

Hydrazonide titanium derivatives

Synthesis, characterization and catalytic activity in olefin polymerization. Molecular structure of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}(\mu\text{-N}_2\text{CPh}_2)]_2$

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

Reaction of the mixed dicyclopentadienyl titanium compound $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{H}_5)\text{Cl}_2$ with LiN(H)NCPh_2 , in toluene at -78°C , gives the hydrazonide(1–) derivatives ('metalloazine') $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{H}_5)\text{Cl}[\text{N(H)NCPh}_2]$ and $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{H}_5)[\text{N(H)NCPh}_2]_2$ in high yield. The titanium trichloro compound $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})]\text{Cl}_3$ reacts with hydrazone $[\text{H}_2\text{N-N=CPh}_2]$ in the presence of one equivalent of NEt_3 to afford the hydrazonide(1–) compound $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})]\text{Cl}_2[\text{N(H)NCPh}_2]$, while in the presence of two equivalents of NEt_3 the cyclopentadienyl-amido derivative $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{-}\eta^1\text{-NNCPh}_2)]\text{Cl}_2$ is obtained. Mono-hydrazonide(1–) compounds $\text{Ti}(\text{CpR})\text{Cl}_2[\text{N(H)NCPh}_2]$ [$\text{CpR} = \eta^5\text{-C}_5\text{Me}_5$, $\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)$] were synthesized by treatment of the corresponding monocyclopentadienyl trichloro derivatives $\text{Ti}(\text{CpR})\text{Cl}_3$ with hydrazone in the presence of one equivalent of NEt_3 . The dinuclear complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}(\mu\text{-N}_2\text{CPh}_2)]_2$ has been prepared by reaction of $\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_2[\text{N(H)NCPh}_2]$ with NEt_3 in toluene and alternatively by reaction of $\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_3$ with hydrazone and two equivalents of NEt_3 . The molecular structure of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}(\mu\text{-N}_2\text{CPh}_2)]_2$ was determined by single-crystal X-ray diffraction methods and contains two $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}]$ units bridged by two hydrazonide(2–) ligands which form a symmetrical ' $\text{Ti}_2(\text{NN})_2$ ' core. These hydrazonide compounds have been activated with MAO and are suited to olefin polymerization.

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Keywords: Hydrazonide; Cyclopentadienyl-amido; Titanium; Olefin polymerization

1. Introduction

Cyclopentadienyl titanium and zirconium derivatives represent the most versatile class of organometallic compounds as homogeneous Ziegler–Natta olefin polymerization catalysts. The most successful precursor catalysts are the dicyclopentadienyl derivatives $\text{MCp}'_2\text{X}_2$ ($\text{M} = \text{Ti, Zr}$; $\text{Cp}' =$ substituted or unsubstituted η^5 -cyclopentadienyl ligand; $\text{X} =$ halo, alkyl), from

which the formally 14-electron cationic active species $[\text{MCp}'_2\text{R}]^+$ is generated in the presence of a cocatalyst [1,2]. Monocyclopentadienyl compounds $\text{MCp}'\text{X}_3$ have also been used with success in the polymerization of different types of olefins [3]. The electronically less saturated and sterically less hindered 10-electron cationic species $[\text{MCp}'\text{R}_2]^+$ might exhibit even higher activities than the dicyclopentadienyl species. Another family of compounds are the cyclopentadienyl-amido complexes which, in recent years, have gained widespread importance as catalysts for the polymerization and copolymerization of olefins [4]. The search for a new α -olefin polymerization catalyst based on non-

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cyclopentadienyl Group 4 metal complexes is a field of recent and increased interest involving academic and industrial research groups [5]. Octahedral zirconium complexes in particular were found to promote olefin polymerization, inducing tacticity in the resulting polymers [6].

We have recently reported an efficient and versatile alternative strategy to prepare cyclopentadienyl-amido derivatives via the reaction of primary amines [7] with the chlorosilyl-substituted cyclopentadienyl compound $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl})\text{Cl}_3]$ [8] in the presence of a base (NEt_3). Similar reactions with diamines afforded a new type of cyclopentadienyl-amido complex bearing a pendant NHR functionality [9]. Part of our current interest is to extend this synthetic methodology to produce new types of amido and linked cyclopentadienyl-amido Group 4 metal compounds.

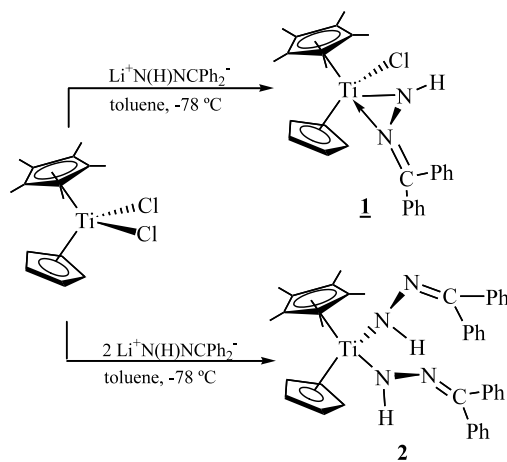
Here we report the synthesis of titanium hydrazonide derivatives ('metalloazines') by reaction of $\text{Ti}(\text{CpR})\text{Cl}_3$ ($\text{CpR} = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Cl}$, $\eta^5\text{-C}_5(\text{CH}_3)_5$, $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$) with hydrazone $\text{H}_2\text{N-N}=\text{CPh}_2$ in the presence of NEt_3 . Alternatively, hydrazonide compounds can be synthesized by ligand metathesis between $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{H}_5)\text{Cl}_2$ and $\text{LiN}(\text{H})\text{NCPH}_2$. The activation of such complexes with methylaluminoxane (MAO) should produce catalytic properties in the olefin polymerization process. Results on olefin polymerization using these derivatives as precursor catalysts and the characterization of the polyolefins obtained are also reported.

2. Results and discussion

2.1. Preparation and characterization of the complexes

The reaction of $\text{LiN}(\text{H})\text{NCPH}_2$, obtained by addition of a solution of Li^nBu in hexane to benzophenonehydrazone in dry THF at -78°C under argon [10], with the mixed dicyclopentadienyl titanium compound $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{H}_5)\text{Cl}_2$, in toluene at -78°C , gives the chloro hydrazonide(1-) derivative ('metalloazine') [10] $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Cl}[\text{N}(\text{H})\text{NCPH}_2]$ (**1**). The bis-hydrazonide(1-) complex $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)[\text{N}(\text{H})\text{NCPH}_2]_2$ (**2**) is easily formed by treatment of $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2$ with two equivalents of the lithium salt (Scheme 1).

