compound **5** was prepared from the reaction of the *o*-$C_6H_4(NHPr)_2$ amine (0.81 g, 4.22 mmol), 8.44 mmol of *n*BuLi and [Ti($\eta^5$-$C_5Me_5$)$Cl_3$] (1.22 g, 4.22 mmol) by the procedure described for **4**, and obtained as a black oil (1.59 g, 3.90 mmol, 92%). $C_{22}H_{33}ClN_2Ti$ (408.54): calcd. C 64.67, H 8.08, N 6.85; found C 64.80, H 8.76, N 6.30. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 7.30$ (m, 2 H, Ph), 6.89 (m, 2 H, Ph), 3.88 (m, 1 H, $N-CH_2$), 3.57 (m, 1 H, $N-CH_2$), 1.75 (s, 15 H, $C_5Me_5$), 1.64 (m, 4 H, $CH_2$), 0.80 (t, 6 H, $CH_3$) ppm. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.26$ (m, 2 H, Ph), 7.01 (m, 2 H, Ph), 4.00 (m, 1 H, $N-CH_2$), 3.81 (m, 1 H, $N-CH_2$), 1.93 (s, 15 H, $C_5Me_5$), 1.59 (m, 4 H, $CH_2$), 0.88 (t, 6 H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 124.5$, 114.1 (Ph), 122.9 (*ipso*- $C_5Me_5$), 54.5 ($N-CH_2$), 23.5 ($CH_2$), 12.5 ($CH_3$), 11.4 ($C_5$*Me*$_5$) ppm; the signal for *ipso* Ph was not observed

**[Ti($\eta^5$-$C_5Me_5$){1,2-$C_6H_4(NCH_2$*t*Bu)$_2$}Cl] (6):** Compound **6** was prepared by reacting of the *o*-$C_6H_4(NHCH_2$*t*Bu)$_2$ amine (0.85 g, 3.42 mmol), 6.85 mmol of *n*BuLi and [Ti($\eta^5$-$C_5Me_5$)$Cl_3$] (1.00 g, 3.45 mmol) by the procedure described for **4**, and obtained as a red-brown oil (0.90 g, 1.94 mmol, 56%). $C_{26}H_{41}ClN_2Ti$ (464.58): calcd. C 67.21, H 8.89, N 6.02; found C 67.26, H 8.84, N 6.17. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 7.23$ (m, 2 H, Ph), 7.19 (m, 2 H, Ph), 3.97 (dd, 4 H, $CH_2$), 1.63 (s, 15 H, $C_5Me_5$), 0.90 (s, 18 H, *t*Bu) ppm. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.38$ (m, 2 H, Ph), 7.36 (m, 2 H, Ph), 3.96 (dd, 4 H, $CH_2$), 1.65 (s, 15 H, $C_5Me_5$), 0.75 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 125.0$, 117.4 (Ph), 122.7 (*ipso*-Ph), 121.0 (*ipso*-$C_5Me_5$), 62.1 ($N-CH_2$), 37.6 (*ipso*-*t*Bu), 29.6 (*t*Bu), 11.1 (*C*$_5$Me$_5$) ppm.

**[Ti{$\eta^5$-$C_5H_4(SiMe_3)$}{1,2-$C_6H_4(NCH_2CH_2CH_3)_2$}Cl] (7):** Compound **7** was prepared by reacting the *o*-$C_6H_4(NHPr)_2$ amine (1.7 g, 8.85 mmol), 17.70 mmol of *n*BuLi and [Ti{$\eta^5$-$C_5H_4(SiMe_3)$}$Cl_3$] (2.50 g, 8.85 mmol) by the procedure described for **4**, and obtained as a black oil (2.5 g, 6.09 mmol, 69%). $C_{20}H_{31}ClN_2SiTi$ (410.52): calcd. C 58.51, H 7.98, N 6.82; found C 58.61, H 7.98, N 6.26. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 7.34$ (m, 2 H, Ph), 6.96 (m, 2 H, Ph), 6.57, 6.40 (2 H, 2 H, AA′BB′ spin system, $C_5H_4$), 3.82 (m, 4 H, $CH_2$), 1.33 (m, 4 H, $CH_2$), 0.60 (t, 6 H, $CH_3$), 0.32 (s, 6 H, $SiMe_3$) ppm. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.43$ (m, 2 H, Ph), 7.08 (m, 2 H, Ph), 6.66, 6.65 (2 H, 2 H, AA′BB′ spin system, $C_5H_4$), 4.08 (m, 4 H, $CH_2$), 1.46 (m, 4 H, $CH_2$), 0.78 (t, 6 H, $CH_3$), 0.25 (s, 6 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta = 137.8$ (*ipso*-Ph), 125.6 (*ipso*-$C_5H_4$), 127.0, 116.7 (Ph), 121.8, 116.4 ($C_5H_4$), 59.3 ($CH_2$), 24.4 ($CH_2$), 11.7 ($CH_3$), −0.04 ($SiMe_3$) ppm.

