Synthesis and Structure of Mononuclear Titanium Complexes Containing *ansa*-Aminopyridinato Ligands

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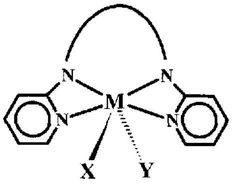
A series of siloxane-bridged bis(2-aminopyridines) were synthesized from dichlorosiloxanes and 2-aminopyridines in the presence of a base via nucleophilic substitution reactions. They were used, after deprotonation, as dianionic (*ansa*-aminopyridinato) ligands to stabilize mononuclear titanium complexes with unusual coordination geometries. An X-ray crystal structure analysis of one of the ligands and of a titanium complex proved mononuclearity and provided information about the binding mode of this novel type of ligands. Ethylene polymerization studies showed low activity, remarkable differences between structurally related complexes, and broad molecular weight distributions. Sterically less demanding substituents and a high basicity of the ligand increase polymerization activity.

The most popular ligands among amido-based Cp-analogous ligands (anionic ligands that donate up to 6 electrons to the metal) are benzamidinato ligands[1]. Related to these ligands are deprotonated 2-aminopyridines (aminopyridinato ligands) if they are bound in a strained η^2-coordination mode. Only a few examples of such mononuclear transition metal complexes have been described[2] so far. An advantage of aminopyridinato ligands compared to benzamidinato ligands is the opportunity to connect two of them easily via a bridge between the amido nitrogen atoms (see Scheme 1). This leads to *ansa*-aminopyrinato complexes. An analogy to *ansa*-metallocenes[3] and to bulky dialkoxy compounds[4,5] may be established.

Scheme 1. Schematic representation of an *ansa*-aminopyridinato complex

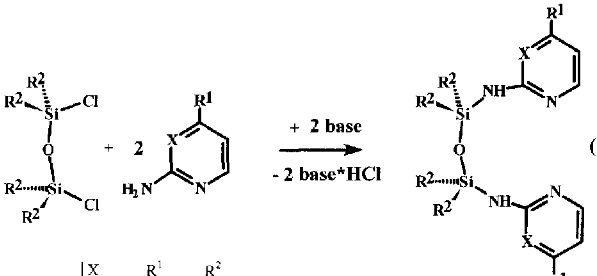


In this paper we report on the synthesis and structure of siloxane-bridged 2-aminopyridines which are used after deprotonation as *ansa*-aminopyridinato ligands to stabilize titanium complexes with an unusual coordination geometry. Furthermore, the application of such complexes in ethylene polymerization is described. Recently, siloxane-bridged metallocene complexes of group-4 metals[6] and siloxane-bridged amido metal complexes were reported. In the latter case a variety of transition metal complexes were described[7]. Manganese and iron complexes, which were characterized by X-ray crystal structure analysis, reveal polynuclearity by co-coordination of the amido nitrogen. This co-coordination is a problem if mononuclear amido metal complexes are desired. It is avoided by using aminopyridinato ligands due to pyridine coordination. Thus, the use of *ansa*-aminopyridinato ligands provide access to a variety of mononuclear early amido transition metal complexes.

Results and Discussion

Ligand Syntheses

Trimethylsilyl-substituted 2-aminopyridines may be easily prepared and have been shown to form complexes with group-4 metals in the desired η^2-coordination mode[2d,2e]. Thus, dichlordisiloxanes are promising synthetic tools to introduce a 3-atomic bridge between two aminopyridine units.



(eq. 1)

	X	R^1	R^2
1	C-H	Me	i-Pr
2	C-H	Me	Me
3	N	H	Me

By a variation of the alkylsilyl substituents and the use of pyrimidine instead of pyridine the electronic and steric influence of the ligands may be changed. **1** and **2** differ in the steric demand of the siloxane bridge. **2** and **3** have equal bridging moeties but a different ligand basicity. The synthesis of **2** and **3** according to equation 1 proceeded smoothly in the presence of triethylamine as a base. In a synthetically analogous approach **1** was obtained in 60% yield after a reaction time of 12 days. The reaction of so-