The titanium trichloro compound $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})]\text{Cl}_3$ [8] reacts in toluene, at room temperature, with hydrazone ($\text{H}_2\text{N-N}=\text{CPh}_2$) in the presence of two equivalents of NEt_3 , with aminolysis of the Si-Cl and one of the Ti-Cl bonds, to afford the cyclopentadienyl-amido derivative $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2-\eta^1\text{-NNCPH}_2)]\text{Cl}_2$ (**6**) in high yield (80%), whereas the same reaction with 1 equivalent of NEt_3 gives the mono-hydrazonide(1-) compound $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})]\text{Cl}_2[\text{N}(\text{H})\text{NCPH}_2]$ (**3**),

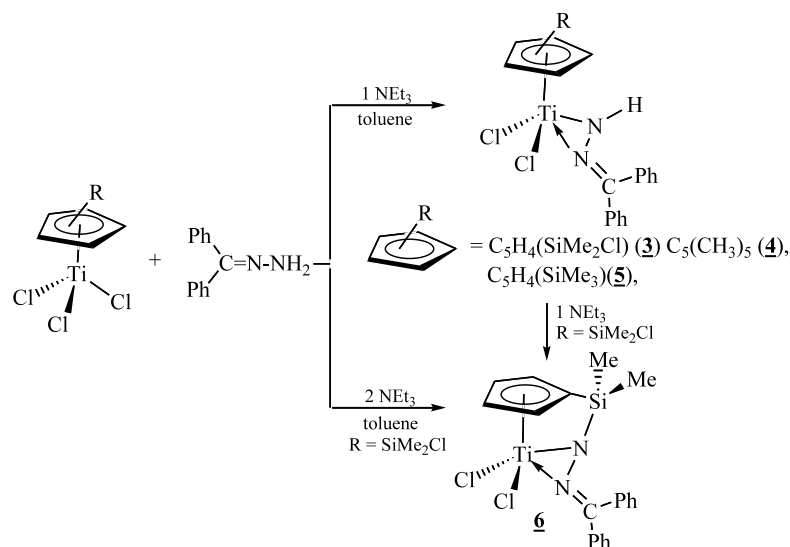


Scheme 1.

isolated as a pale orange solid in 61% yield (Scheme 2). These results allow us to suggest that the Ti-Cl bond undergoes a selective aminolysis reaction with hydrazone to give the amido titanium derivative **3**. Selective reactivity of the M-Cl bond toward highly polar lithium amide has also been described, while similar reactivity of both Si-Cl and Ti-Cl bonds with water and amine reagents was previously observed for other titanium and zirconium derivatives [8]. From compound **3**, the cyclopentadienyl-silyl-amido compound **6** is formed by subsequent elimination of HCl after aminolysis of the Si-Cl bond, mediated by the presence of NEt_3 in the reaction mixture [7a]. Analogous mono-hydrazonide(1-) compounds $\text{Ti}(\text{CpR})\text{Cl}_2[\text{N}(\text{H})\text{NCPH}_2]$ [$\text{CpR} = \eta^5\text{-C}_5\text{Me}_5$ (**4**), $\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)$ (**5**)] can be synthesized by reaction of the corresponding monocyclopentadienyl trichloro derivatives $\text{Ti}(\text{CpR})\text{Cl}_3$ with hydrazone in the presence of one equivalent of NEt_3 (Scheme 2). Treatment of **5** with NEt_3 in toluene gives the dinuclear complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}(\mu\text{-N}_2\text{CPh}_2)]_2$ (**7**) as an analytically pure red compound, in which two titanium atoms are doubly bridged by a hydrazonide(2-) ligand. Compound **7** is also synthesized by reaction of $\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_3$ with hydrazone and two equivalents of NEt_3 in toluene (Scheme 3). Unlike **5**, a toluene solution of compound **4** remains unaltered in the presence of an excess of NEt_3 and the formation of a dinuclear analogue to **7** is not observed, probably due to the high steric demand of the substituted cyclopentadienyl ring.

Complexes **1-7** are air and moisture-sensitive, both in solution and in the solid state. They can, however, be stored unaltered for weeks if strictly anaerobic conditions are maintained. They are soluble in chlorinated solvents (chloroform and dichloromethane) as well as in aromatic hydrocarbons (benzene, toluene) and slightly soluble in hexane and pentane.

The IR spectra of all of these complexes show characteristic absorptions for $\nu(\text{Ti-N})$ around 700

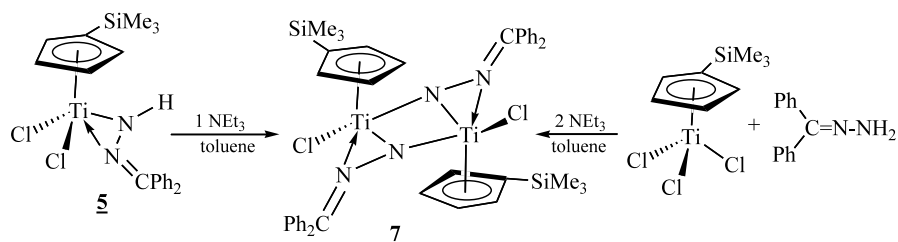


Scheme 2.

cm^{-1} and $\nu(\text{N}-\text{H})$ vibrations between 3200 and 3400 cm^{-1} . These spectra do not show any $\nu(\text{N}=\text{C})$ vibrations above 1600 cm^{-1} , possibly due to an electronic delocalization over the $\text{C}-\text{N}-\text{N}-$ unit [11,12b]. ^1H -NMR spectra (C_6D_6 or CDCl_3 , room temperature) for complexes **1** and **2** show singlets for the pentamethyl- and cyclopentadienyl ring protons, while for complexes **3**, **5**, and **6** one AA'BB' spin system (two resonances) for the C_5H_4 ring protons and one singlet for the SiMe_2 or SiMe_3 groups are observed, as would be expected from the symmetry of the proposed structures for these compounds. The same spectroscopic features are also observed in the ^{13}C -NMR spectra. A feature associated with the ^1H -NMR spectra of these compounds is the resonance for the amido proton. They exhibit one signal (δ 8.5–10.5) shifted downfield with respect to the $(\text{H}_2)\text{N}-\text{N}=\text{CPh}_2$ resonance (δ 4.53), indicating that the hydrazonide(1 $-$) ligand adopts an amido coordination mode [11]. The ^1H - and ^{13}C -NMR spectra also show the presence of two non-equivalent phenyl groups indicating a coplanar $\text{Ti}-\text{N}-\text{N}-\text{C}-\text{C}_{ipso}(\text{Ph}_2)$ fragment pointing to sp^2 hybridization for the nitrogen and carbon atoms and suggesting a $\text{Ti}-\text{N}$ π -bond interaction with hindered rotation around the $\text{C}=\text{N}$ bond.