**[Ti{$\eta^5$-$C_5H_4(SiMe_3)$}{1,2-$C_6H_4(NCH_2$*t*Bu)$_2$}Cl] (8):** Compound **8** was prepared by reacting the *o*-$C_6H_4(NHCH_2$*t*Bu)$_2$ amine (0.50 g, 2.00 mmol), 4.03 mmol of *n*BuLi and [Ti{$\eta^5$-$C_5H_4(SiMe_3)$}$Cl_3$] (0.59 g, 2.00 mmol) by the procedure described for **4**, and obtained as a red-brown oil (0.60 g, 1.28 mmol, 64%). The isolated oil consisted mainly of **8**, but it contained some unremovable LiCl as an impurity and therefore correct elemental analysis data could not be obtained, although satisfactory spectroscopic data were obtained. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 7.31 (m, 2 H, Ph), 7.24 (m, 2 H, Ph), 6.73, 6.38 (2 H, 2 H, AA′BB′ spin system, $C_5H_4$), 4.02 (dd, 4 H,, $CH_2$), 0.68 (s, 18 H, *t*Bu), 0.37 (s, 9 H, $SiMe_3$) ppm. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.47 (m, 2 H, Ph), 7.40 (m, 2 H, Ph), 6.69, 6.55 (2 H, 2 H, AA′BB′ spin system, $C_5H_4$), 4.25, 4.11 (2 H, $CH_2$), 0.77 (s, 18 H, *t*Bu), 0.26 (s, 9 H, $SiMe_3$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 122.5 (*ipso*-Ph), not observed (*ipso*-$C_5H_4$), 127.8, 119.1 (Ph), 123.0, 116.3 ($C_5H_4$), 67.6 ($CH_2$), 35.9 (*ipso*-*t*Bu), 28.9 (*t*Bu), 0.14 ($SiMe_3$) ppm.

**[Zr(η$^5$-$C_5H_5$){1,2-$C_6H_4$($NCH_2$*t*Bu)$_2$}Cl] (9):** *n*BuLi (5.04 mL of an 1.6 M solution, 8.06 mmol) was added dropwise to a stirred solution of *o*-$C_6H_4$($NHCH_2$*t*Bu)$_2$ (1.0 g, 4.03 mmol) in 50 mL of hexane at −78 °C. After the addition was complete, the reaction mixture was stirred for 6 hours and then slowly warmed to room temperature. The white solid formed was filtered and washed with cold hexane. This solid was added to a solution of [Zr(η$^5$-$C_5H_5$)$Cl_3$]·DME (1.4 g, 4.03 mmol) in 50 mL of toluene at −78 °C. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature with stirring for 12 h. The solid formed was insoluble in hexane which made its characterization difficult. Complex **9** was obtained as a yellow solid (0.27 g, 0.62 mmol, 15.4%). $C_{21}H_{31}ClN_2Zr$ (437.67): calcd. C 57.58, H 7.08, N 6.40; found C 57.32, H 8.22, N 6.40. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 7.39 (m, 2 H, Ph), 7.18 (m, 2 H, Ph), 5.98 (s, 5 H, $C_5H_5$), 3.80 (dd, 4 H, $CH_2$), 0.78 (s, 18 H, *t*Bu) ppm. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.32 (m, 2 H, Ph), 7.17 (m, 2 H, Ph), 5.82 (s, 5 H, Cp), 3.70 (dd, 4 H, $CH_2$), 0.72 (s, 18 H, *t*Bu) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 123.5−120.1 (Ph), 124.5 (*ipso*-Ph), 114.0 ($C_5H_5$), 63.2 ($CH_2$), 35.4 (*ipso*-*t*Bu), 28.8 (*t*Bu) ppm.