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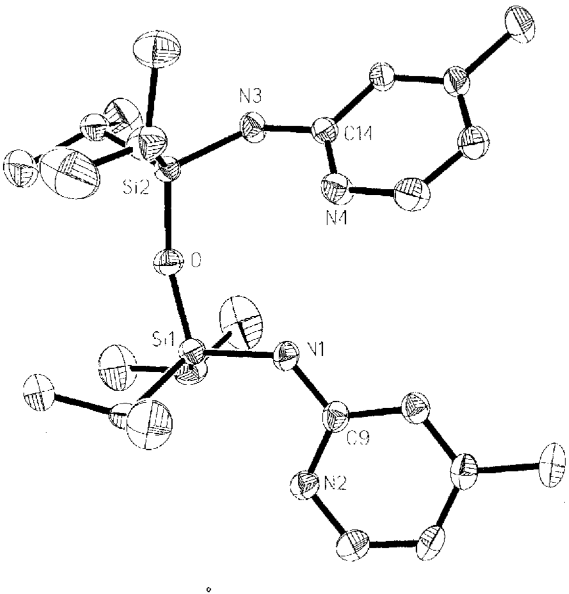
dium 4-picoline-2-ylamide with 1,3-dichloro-1,1,3,3-tetraisopropylsisiloxane afforded **1** (90% yield) in one hour. Recrystallization of **1**, **2**, and **3** from hexane furnished pure colorless crystalline materials. ^{1}H-, ^{13}C-, and ^{29}Si-NMR data as well as the elemental analyses are consistent with the structures of **1**–**3** (equation 1). Single crystals of **1** suitable for an X-ray crystal structure analysis could be grown by slow cooling of a saturated ether solution. A perspective ORTEP drawing of the molecular structure of **1** is shown in Figure 1 including selected bond lengths and angles. Crystallographic details are listed in Table 1. The sterically demanding isopropyl groups are arranged in a non-eclipsed manner and force **1** into a cisoid arrangement. Thus, the ligand is preorientated to bind in the desired chelating mode. A remarkable structural feature is the almost linear Si–O–Si bond angle [165.4(2)] indicative of strong dπ–pπ interactions between silicon and oxygen or electrostatic repulsive forces between the strong polarized Si–O bonds. The averaged N_{amido}–C–$N_{pyridine}$ bond angle (116°) is significantly smaller than the expected value of 120° (Csp^2 atom). **1** is predicted to form inter- or intramolecular H bonds because it contains a potential proton donor and an acceptor functionality. Due to the good solubility of **1** in hydrocarbons the H bond interactions are expected to be weak. An intramolecular hydrogen bond[8] N1–HN1···N4 (with a HN1···N4 distance of 2.20 Å) and a very weak intermolecular interaction N3–HN3···N2′ (with a HN3···N2′ distance of 2.90 Å) are forming an infinite chain in the solid state.

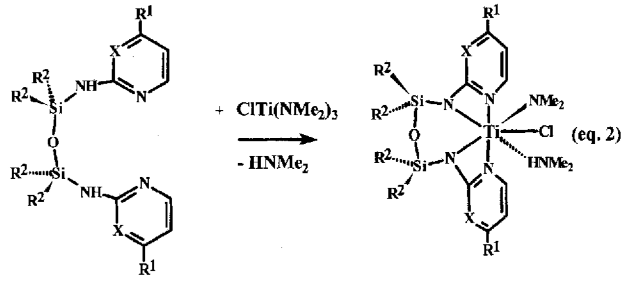
Figure 1. Structural representation of **1**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability



Selected bond lengths [Å] and angles [°]: C(14)–N(4) 1.336(5), C(14)–N(3) 1.377(5), N(1)–Si(1) 1.729(4), N(3)–Si(2) 1.741(4), O–Si(1) 1.623(4), O–Si(2) 1.626(3), N(2)–C(9)–N(1) 116.7(4), N(4)–C(14)–N(3) 115.8(3), C(9)–N(1)–Si(1) 129.1(3), C(14)–N(3)–Si(2) 128.1(3), Si(1)–O–Si(2) 165.4(2), O–Si(1)–N(1) 103.4(2), O–Si(2)–N(3) 111.9(2).

Complex syntheses and structures

Dimethylamido complexes of group-4 metals are known to be useful starting materials for the formation of metal complexes containing amido-chelating ligands via dimethylamine elimination[9]. The reactions of **1**, **2**, and **3** with one equivalent of $ClTi(NMe_2)_3$ (**4**), which can be easily obtained by a conproportionation reaction between $TiCl_4$ and $Ti(NMe_2)_4$ or by a salt elimination route starting from $TiCl_4$ and $LiNMe_2$[10], afford clean crystalline products of **5**, **6**, and **7** (eq. 2).