η^2 - N,N' -Hydrazonide(1 $-$) and η^2 - N,N' -alkyl hydrazonide(1 $-$) dicyclopentadienyl zirconium deriva-

tives have been synthesized by migratory insertion of a ligand into a zirconium coordinate diazoalkane molecule [11] and some η^2 - N,N' -hydrazonide(2 $-$) titanium complexes are also known [12]. Alternatively, η^1 - N,N' coordination has been suggested for the intermediate titanium species $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{NNCPh}_2)$ [12a,12c] and the compound $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PMe}_3)(\text{NNCPh}_2)$ [13]. Although a similar η^1 - N,N' coordination mode could not be ruled out for the hydrazonide ligands in the dicyclopentadienyl compounds **1** and **2** due to the smaller ionic radii of titanium compared with zirconium and the greater space requirement of the C_5Me_5 ligand, an η^2 - N,N' bonding of the hydrazonide ligand to the titanium atom is proposed for these compounds (Scheme 1). The spectroscopic data for the monocyclopentadienyl derivatives **3**–**6** are support the proposed structure with a mirror plane containing the $\text{Ti}-\text{N}-\text{N}-\text{C}-\text{C}_{ipso}(\text{Ph}_2)$ unit (the coplanar $\text{Ti}-\text{N}(-\text{Si})-\text{N}-\text{C}-\text{C}_{ipso}(\text{Ph}_2)$ fragment for compound **6**) bisecting the $\text{Cl}-\text{Ti}-\text{Cl}$ angle and the cyclopentadienyl ring (Scheme 2) [11b,14,15] making both phenyl groups non-equivalent in the corresponding NMR spectra. Compound **6** symbolizes a structural variation of the classical cyclopentadienyl-amido titanium derivatives [16] in which the hydrazonide moiety has been employed as a donor ligand in place of the amido ligand.



Scheme 3.

The reactions of **1**, **3** and **4** with alkylating reagents have been studied. However, all attempts made to alkylate these complexes under varying conditions always gave unresolvable mixtures of unidentified compounds.

2.2. Molecular structure of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}(\mu\text{-N}_2\text{CPh}_2)]_2$ (**7**)

The structure of complex **7** was confirmed by a single-crystal X-ray diffraction study. Fig. 1 shows an ORTEP view of the structure along with the atom-labelling scheme. Selected bond distances and angles with their standard deviations are listed in Table 1.

The structure shows **7** as a dimeric complex where two 'Ti($\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3\text{Cl}$)' units are bridged by two diphenyl hydrazonide(2–) ligands. In the asymmetric unit cell two independent crystallographic molecules **A** and **B** were found around a centre of inversion. Both are equivalent within estimated S.D.'s. We focus the discussion therefore on molecule **A**. Each hydrazonide(2–) ligand is bonded *side-on* to one titanium atom and *end-on* to the other titanium centre. If the centroid of the cyclopentadienyl ring and the midpoint of the hydrazonide(2–) N–N bond is considered as a single coordination site, the coordination geometry around the titanium centre can be best described as tetrahedral. In the *side-on* disposition, the Ti–N bond length for the bridge nitrogen is slightly shorter [Ti1–N2 2.021(3) Å] than that for the nitrogen carrying the CPh₂ substituent [Ti1–N1 2.148(3) Å]. The Ti1–N2 and Ti1–N1 bond

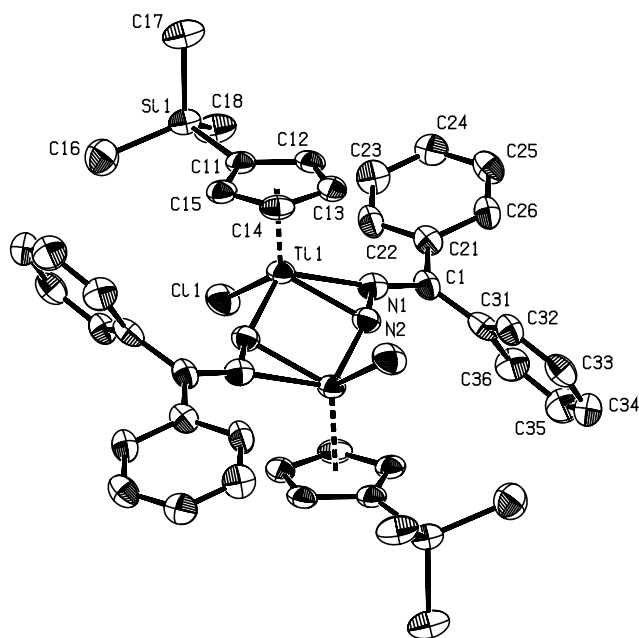


Fig. 1. ORTEP drawing view of the molecular structure of molecule **A** in compound **7** along with the atomic labelling scheme. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table 1
Selected interatomic distances (Å) and angles (°) for complex **7**

	A ^a	B ^a
<i>Bond distances</i>		
Ti1–C11	2.3480(11)	2.3393(11)
Ti1–N1	2.148(3)	2.153(3)
Ti1–N2	2.021(3)	1.996(3)
Ti1–C11	2.392(4)	2.402(3)
Ti1–C12	2.343(4)	2.355(4)
Ti1–C13	2.337(4)	2.345(4)
Ti1–C14	2.353(4)	2.339(3)
Ti1–C15	2.363(4)	2.350(3)
Ti1–N2 _a	1.870(3)	1.898(3)
N1–N2	1.324(4)	1.339(4)
N1–C1	1.323(4)	1.315(4)
<i>Bond angles</i>		
C11–Ti1–N1	92.00(8)	92.42(7)
C11–Ti1–N2	112.45(9)	116.35(8)
C11–Ti1–N2 _a	95.74(9)	96.48(9)
N1–Ti1–N2	36.89(11)	37.41(10)
N1–Ti1–N2 _a	119.71(11)	117.48(11)
N2–Ti1–N2 _a	86.44(12)	85.38(12)
Ti1–N1–N2	66.35(17)	64.93(16)
Ti1–N1–C1	169.1(2)	171.3(2)
N2–N1–C1	124.0(3)	123.8(3)
Ti1–N2–N1	76.76(17)	77.66(17)
Ti1 _a –N2–N1	154.0(2)	149.6(2)
Ti1–N2–Ti1 _a	93.56(13)	94.62(13)

The translation of symmetry code to equivalent positions is:
_a = –x, 1–y, 1–z.