**Synthesis of [Zr(η$^5$-$C_5Me_5$){1,2-$C_6H_4$($NCH_2$*t*Bu)$_2$}Cl] (10):** Compound **10** was prepared by reacting the *o*-$C_6H_4$($NHCH_2$*t*Bu)$_2$ amine (1.0 g, 4.03 mmol), 8.06 mmol of *n*BuLi and [Zr(η$^5$-$C_5Me_5$)$Cl_3$] (1.34 g, 4.03 mmol) by the procedure described for **5** and obtained as a black solid (1.66 g, 3.27 mmol, 81%). $C_{26}H_{41}N_2ZrCl$ (507.93): calcd. C 61.48, H 8.07, N 5.51; found C 61.56, H 8.69, N 5.64. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 7.09 (m, 2 H, Ph), 7.02 (m, 2 H, Ph), 3.65 (dd, 4 H, $CH_2$), 1.66 (s, 15 H, $C_5Me_5$), 0.97 (s, 18 H, *t*Bu) ppm. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.28 (m, 4 H, Ph), 3.63 (s, 4 H, $CH_2$), 1.72 (s, 15 H, $C_5Me_5$), 0.87 (s, 18 H, *t*Bu) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 122.5, 117.2 (Ph), 117.8 (*ipso*- $C_5$*Me*$_5$), 62.1 ($CH_2$), 34.9 (*ipso*-*t*Bu), 28.9 (*t*Bu), 10.0 ($C_5$*Me*$_5$) ppm; *ipso*-Ph signal not observed.

**Polymerization Procedure:** Ethylene polymerization was carried out in 100 mL Schlenk flasks with magnetic stirring. Polymerization was carried out as follows: toluene and MAO were injected into the Schlenk flask with magnetic stirring at the desired temperature (25 °C). The solution was then saturated with 1 atmosphere of ethylene, and the monomer pressure was kept constant over the polymerization runs. Polymerization begins with the addition of a toluene solution of the titanium compound into the flask. After the desired reaction time was reached, polymerization was terminated by venting the ethylene gas and quenching with a small volume of a solution of MeOH/HCl. The polymers were isolated by filtration, washed with MeOH, and then dried in vacuo at 50 °C.

Polymerization of styrene was performed in toluene at 50 °C. Polymerization was carried out as follows: toluene (30 mL), styrene (5 mL), and MAO were injected into the Schlenk flasks with magnetic stirring at the desired temperature. The titanium compound dissolved in toluene (5 mL) was added last. All manipulations were performed under an argon atmosphere. The reaction was stopped after 15 minutes by addition of MeOH/HCl, and the polymer prod-

Table 4. Summary of the crystallographic data for compounds **3** and **7**

| | **3** | **7** |
|---|---|---|
| Empirical formula | $C_{17}H_{23}ClN_2Ti$ | $C_{20}H_{31}ClN_2SiTi$ |
| Formula mass | 338.69 | 410.88 |
| Crystal system | monoclinic | triclinic |
| Space group | $P2_1/c$ (no. 14) | $P\bar{1}$ (no. 2) |
| *a* (Å) | 13.0339(2) | 10.0673(2) |
| *b* (Å) | 12.9656(2) | 10.3242(2) |
| *c* (Å) | 10.7520(1) | 11.1287(2) |
| $\alpha$ (°) | 90 | 87.5786(14) |
| $\beta$ (°) | 110.4105(8) | 72.5554(14) |
| $\gamma$ (°) | 90 | 88.8736(8) |
| *V* (Å$^3$) | 1702.93(4) | 1102.47(4) |
| *Z* | 4 | 2 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.321 | 1.238 |
| $\mu$ [mm$^{-1}$] | 0.655 | 0.569 |
| *T* [K] | 123 | 153 |
| *F*(000) | 712 | 436 |
| Crystal size (mm) | 0.61 × 0.25 × 0.23 | 0.38 × 0.25 × 0.20 |
| $\Theta$ range (°) | 2.29/25.41 | 1.92/25.28 |
| Index ranges | *h*: ±15/*k*: ±15/*l*: ±12 | *h*: ±12/*k*: ±12/*l*: ±13 |
| Reflections collected | 36764 | 15832 |
| Independent reflections [$I_o > 2\sigma(I_o)$/all data/$R_{int}$] | 2764/3131/0.038 | 3616/3989/0.027 |
| Data/restraints/parameters | 3131/0/282 | 3989/0/350 |
| *R*1 [$I_o > 2\sigma(I_o)$/all data] | 0.0251/0.0313 | 0.0251/0.0293 |
| *wR*2 [$I_o > 2\sigma(I_o)$/all data] | 0.0605/0.0632 | 0.0623/0.0648 |
| *GOF* | 1.027 | 1.077 |
| Weights *a*/*b* | 0.0275/0.9782 | 0.0245/0.4603 |
| $\Delta\rho_{max/min}$ [e·Å$^{-3}$] | 0.26/−0.25 | 0.26/−0.25 |