	X	R^1	R^2
5	C-H	Me	i-Pr
6	C-H	Me	Me
7	N	H	Me

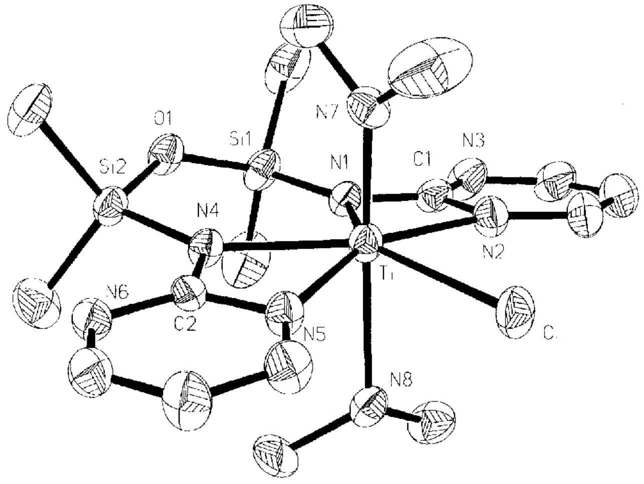
The ^{1}H- and ^{13}C-NMR data of **5**, **6**, and **7** are similar considering the fact that characteristic ligand signals are slightly different. Thus, only the spectra of **7** are discussed. Its ^{1}H-NMR spectra exhibit two single signals in the methylsilyl range and a single signal set for the other *ansa*-aminopyridinato ligand signals. Furthermore, characteristic signals of a dimethylamido and a lone-pair-coordinated dimethylamino ligand are observed. Thus, **7** possesses mirror symmetry in solution. The mirror plane is occupied by the O, Ti, N_{amido}, N_{amine}, and the Cl atom. The *ansa*-aminopyridinato ligand coordinates coplanarly to this plane by generating a second plane (ligand plane) which is also occupied by the Ti and the Cl atoms. The dimethylamido and the dimethylamino ligand are coordinated above and below the second plane. Thus, the different chemical environments of the methylsilyl signals can be explained. NOE experiments show that the dimethylamino ligand signal interacts with the downfield shifted methylsilyl signal.

In order to prove mononuclearity and the coordination mode determined on the basis of spectroscopical data an X-ray crystal structure analysis was carried out. Single crystals suitable for this purpose could be obtained after recrystallization of **7** in hexane. The analysis established a monomeric structure as shown in Figure 2 (including principal bond lengths and angles). Some important crystallographic features are compiled in Table 1. The coordination geometry of **7** is best described as distorted pentagonal-bipyramidal. The equatorial plane is occupied by the *ansa*-aminopyridinato and the chloro ligand as revealed by the NMR studies. The dimethylamino and the dimethylamido ligands are coordinated above and below this plane. The *ansa*-aminopyridinato ligand is planar with a maximal deviation smaller than 0.3 Å. The amido nitrogen atoms (N1,

Table 1. Crystallographic Data for **1** and **7**

compd.	**1**	**7**
formula	$C_{24}H_{41}N_4OSi_2$	$C_{16}H_{31}ClN_8OSi_2Ti$
mol. mass	457.8	491.0
cryst. color	colorless	brown
cryst. descript	prism	needle-like
cryst. size (mm)	0.4 × 0.3 × 0.2	0.4 × 0.1 × 0.1
cryst. system	monoclinic	monoclinic
space group	*Cc*	$P2_1/n$
lattice constants		
a (Å)	20.129(4)	8.301(2)
b (Å)	17.868(4)	24.968(5)
c (Å)	8.317(2)	12.167(2)
β (deg)	113.21(3)	100.75(3)
Z	4	4
T (K)	293(2)	293(2)
μ (mm^{-1})	0.150	0.573
absorp. corr.	no	no
θ range (deg)	2.20 - 24.31	1.89 - 24.11
largest diff. (e $Å^{-3}$) peak / hole	0.25 / -0.28	0.26 / -0.27
no. of rflns. (measd.)	4067	6291
no. of rflns. (indep.)	3010	3360
R (int)	0.055	0.048
no. of rflns. (obsd.) $I > 2\sigma(I)$	2270	1765
no. of parameters	298	267
$R1$ $[I > 2\sigma(I)]$	0.044	0.041
$wR2$ (all data)	0.114	0.098

Figure 2. Perspective ORTEP drawing of the molecular structure of **7**. All nonhydrogen atoms are represented by thermal ellipsoids drawn to encompass 30% probability