^a The labels are given for **A**. For further details see text and Section 4.

distances are, respectively, slightly longer and shorter than those of the known titanium compounds $\text{Ti}[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\eta^2\text{-NNMe}_2)]\text{X}_2$ (X=Cl, Me) [15b] and comparable to those of the $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-NHNMe}_2)\text{Cl}_2$ and $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-NPhNH}_2)\text{Cl}_2$ [14]. The Ti1–N1–N2 system is an almost isosceles triangle and the titanium, nitrogen and C1 atoms lie in a plane. The angles in the triangle are Ti1–N1–N2 66.35(17)°, Ti1–N2–N1 76.76(17)° and very acute at the metal centre N1–Ti1–N2 36.89(11)°. Comparable structures for analogous titanium and other transition metal derivatives have been found [17]. The 'Ti1N2N1' and 'Ti1_aN2_aN1_a' fragments are connected through two Ti–N bonds, which show equal distances [Ti1–N2_a 1.870(3) Å] forming an almost planar 'Ti1N2Ti1_aN2_a' ring. The short Ti1–N2_a bond distance in the range 1.80–1.90 Å suggests a pπ–dπ-interaction between the titanium and nitrogen atoms [18]. The N–N [N1–N2 1.324(4) Å] and N–C [N1–C1 1.323(4) Å] bond distances are shorter than the single bonds, indicating significant multiple N–N and N–C bond character. These structural features indicate an electronic delocalization over the Ti1_aN2N1C1 unit.

Analogous structures have been reported by Floriani and Leigh for similar titanium derivatives. The com-

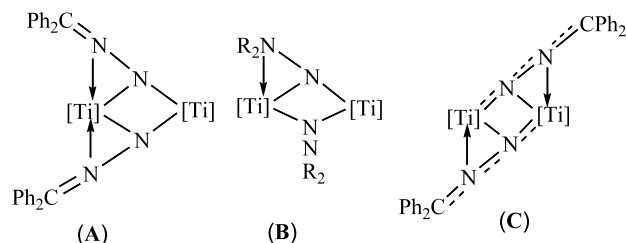


Fig. 2. Comparison of the 'TiN₂TiN₂' structure core defined in the compounds [Ti(η^5 -C₅H₅)Cl]₂(μ -N₂CPh₂) [12c] (A), [Ti(η^5 -C₅H₅)Cl(NNPh₂)]₂ [19] (B) and [Ti(η^5 -C₅H₄SiMe₃)Cl(μ -N₂CPh₂)]₂ (7) (C).

pound [Ti(η^5 -C₅H₅)Cl]₂(μ -N₂CPh₂)₂ [12c] contains two hydrazonide ligands η^2 -N,N' bonded to the same titanium atom, while the second titanium centre is bonded at very short distances to the terminal nitrogens only (Fig. 2A). The complex [Ti(η^5 -C₅H₅)Cl(NNPh₂)]₂ [19] shows one hydrazonide ligand symmetrically *end-on* bridging while the other hydrazonide ligand is both bridging and bonded *side-on* to one of the titanium atoms (Fig. 2B). Compound 7 exhibits a different 'TiN₂TiN₂' structure core with the disposition for the two η^2 -N,N' hydrazonide ligands as shown in Fig. 2C. The *side-on* structure has been previously observed, but the presence of two symmetric titanium environments in the same dinuclear compound is unique. The steric hindrance caused by the ring must influence the final structural disposition. For unsubstituted cyclopentadienyl derivatives the existence of metastable forms in solution has been proposed [19] which under crystallization yield a determined disposition in the solid state. For substituted cyclopentadienyl rings, the symmetrical disposition must be favoured as the thermodynamically more stable form in solution (for 7 we only observed by NMR spectroscopy the formation of a symmetrical disposition) and in the solid state. When the steric demands of the cyclopentadienyl ring increase the formation of the dinuclear compound is not observed. When a similar reaction to prepare 7 is carried out with the pentamethyl-cyclopentadienyl derivative, even in the presence of an excess of hydrazone and NEt₃, only the mononuclear compound 4 is formed.

The formation of 7 could be explained by the dimerization of two transient η^1 -hydrazonide compounds 'Ti(η^5 -C₅H₄SiMe₃)Cl(NNCPh₂)' [12a,12c]. The titanium(III) complex Ti(η^5 -C₅H₅)₂(PMe₃)(NNCPh₂) [13] in which the diazoalkane moiety adopts an η^1 -coordination has been described. The structural parameters concerning the 'TiNNC' fragment in the titanium(III) complex are very comparable with those found for the 'Ti1_a-N2-N1-Cl' unit in 7 and fall in the range observed for [Ti(η^5 -C₅H₅)Cl(NNPh₂)]₂ [19]. The difference in length between the Ti1-N2 and Ti1-N2_a (0.151 Å) in 7 suggests an asymmetric bridging imido character for the terminal nitrogen of the hydrazide

ligands. The Ti1-N1 bond distance is of the order of that found for donor N→Ti bonds [18]. The Ti1_a-N2-N1 angle at 154.0(2)° is closer than the corresponding angle in the compound [Ti(η^5 -C₅H₅)Cl(NNPh₂)]₂ [19] for which an almost linear disposition (171.4(2)°) has been proposed.

The Cp rings are planar. The Ti-C_{ring} distances range from 2.392(4) to 2.337(4) Å and the Ti-Cl distance is 2.3480(11) Å. These distances are very similar to those found in typical titanium chloro-cyclopentadienyl derivatives.