uct was coagulated with a large excess of acidified methanol and recovered by filtration.

**Characterization of Polymers:** The thermal properties of the samples were studied in a Du Pont 2920 MDSC instrument calibrated by measuring the melting point of indium. 5−10 mg each of the dried polymer were fused into standard aluminium pans and measured using the following temperature program for polyethylene samples: first a heating phase (10 °C/min) from 50 to 200 °C, followed by a cooling phase (−10 °C/min) to 50 °C. The peak maximum of the second heating curve was taken as the melting point ($T_\mathrm{m}$). To determinate the degree of crystallinity (α) the relationship $\Delta H_\mathrm{m}/\Delta H^\circ_\mathrm{m}$ was used. $\Delta H_\mathrm{m}$ was derived from the data of the second heating course of the DSC, and $\Delta H^\circ_\mathrm{m}$ was assumed to be the fusion enthalpy[33] (290 J/g) for 100% crystalline polyethylene.

Polystyrene samples were subjected to the following steps: heating at 10 °C/min from 30 to 270 °C and then cooling at 10 °C/min from this temperature to 30 °C, followed by heating at 10 °C/min from 30 to 270 °C to obtain the melting peak temperature ($T_\mathrm{m}$).

The NMR samples were prepared by dissolving the polystyrene sample in tetrachloro-1,2-dideuterioethane. The spectra were recorded at 25 °C.

**X-ray Structure Determination of 3 and 7:** Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 4. Crystals of complex **3** (**7**) suitable for an X-ray single crystal structure determination were obtained from hexane. Preliminary examination and data collection were carried out on a kappa-CCD device (Nonius) at the window of a rotating anode (NONIUS FR591; 50 kV; 60 mA; 3.0 kW) and graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å).[34] The unit-cell parameters were obtained by full-matrix least-squares refinement of 3274 (3935) reflections. Data collection was performed at 123 (153) K with an exposure time of 60 (80) s per frame, 7 (7) sets; 501 (335) frames; phi and omega scans; 2.0° (2.0°) scan-width. A total number of 36764 (15832) reflections were integrated. Raw data were corrected for Lorentz and polarization effects. If necessary, corrections for absorption and decay effects were applied during the scaling procedure.[35] After merging, a sum of 3131 (3989) independent reflections remained and used for all calculations. The structure was solved by a combination of direct methods[36] and difference-Fourier syntheses.[37] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the final Fourier maps and refined with isotropic displacement. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2$ with the SHELXL-97 weighting scheme and stopped at maximum shift/err < 0.001. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.[38] All other calculations (including ORTEP graphics) were carried out with the program PLATON.[39]

CCDC-206875 (for **3**) and -206874 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] P. C. Wailes, R. S. P. Coates, H. Weigold, *Organometallic Chemistry of Titanium, Zirconium and Hafnium*, Academic Press, New York, **1974**. [1b] D. J. Cardin, M. F. Lappert, C. L. Raston, P. I. Riley, in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), vol. 3, Pergamon, Oxford, **1982**. [1c] D. J. Cardin, M. F. Lappert, C. L. Raston, *Chemistry of Organo-Zirconium and -Hafnium Compounds*, John Wiley & Sons, New York, **1986**. [1d] *Comprehensive Organometallic Chemistry II. A Review of the Literature* (1982−1994) (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), vol. 4, Pergamon, Oxford, **1994**. [1e] *Metallocene: Synthesis, Reactivity and Applications* (Eds.: A. Togni, R. L. Halterman), vol. 1 and 2, Wiley-VCH, New York, **1998**.

[2] [2a] H. C. S. Clark, F. G. N. Cloke, P. B. Hitchcock, J. B. Love, A. P. Wainwright, *J. Organomet. Chem.* **1995**, *501*, 333−340. [2b] F. G. N. Cloke, P. B. Hitchcock, J. B. Love, *J. Chem. Soc., Dalton Trans.* **1995**, 25−30. [2c] J. D. Scollard, D. H. McConville, J. J. Vittal, *Organometallics* **1995**, *14*, 5478−5480. [2d] T. H. Warren, R. R. Schrock, W. M. Davis, *Organometallics* **1996**, *15*, 562−569. [2e] K. Aoyagi, P. Gantzel, K. Kalai, T. D. Tilley, *Organometallics* **1996**, *15*, 923−927. [2f] A. D. Horton, J. de With, A. J. van der Linden, H. van de Weg, *Organometallics* **1996**, *15*, 2672−2674. [2g] F. Guérin, D. H. McConville, N. C. Payne, *Organometallics* **1996**, *15*, 5085−5089. [2h] F. Guérin, D. H. McConville, J. J. Vittal, *Organometallics* **1996**, *15*, 5586−5590. [2i] R. Duchateau, C. T. van Wee, A. Meetsma, P. T. van Duijnnen, J. H. Teuben, *Organometallics* **1996**, *15*, 2279−2290. [2j] J. D. Scollard, D. H. McConville, J. J. Vittal, *Organometallics* **1997**, *16*, 4415−4420. [2k] A. D. Horton, J. de With, *Organometallics* **1997**, *16*, 5424−5436. [2l] R. Baumann, R. Stumpf, W. M. Davis, L.-C. Liang, R. R. Schrock, *J. Am. Chem. Soc.* **1999**, *121*, 7822−7836. [2m] C. Cao, J. T. Ciszewski, A. Odom, *Organometallics* **2001**, *20*, 5011−5013. [2n] J. Scholz, H. Görls, *J. Organomet. Chem.* **2002**, *648*, 87−92. [2o] R. M. Gauvin, J. Kress, *J. Mol. Catal. A* **2002**, *182−183*, 411−417.

[3] [3a] J. D. Scollard, D. H. McConville, *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009. [3b] J. D. Scollard, D. H. McConville, S. J. Rettig, *Organometallics* **1997**, *16*, 1810−1812. [3c] R. Baumann, W. M. Davis, R. R. Schrock, *J. Am. Chem. Soc.* **1997**, *119*, 3830−3831. [3d] V. C. Gibson, B. S. Kimberley, A. J. P. White, D. J. Williams, P. Howard, *Chem. Commun.* **1998**, 313−314. [3e] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* **1999**, *38*, 428−447. [3f] P. Mehrkhodavandi, P. Bonitatebus Jr., R. R. Schrock, *J. Am. Chem. Soc.* **2000**, *122*, 7841−7842. [3g] P. Mehrkhodavandi, R. R. Schrock, *J. Am. Chem. Soc.* **2001**, *123*, 10746−10747.

[4] [4a] R. Gómez, R. Duchateau, A. N. Chernega, J. H. Teuben, F. T. Edelman, M. L. H. Green, *J. Organomet. Chem.* **1995**, *491*, 153−158. [4b] F. G. Cloke, T. J. Geldbach, P. B. Hitchcock, J. B. Love, *J. Organomet. Chem.* **1996**, *506*, 343−345. [4c] G. Jiménez-Pindado, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.* **1998**, 393−400. [4d] F. Amor, P. Gómez-Sal, P. Royo, J. Okuda, *Organometallics* **2000**, *19*, 5168−5173. [4e] J. Scholz, G. A. Hadi, K.-H. Thiele, H. Görls, R. Weimann, H. Schumann, J. Sieler, *J. Organomet. Chem.* **2001**, *626*, 243−259.