2.3. Olefin polymerization

Treatment of the titanium hydrazonide compounds with MAO affords catalytic species which polymerize ethylene, propylene and styrene. The reaction conditions and results are summarized in Tables 2–4. We carried out ethylene polymerizations at 25 and 50 °C and at 1 and 5 atm of ethylene pressure. The complexes exhibit activities comparable to those observed for Ti(η^5 -C₅H₅)Cl₃/MAO and higher than those observed for Ti(η^5 -C₅Me₅)Cl₃/MAO [20]. The polymerization data in Table 1 reveal that the chloro dicyclopentadienyl compound 1/MAO (entry 5) shows the highest activity at 25 °C and 1 atm of monomer pressure. Among the monocyclopentadienyl compounds 3, 5 and 6, the catalytic efficiency in terms of activity decreases in the order Ti[η^5 -C₅H₄(SiMe₂Cl)]Cl₂[N(H)NCPh₂]/MAO > Ti[η^5 -C₅H₄(SiMe₃)]Cl₂[N(H)NCPh₂]/MAO > Ti[η^5 -C₅H₄(SiMe₂- η^1 -NNCPh₂)]Cl₂/MAO with the cyclopentadienyl-amido system showing the same activity at 25 and 50 °C. The polyethylenes (PE's) produced by these catalysts exhibit single DSC endotherms consistent with a single active species for each catalyst. The melting point *T_m* of a PE depends upon its molecular weight and linearity [21]. The *T_m* of the obtained polymers (about 115 °C consistently made at all polymerization experiments) with the mono- and dicyclopentadienyl titanium hydrazonide derivatives are lower than those reported for linear high molecular weight polyethylene (HLPE, about 134°). This finding suggests a low molecular weight of the polymer products obtained or a branched polyethylene. The cyclopentadienyl-amido compound showed a similar *T_m* value with increasing *T_p*.

The synthesized complexes were activated with MAO and also tested for homogeneous propylene polymerization at 50 °C and 5 atm of monomer pressure. Table 3 summarized the results obtained. The activities in the polymerization of propylene are lower than for the production of polyethylene and polystyrene. The polypropylenes produced by these compounds are all atactic in nature, as indicated by the absence of melting transitions.

Polymerizations of styrene with the dicyclopentadienyl (1/MAO and 2/MAO) and mono-cyclopentadienyl

Table 2

Polymerization results of ethylene with the hydrazone titanium derivatives and MAO

Entries	Catalysts	Al/Ti ^a	<i>T</i> ^a (°C)	<i>P</i> (atm)	Activity ^b	<i>T</i> _m (°C) ^c , Δ <i>H</i> _m (J g ^{−1})
1	6	100	25	1	14	115.45, 83.75
2	6	100	50	5	14	115.77, 163.4
3	3	100	25	1	55	117.35, 150.70
4	5	100	25	1	44	116.76, 199.0
5	1	100	25	1	66	116.41, 212.10
6	2	100	25	1	28	116.44, 190.80

^a Molar ratio of Al–Ti.^b gPE (mmol Ti atm h)^{−1}.^c Determined by DSC.

compounds (**3**/MAO, **5**/MAO and **6**/MAO) were performed in toluene at 50 °C and the observed results are summarized in Table 4. The **1**/MAO and **2**/MAO systems were inactive in the styrene polymerization process and the activity for the **3**/MAO, **5**/MAO and **6**/MAO catalytic systems decreases in the order Ti[η⁵-C₅H₄(SiMe₂-η¹-NNCPh₂)]Cl₂/MAO > Ti[η⁵-C₅H₄(SiMe₂Cl)]Cl₂[N(H)NCPh₂]/MAO > Ti[η⁵-C₅H₄(SiMe₃)]Cl₂[N(H)NCPh₂]/MAO, with the activities in the production of polystyrene of the same order as polyethylene. The polystyrene polymers obtained are syndiotactic as indicated by the DSC analysis.

3. Conclusions

We describe here the preparation of dicyclopentadienyl hydrazone titanium derivatives by reaction of Ti(η⁵-C₅Me₅)(C₅H₅)Cl₂ with LiN(H)NCPh₂. Monocyclopentadienyl hydrazone titanium complexes have also been synthesized by Ti–Cl bond aminolysis reactions of Ti(CpR)Cl₃ with hydrazone [H₂N–N=CPh₂] in the presence of amine to bind the eliminated HCl. When one equivalent of NEt₃ is used, the hydrazone(1–) compounds Ti(CpR)Cl₂[N(H)NCPh₂] [CpR = η⁵-C₅H₄(SiMe₂Cl), η⁵-C₅Me₅, η⁵-C₅H₄(SiMe₃)] are obtained, while in the presence of two equivalents of NEt₃ the dinuclear complex [Ti(η⁵-C₅H₄SiMe₃)Cl(μ-

Table 4

Polymerization results of styrene ^a with the hydrazone titanium derivatives and MAO

Entries	Catalysts	Activity ^b	<i>T</i> _m (°C) ^c , Δ <i>H</i> _m (J g ^{−1})
1	6	17	243.99, 29.23
2	3	11	241.62, 24.86
3	5	6	242.03, 33.04
4	1	–	–
5	2	–	–

^a Reaction conditions: 4 × 10^{−5} mol of titanium compound precursor; solvent = toluene (35 ml); monomer = styrene (5 ml); temperature = 50 °C.

^b gPE (mmol Ti atm h)^{−1}.^c Determined by DSC.

N₂CPh₂)]₂ or the cyclopentadienyl-amido derivative Ti[η⁵-C₅H₄(SiMe₂-η¹-NNCPh₂)]Cl₂ were obtained, depending on the nature of the cyclopentadienyl substituent. The crystal structure of the [Ti(η⁵-C₅H₄SiMe₃)Cl(μ-N₂CPh₂)]₂ compound has been determined by X-ray diffraction methods. The structure shows a dimeric compound containing two titanium atoms doubly bridged by a hydrazone(2–) ligand in a symmetrical disposition. The catalytic activity for olefin polymerization of these compounds activated with MAO has been tested and studied.