[5] [5a] P. J. Shapiro, E. E. Bunel, W. E. Piers, J. E. Bercaw, *Synlett* **1990**, *2*, 74−84. [5b] J. Okuda, *Chem. Ber.* **1990**, *123*, 1649. [5c] J. C. Stevens, F. J. Timmers, D. R. Wilson, G. F. Schmidt, P. N. Nickias, R. K. Rosen, G. W. Knight, S. Lai, *Eur. Patent. Appl.* EP **1991**, *416*, 815 (Dow) (*Chem. Abstr.* **1991**, *115*, 93163). [5d] J. M. Canich, *Eur. Patent. Appl.* EP **1991**, *420*, 436 (Exxon) (*Chem. Abstr.* **1991**, *115*, 184145). [5e] R. B. Panell, J. A. M. Canich, G. G. Hlatky (Exxon) *PCT Int. Appl.* **1994**, WO 94/00500. [5f] P. N. Nickias, M. H. McAdon, J. T. Patton (Dow) *PCT Int. Appl.* **1997**, WO 97/15583. [5g]A. L. Mcknight, R. W. Waymouth, *Chem. Rev.* **1998**, *98*, 2587−2598. [5h] J. Jin, D. R. Wilson, E. Y.-X. Chen, *Chem. Commun.* **2002**, 708−709.

[6] J. Cano, P. Royo, M. Lanfranchi, M. A. Pellinghelli, A. Tiripicchio, *Angew. Chem. Int. Ed.* **2001**, *40*, 2495−2497.

[7] M. González-Maupoey, T. Cuenca, L. M. Frutos, O. Castaño, E. Herdtweeck, *Organometallics* **2003**, *22*, 2694−2704.

[8] [8a] M. Maeda, S. Sasaki, T. Fukumura, E. Fukuzawa, K. Watanabe, M. Kojima, T. Tahara, K. Masuda, Y. Ichiya, *Chem. Pharm. Bull.* **1992**, *40*, 1793−1798. [8b] H. Braunschweig, B. Gehrhus, P. Hitchcock, M. F. Lappert, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1922−1928.

[9] [9a] B. Gehrhus, P. B. Hitchock, M. F. Lappert, J. Heinicke, R. Bolse, D. Bläser, *J. Organomet. Chem.* **1996**, *521*, 211−220. [9b] S. Danièle, P. B. Hitchcock, M. Lappert, P. G. Merle, *J. Chem. Soc., Dalton Trans.* **2001**, 13−19.

[10] A. Bulbarela, H. Tlahuext, H. R. Morales, L. Cuéllar, G. Uribe, R. Contreras, *Magn. Reson. Chem.* **1986**, *24*, 1093.109.

[11] B. Richter, J. Scholz, J. Sieler, K.-H. Thiele, *Angew. Chem.* **1995**, *107*, 2865; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2649.

[12] [12a] H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *J. Am. Chem. Soc.* **1985**, *107*, 2410−2413. [12b] H. Yasuda, A. Nakamura, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 723−742. [12c] T. Okamoto, H. Yasuda, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *J. Am. Chem. Soc.* **1988**, *110*, 5008−5011. [12d] H. Kagawuchi, Y. Yamamoto, K. Asaoka, K. Tatsumi, *Organometallics* **1998**, *17*, 4380−4386. [12e] J. Scholz, H. Görls, *Polyhedron* **2002**, *21*, 305−312.

[13] M. L. H Green, J. Sassmannhausen, *Chem. Commun.* **1999**, 115−116.

[14] A. Nakamura, K. Mashima, *J. Organomet. Chem.* **2001**, *621*, 224−230.

[15] [15a] M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, Wiley, New York, **1980**. [15b] R. A. Jones, M. H. Seeberger, J. L. Atwood, W. E. Hunter, *J. Organomet. Chem.* **1983**, *247*, 1−6. [15c] R. M. Pupi, J. N. Coalter, J. L. Petersen, *J. Organomet. Chem.* **1995**, *497*, 17−25. [15d] N. A. H. Male, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.* **1997**, 2487−2494.

[16] G. van Koten, K. Vrieze, *Adv. Organomet. Chem.* **1982**, *21*, 151−239.

[17] [17a] J. M. Boncella, S. Wang, D. D. VanderLende, R. L. Huff, K. A. Abboud, W. M. Vaughn, *J. Organomet. Chem.* **1997**, *530*, 59−70. [17b] C. G. Ortiz, K. A. Abboud, J. M. Boncella, *Organometallics* **1999**, *18*, 4253−4260. [17c] K. Mashima, Y. Matsuo, K. Tani, *Organometallics* **1999**, *18*, 1471−1481.

[18] A. Galindo, A. Ienco, C. Mealli, *New J. Chem.* **2000**, *14*, 73−75.

[19] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283−315.

[20] [20a] Y. Jeo, J. Heo, W. M. Lee, T. Chang, K. Kim, *Organometallics* **1999**, *18*, 4107−4113. [20b] T. I. Gountchev, T. D. Tilley, *Inorg. Chim. Acta* **2003**, *345*, 81−88. [20c] R. M. Gauvin, R. Choukroun, B. Donadieu, J. Kress, *Eur. J. Inorg. Chem.* **2001**, 2337−2346.

[21] [21a] C. H. Lee, Y. H. La, S. J. Park, J. W. Park, *Organometallics* **1998**, *17*, 3648−3655. [21b] C. Lorber, B. Donnadieu, R. Choukroun, *Organometallics* **2000**, *19*, 1963−1966. [21c] C. H. Lee, Y. H. La, S. J. Park, J. W. Park, *Organometallics* **1999**, *18*, 344−351.

[22] A. Karam, M. Jimeno, J. Lezama, E. Catarí, A. Figueroa, B. R. Gascue, *J. Mol. Catal. A* **2001**, *176*, 65−72.

[23] [23a] P. Longo, A. Proto, A. Zambelli, *Macromol. Chem. Phys.* **1995**, *196*, 3015−3029. [23b] S. Saccheo, G. Goia, A. Grassi, D. E. Bowen, R. F. Jordan, *J. Mol. Catal. A* **1998**, *128*, 111−118. [23c] W. Kamisky, *J. Chem. Soc., Dalton Trans.* **1998**, 1413−1418.

[24] [24a] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* **1986**, *19*, 2464−2465. [24b] N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* **1988**, *21*, 3356−3360. [24c] N. Tomotsu, N. Ishihara, T. H. Newman, M. T. Malanga, *J. Mol. Catal. A* **1998**, *128*, 167−190.

[25] R. Kleinschmidt, Y. Griebenow, G. Fink, *J. Mol. Catal. A* **2000**, *157*, 83−90.

[26] [26a] J. Richter, F. T. Edelman, M. Noltemeyer, H. G. Schmidt, M. Shmulinson, M. S. Eisen, *J. Mol. Catal. A* **1998**, *130*, 149−162. [26b] S. J. Kim, I. N. Jung, B. R. Yoo, S. H. Kim, J. Ko, D. Byun, S. O. Kang, *Organometallics* **2001**, *20*, 2141.

[27] A. V. Firth, J. C. Stewart, A. J. Hoskin, D. W. Stephan, *J. Organomet. Chem.* **1999**, *591*, 185.

[28] [28a] R. D. Gorsich, *J. Am. Chem. Soc.* **1958**, *80*, 4744−4744. [28b] R. D. Gorsich, *J. Am. Chem. Soc.* **1960**, *82*, 4211−4214.

[29] M. Mena, M. A. Pellinghelli, P. Royo, R. Serrano, A. Tiripicchio, *J. Chem. Soc., Chem. Commun.* **1986**, 1118−1119.

[30] P. Jutzi, M. Kuhn, *J. Organomet. Chem.* **1979**, *173*, 221−229.

[31] E. C. Lund, T. Livinghouse, *Organometallics* **1990**, *9*, 2426−2427.

[32] A. Martín, M. Mena, F. Palacios, *J. Organomet. Chem.* **1994**, *480*, C10−C11.

[33] [33a] G. Luft, M. Dorn, *Angew. Macromol. Chem.* **1991**, *188,* 177. [33b] J. G. Fatou, *Morphology and Crystallization in Polyolefins*, in *Handbook of Polyolefins* (Eds.: C. Vasile, R. B. Seymour), chapter 8, Marcel Dekker, **1993**.

[34] Data Collection Software for Nonius KappaCCD devices, Delft, The Netherlands, **2000**.

[35] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326.

[36] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C Burla, G. Polidori, M. Camalli, *SIR92, J. Appl. Cryst.* **1994**, *27*, 435−436.

[37] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1998**.

[38] A. J. C. Wilson (Ed.), *International Tables for Crystallography*, Kluwer Academic Publisher, Dordrecht, The Netherlands, **1992**, vol. C, Tables 6.1.1.4 (pp. 500−502), 4.2.6.8 (pp. 219−222), 4.2.4.2 (pp. 193−199).

[39] A. L. Spek, *PLATON A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2001**.

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