Table 3

Polymerization results of propylene with the hydrazone titanium derivatives and MAO

Entries	Catalysts	Al/Ti ^a	<i>T</i> ^a (°C)	<i>P</i> (atm)	Activity ^b
1	6	100	50	5	4
2	3	100	50	5	–
3	5	100	50	5	0.5
4	1	100	50	5	1
5	2	100	50	5	0.6

^a Molar ratio of Al–Ti.^b gPE (mmol Ti atm h)^{−1}.

4. Experimental

All manipulations were performed under Ar using Schlenk and high-vacuum line techniques or a glovebox model HE-63. The solvents were purified by distillation under Ar 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. $\text{H}_2\text{N}-\text{N}=\text{CPh}_2$ and NEt_3 were purchased from commercial sources and used after purification and distillation. LiN(H)NCPh_2 [10], $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{H}_5)\text{Cl}_2$ [22], $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})]\text{Cl}_3$ [8], $\text{Ti}[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Cl}_3$ [23] and $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)]\text{Cl}_3$ [24] were prepared by known procedures. C, H and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus CHN–O–Rapid microanalyzer. The analytical data found for compound **2** deviated from expected values since LiCl could not be completely eliminated from the mixture. IR spectra were recorded (Nujol mulls) on a Perkin–Elmer Spectrum 2000 spectrophotometer; only selected IR data are reported. NMR spectra, measured at 25 °C, were recorded on a Varian Unity 300 (^1H at 300 MHz and ^{13}C at 75 MHz) and 500 Plus (^1H at 300 MHz and ^{13}C at 125 MHz) spectrometers and chemical shifts are referenced to residual protons and carbon signals of the solvent.

4.1. $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Cl}[N(\text{H})\text{NCPh}_2]$ (**1**)

LiN(H)NCPh_2 (1.00 g, 4.94 mmol) in 20 ml of THF was added to a solution of $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{H}_5)\text{Cl}_2$ (1.58 g, 4.94 mmol) in 50 ml of $\text{C}_6\text{H}_5\text{CH}_3$ at -78 °C. The reaction mixture was warmed to room temperature (r.t.) and then stirred for 12 h, resulting in a dark violet solution along with a white residue. The mixture was filtered and the solvent was removed under reduced pressure to give a dark violet crystalline solid. Recrystallization from $\text{C}_6\text{H}_5\text{CH}_3$ – C_6H_{14} at -40 °C gave **1** as an analytically pure sample (1.32 g, 2.76 mmol, 56% yield). Anal. Calc. for $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{Ti}$: C, 70.23; H, 6.47; N, 5.85. Found: C, 69.74; H, 6.45; N, 5.88%. $^1\text{H-NMR}$ (C_6D_6): δ 10.53 (s, 1H, NH), 7.87 (*ortho*-Ph), 7.30–7.00 (Ph), 6.21 (s, 5H, C_5H_5), 1.55 (s, 15H, C_5Me_5). $^1\text{H-NMR}$ (CDCl_3): δ 10.48 (s, 1H, NH), 7.57–7.10 (Ph), 6.20 (s, 5H, C_5H_5), 1.71 (s, 15H, C_5Me_5). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 140.2 (C=N), 134.8 (C_{ipso} , Ph), 130.5 (C_{ipso} , Ph), 129.4–127.2 (Ph), 122.4 (C_5Me_5), 116.2 (C_5H_5), 12.3 (C_5Me_5). IR (Nujol mulls, cm^{-1}): 690 $\nu(\text{Ti}-\text{N})$, 3200 $\nu(\text{N}-\text{H})$.

4.2. $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_5)[N(\text{H})\text{NCPh}_2]_2$ (**2**)

The procedure described for the preparation of compound **1**, using LiN(H)NCPh_2 (1.43 g, 7.00 mmol) and $\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_5\text{H}_5)\text{Cl}_2$ (1.12 g, 3.50 mmol) gave **2** as a dark violet solid (1.26 g, 1.97 mmol, 56% yield).

Anal. Calc. for $\text{C}_{41}\text{H}_{42}\text{N}_4\text{Ti}$: C, 77.14; H, 6.89; N, 8.77. Found: C, 75.21; H, 6.67; N, 8.69%. $^1\text{H-NMR}$ (C_6D_6): δ 8.75 (s, 2H, NH), 7.89, 7.22 (*ortho*-Ph), 7.20–7.00 (Ph), 6.33 (s, 5H, C_5H_5), 1.40 (s, 15H, C_5Me_5). $^1\text{H-NMR}$ (CDCl_3): δ 8.47 (s, 2H, NH), 7.60–7.07 (Ph), 6.23 (s, 5H, C_5H_5), 1.52 (s, 15H, C_5Me_5). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 140.8 (C=N), 136.4, 136.2 (C_{ipso} , Ph), 131.1–126.1 (Ph), 120.0 (C_5Me_5), 115.5 (C_5H_5), 11.8 (C_5Me_5). IR (Nujol mulls, cm^{-1}): 699.5 $\nu(\text{Ti}-\text{N})$, 3420 $\nu(\text{N}-\text{H})$.

4.3. $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})]\text{Cl}_2[N(\text{H})\text{NCPh}_2]$ (**3**)

A solution of $\text{H}_2\text{N}-\text{N}=\text{CPh}_2$ (1.88 g, 9.6 mmol) in $\text{C}_6\text{H}_5\text{CH}_3$ (30 ml) was quickly added to a $\text{C}_6\text{H}_5\text{CH}_3$ solution (30 ml) of $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})]\text{Cl}_3$ (3.0 g, 9.6 mmol) and NEt_3 (1.35 ml, 9.6 mmol) at r.t. The reaction mixture was stirred for 12 h resulting in an orange–yellow solution and a white residue. After filtration, the solvent was completely removed to give an orange–yellow solid. Repeated recrystallization from $\text{C}_6\text{H}_5\text{CH}_3$ – C_6H_{14} at -40 °C gave **3** as an analytically pure sample (2.78 g, 5.88 mmol, 61% yield). Anal. Calc. for $\text{C}_{20}\text{H}_{21}\text{Cl}_3\text{N}_2\text{SiTi}$: C, 50.84; H, 5.94; N, 4.45. Found: C, 50.44; H, 5.77; N, 4.63%. $^1\text{H-NMR}$ (C_6D_6): δ 9.66 (s, 1H, NH), 8.29, 7.75 (*ortho*-Ph), 7.15–6.80 (Ph), 6.50, 6.09 (2H, 2H, AA'BB' spin system, C_5H_4), 0.57 (s, 6H, SiMe_2). $^1\text{H-NMR}$ (CDCl_3): δ 10.15 (s, 1H, NH), 8.00, 7.98 (*ortho*-Ph), 7.60–7.20 (Ph), 6.98, 6.75 (2H, 2H, AA'BB' spin system, C_5H_4), 0.67 (s, 6H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 144.1 (C=N), 135.7, 134.3 (C_{ipso} , Ph), 131–128 (Ph), 125.7, 120.3 (C_5H_4), $C_{\text{ipso}}-\text{C}_5\text{H}_4$ not observed, 2.8 (SiMe_2). IR (Nujol mulls, cm^{-1}): 692 $\nu(\text{Ti}-\text{N})$, 3200 $\nu(\text{N}-\text{H})$.

4.4. $\text{Ti}[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Cl}_2[N(\text{H})\text{NCPh}_2]$ (**4**)

Following the same procedure described for the preparation of **3**, using 0.34 g (1.73 mmol) of $\text{H}_2\text{N}-\text{N}=\text{CPh}_2$, 0.5 g (1.73 mmol) of $\text{Ti}[\eta^5\text{-C}_5(\text{CH}_3)_5]\text{Cl}_3$ and 0.24 ml (1.73 mmol) of NEt_3 compound **4** was obtained as an analytically pure sample (0.30 g, 6.68 mmol, 42% yield). Anal. Calc. for $\text{C}_{23}\text{H}_{26}\text{Cl}_2\text{N}_2\text{Ti}$: C, 61.52; H, 6.24; N, 6.24. Found: C, 62.26; H, 6.51; N, 6.04%. $^1\text{H-NMR}$ (C_6D_6): δ 9.21 (s, 1H, NH), 8.27 (*ortho*-Ph), 7.30–6.80 (Ph), 1.87 (s, 15H, C_5Me_5). $^1\text{H-NMR}$ (CDCl_3): δ 9.26 (s, 1H, NH), 7.85 (*ortho*-Ph), 7.55–7.15 (Ph), 2.07 (s, 15H, C_5Me_5). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 142.7 (C=N), 137.8, 137.3 (C_{ipso} , Ph), 136–126 (Ph), 125.6 (C_5Me_5), 12.6 (C_5Me_5). IR (Nujol mulls, cm^{-1}): 695 $\nu(\text{Ti}-\text{N})$, 3280 $\nu(\text{N}-\text{H})$.

4.5. $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)]\text{Cl}_2[N(\text{H})\text{NCPh}_2]$ (**5**)

Following the same procedure described for the preparation of **3**, using 0.58 g (2.95 mmol) of $\text{H}_2\text{N}-$

$\text{N}=\text{CPh}_2$, 0.86 g (2.95 mmol) of $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)]\text{Cl}_3$ and 0.41 ml (2.95 mmol) of NEt_3 compound **5** was obtained as an analytically pure sample (0.77 g, 1.70 mmol, 58% yield). Anal. Calc. for $\text{C}_{21}\text{H}_{24}\text{Cl}_2\text{N}_2\text{SiTi}$: C, 55.90; H, 5.32; N, 6.21. Found: C, 55.24; H, 6.09; N, 5.57%. $^1\text{H-NMR}$ (C_6D_6): δ 9.48 (s, 1H, NH), 8.32, 7.05 (*ortho*-Ph), 7.20–6.80 (Ph), 6.50, 6.11 (2H, 2H, AA'BB' spin system, C_5H_4), 0.24 (s, 9H, SiMe_3). $^1\text{H-NMR}$ (CDCl_3): δ 9.85 (s, 1H, NH), 8.00, 7.95 (*ortho*-Ph), 7.50–7.20 (Ph), 6.93, 6.70 (2H, 2H, AA'BB' spin system, C_5H_4), 0.25 (s, 9H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 143.5 (C=N), 135.8, 134.5 (C_{ipso} , Ph), 131–127.9 (Ph), 126.4, 119.8 (C_5H_4), $\text{C}_{ipso}\text{-C}_5\text{H}_4$ not observed, -0.3 (SiMe_3). IR (Nujol mulls, cm^{-1}): 694 $\nu(\text{Ti-N})$, 3250 $\nu(\text{N-H})$.

4.6. $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{-}\eta^1\text{-NNCPh}_2)]\text{Cl}_2$ (**6**)

A solution of $\text{H}_2\text{N-N}=\text{CPh}_2$ (0.63 g, 3.20 mmol) in $\text{C}_6\text{H}_5\text{CH}_3$ (30 ml) was quickly added to a $\text{C}_6\text{H}_5\text{CH}_3$ solution (30 ml) of $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})]\text{Cl}_3$ (1.0 g, 3.20 mmol) and NEt_3 (0.89 ml, 6.40 mmol) at r.t. The reaction mixture was stirred for 12 h resulting in an orange–red solution and a white residue. After filtration, the solvent was completely removed to give a red solid. Repeated recrystallization from $\text{C}_6\text{H}_5\text{CH}_3\text{-C}_6\text{H}_{14}$ at -40°C gave **6** as an analytically pure sample (1.10 g, 2.53 mmol, 80% yield). Anal. Calc. for $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{N}_2\text{SiTi}$: C, 55.21; H, 4.60; N, 6.44. Found: C, 55.61; H, 5.04; N, 6.02%. $^1\text{H-NMR}$ (C_6D_6): δ 8.17, 7.41 (*ortho*-Ph), 7.26–6.95 (Ph), 5.65, 5.56 (2H, 2H, AA'BB' spin system, C_5H_4), 0.80 (s, 6H, SiMe_2). $^1\text{H-NMR}$ (CDCl_3): δ 8.06, 8.04 (*ortho*-Ph), 7.60–7.45 (Ph), 5.59, 5.54 (2H, 2H, AA'BB' spin system, C_5H_4), 0.61 (s, 6H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 152.0 (C=N), 135.8, 135.3 (C_{ipso} , Ph), 132–127 (Ph), 118.1, 117.0 (C_5H_4), 2.65 (SiMe_2) $\text{C}_{ipso}\text{-C}_5\text{H}_4$ not observed. IR (Nujol mulls, cm^{-1}): 694 $\nu(\text{Ti-N})$.

4.7. $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}(\mu\text{-N}_2\text{CPh}_2)]_2$ (**7**)

Following the same procedure described for the preparation of **3**, using 0.67 g (3.43 mmol) of $\text{H}_2\text{N-N}=\text{CPh}_2$, 1.0 g (3.43 mmol) of $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_3)]\text{Cl}_3$ and 0.95 ml (6.86 mmol) of NEt_3 compound **7** was obtained as an analytically red pure sample (0.86 g, 1.04 mmol, 30% yield). Anal. Calc. for $\text{C}_{21}\text{H}_{23}\text{ClN}_2\text{SiTi}$: C, 60.80; H, 5.59; N, 6.75. Found: C, 60.82; H, 5.80; N, 6.50%. $^1\text{H-NMR}$ (C_6D_6): δ 8.29, 7.56 (*ortho*-Ph), 7.40–7.00 (Ph), 5.72, 5.59 (2H, 2H, AA'BB' spin system, C_5H_4), 0.36 (s, 9H, SiMe_3). $^1\text{H-NMR}$ (CDCl_3): δ 8.08, 7.63 (*ortho*-Ph), 7.58–7.48 (Ph), 5.49 (br, 4H, C_5H_4), 0.12 (s, 9H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6): δ 150.9 (C=N), 136.0, 135.8 (C_{ipso} , Ph), 131–128.8 (Ph), 119.8 ($\text{C}_{ipso}\text{-C}_5\text{H}_4$), 118.1, 116.8 (C_5H_4), 0.12 (SiMe_3). IR (Nujol mulls, cm^{-1}): 696 $\nu(\text{Ti-N})$.

4.8. X-ray single crystal structure determination of **7**

General remarks: Suitable single crystals for the X-ray diffraction study were grown -40°C from a saturated solution in $\text{C}_6\text{H}_5\text{CH}_3\text{-C}_6\text{H}_{14}$ 1:1. A clear red crystal fragment was selected, coated with perfluorinated ether, fixed in a capillary and transferred to the diffractometer and the cold nitrogen stream (Oxford Cryosystem). The intensity data were collected at 173 K. Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo-K_α radiation. Data were corrected for Lp effects. Potential absorption and uncertain decay effects of the crystal were corrected during the scaling procedure. **Data collection:** Data collection were performed within the Θ -range of $1.88 < \Theta < 25.38^\circ$ with an exposure time of 120 s per image (four sets, 324 images, $dx = 40$ mm, $\Delta\varphi/\Delta\Omega = 2.0^\circ$). A total number of 29 790 reflections were integrated. After merging a sum of 7585 independent reflections remained and was used for all calculations [25a]. The unit cell parameters were obtained after the scaling procedure from 6990 independent reflections. **Solution and refinement:** The structure was solved by a combination of direct methods and difference-Fourier syntheses. Full-matrix least-square refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at $\text{shift/err} < 0.001$. All non-hydrogen atoms of the Ti complex were refined anisotropically. All hydrogen atoms were found in the difference-Fourier map and refined with individual isotropic thermal displacement parameters. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for X-Ray Crystallography [25b]. All calculations were performed on a DEC 3000 AXP workstation and an Intel Pentium II PC with the STRUX-V [25c] system including the programs PLATON [25d], SIR-92 [25e], and SHELXL-97 [25f]. Crystal data, intensity collection data and refinement parameters are given in Table 5. The asymmetric unit contains two crystallographic independent molecules (**A** and **B**); each located around a centre of inversion.

4.9. Polymerization procedures

Toluene for polymerization was distilled in the presence of Na and benzophenone under a nitrogen atmosphere. Ethylene and propylene of polymerization grade were used as received. Styrene was purified by distillation at reduced pressure from calcium hydride. MAO was prepared from commercially available MAO (Witco 10%) by removing $\text{C}_6\text{H}_5\text{CH}_3$ and the excess amount of AlMe_3 under vacuum. Polymerization runs were performed in a thermostated reactor (Buchiglauster) fitted

Table 5
Crystallographic data for complex 7

	7
Chemical formula	C ₄₂ H ₄₆ Cl ₂ N ₄ Si ₂ Ti ₂
Formula weight	829.65
<i>T</i> (K)	173
Colour/shape	Red/fragment
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	9.6780(2)
<i>b</i> (Å)	12.3549(2)
<i>c</i> (Å)	18.2507(5)
α (°)	79.4657(8)
β (°)	80.6063(7)
γ (°)	82.1580(15)
<i>V</i> (Å ³)	2103.88(8)
<i>Z</i>	2
ρ_{calc} (g cm ^{−3})	1.310
μ (mm ^{−1})	0.598
<i>F</i> (000)	864
Crystal size (mm)	0.25 × 0.13 × 0.05
Θ Range (°)	1.88–25.38
Data collected	−11 ≤ <i>h</i> ≤ 11, −14 ≤ <i>k</i> ≤ 14, −21 ≤ <i>l</i> ≤ 21
Reflections integrated	29 790
Independent reflections	7584 (all) [<i>R</i> _{int} = 0.040]
Observed reflections	5943 (observed)
[<i>I</i> > 2σ(<i>I</i>)]	
Parameters refined	653
<i>R</i> ₁ (observed/all)	0.0519/0.0731
<i>wR</i> ₂ (observed/all)	0.1045/0.1145
Goodness-of-fit (observed/all)	1.038/1.038
Max/min Δσ (e Å ^{−3})	+1.29/−0.69

with a 500 ml glass vessel, using C₆H₅CH₃ as the solvent. The conditions were adjusted as required for each experiment. The ethylene and propylene pressures were kept constant during polymerization by a continuous supply of monomer gas. The reactor was first charged with MAO and C₆H₅CH₃, followed by an injection of a C₆H₅CH₃ solution of the complex and MAO. After the solution was saturated with monomer, the polymerization process was started. Polymerization was stopped by pouring the reaction mixture into acidified EtOH. The polymer was filtered, washed with EtOH and dried under vacuum at 60 °C overnight.

4.10. Characterization of polymers

The thermal properties of the samples were studied. The m.p.s of the polymers were determined using a DSC 2920 TA instrument. Five to 8 mg of each dried polymer was fused into standard Al pans and measured using the following program: first, heating phase (10 °C min^{−1}) from 30 to 200 °C, and then cooling phase from 200 to 30 °C (10 °C min^{−1}).

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 186721 for compound 7. Copies of this data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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