Selected bond lengths [Å] and angles [°]: C(1)−N(1) 1.332(5), C(1)−N(2) 1.352(5), C(1)−N(3) 1.359(5), C(1)−Ti 2.618(5), C(2)−N(4) 1.328(5), C(2)−N(6) 1.346(5), C(2)−N(5) 1.374(5), C(2)−Ti 2.628(4), N(1)−Si(1) 1.731(3), N(1)−Ti 2.129(3), N(2)−Ti 2.171(4), N(4)−Si(2) 1.730(3), N(4)−Ti 2.146(3), N(5)−Ti 2.162(3), N(7)−Ti 1.899(4), N(8)−Ti 2.359(4), O(1)−Si(2) 1.633(3), O(1)−Si(1) 1.641(3), Cl−Ti 2.503(2), N(1)−C(1)−N(2) 109.9(4), N(1)−C(1)−N(3) 126.5(5), N(2)−C(1)−N(3) 123.6(4), N(4)−C(2)−N(6) 126.7(4), N(4)−C(2)−N(5) 109.5(4), N(6)−C(2)−N(5) 123.8(4), Si(1)−N(1)−Ti 141.1(2), Si(2)−N(4)−Ti 142.5(2), Si(2)−O(1)−Si(1) 135.2(2), O(1)−Si(1)−N(1) 105.6(2), O(1)−Si(2)−N(4) 104.3(2), N(7)−Ti−N(1) 97.11(14), N(7)−Ti−N(4) 93.0(2), N(1)−Ti−N(4) 81.99(13), N(7)−Ti−N(5) 93.5(2), N(1)−Ti−N(5) 142.57(13), N(4)−Ti−N(5) 61.63(12), N(7)−Ti−N(2) 93.90(14), N(1)−Ti−N(2) 61.46(13), N(4)−Ti−N(2) 143.37(14), N(5)−Ti−N(2) 153.2(2), N(7)−Ti−N(8) 173.9(2), N(1)−Ti−N(8) 88.88(14), N(4)−Ti−N(8) 89.17(13), N(5)−Ti−N(8) 82.43(14), N(2)−Ti−N(8) 87.78(13), N(7)−Ti−Cl 94.66(12), N(1)−Ti−Cl 136.88(10), N(4)−Ti−Cl 138.59(9), N(5)−Ti−Cl 77.30(10), N(2)−Ti−Cl 76.48(11), N(8)−Ti−Cl 79.97(12).

N4, N7) have an almost planar geometry, as found in virtually all structurally characterized amido transition metal complexes[11]. The Si−O−Si angle in **7** [135.2(2)°] is significantly smaller than the analogous angle in **1** [165.4(2)°]. Thus, metals larger than titanium might be stabilized by this type of ligands without straining the ligand backbone. The study of the "chemistry" is under investigation.

The unusual coordination mode of the *ansa*-aminopyridinato ligands is also expressed by the titanium−nitrogen bond parameters. The $Ti-N_{amido}$ bond lengths [N(1)−Ti 2.129(3), N(4)−Ti 2.146(3), and the $Ti-N_{pyridine}$ distances (N(2)−Ti 2.171(4), N(5)−Ti 2.162(3)] are almost identical and thus the $N_{amido}-C_{ipso}-N_{pyridine}-Ti$ ring might be considered as delocalized. These findings are in accordance with observations made with benzamidinato ligands[1]. The averaged Ti−N bond length in titanium benzamidinato complexes is 2.12(2) Å[12]. The $Ti-N_{amido}$ distance in **7** is approximately 0.1 Å longer than such bond lengths normally [1.889(2) Å[13]] whereas the $Ti-N_{pyridine}$ distance in **7** reflects a value significantly shorter (0.1 Å) than the averaged general $Ti-N_{pyridine}$ bond length [2.247(7)[14]]. Such a bonding pattern is in contrast to titanium complexes that contain "non-bridged" aminopyridinato ligands[2d] where a nondelocalized binding mode with an usual $Ti-N_{pyridine}$ bond distance is observed.

Polymerization Studies

Besides studies of metallocene-related organometallic compounds the interest in the use of *ansa*-aminopyridinato complexes is focused on applications in α-olefin polymerization. Thus, preliminary ethylene polymerization studies were carried out with regard to two questions: Do complexes of the type **5**, **6**, and **7** catalyze the polymerization of ethylene? Which ligand characteristics increase polymerization activity? In order to extend Ziegler-Natta-based homogeneous catalytical applications recent activities were focused on nonmetallocene systems like alkoxy-[4] and amido-based[15] supporting ligands. Whereas alkoxy group-4 metal complexes were reported to be highly active in polymerization of α-olefins, such an activity was rarely observed for amido metal-based complexes[16]. Table 2 compiles the results of homogeneous ethylene polymerizations obtained by using **5**, **6**, and **7** as catalyst. MAO (methylaluminoxane in toluene) was used as a cocatalyst.

Although the complexes **5**, **6**, and **7** have a similar ligand core they show significant differences in polymerization activity. An increase in ligand basicity and a decrease in the steric demand of the ligand backbone seem to improve the activity. The unusually broad molecular weight distribution indicates that no single site reaction was involved. This finding is attributed to the presence of the amido and amine ligands. Heterogeneity during the polymerization process by

Table 2. Ethylene polymerization results by using selected titanium complexes and MAO as cocatalyst

Catalyst[a]	Ratio Al:Ti	Productivity[b] kg mol^{-1} h^{-1} bar^{-1}	M_n[c] kg mol^{-1}	M_w[d] kg mol^{-1}	(M_w/M_n)-1
4	2000	10.3	6.28	131	19.9
5	2000	0.05	3.94	326	81.8
6	2000	9.8	3.52	50	13.2
7	2000	6.4	3.26	124	37.1

[a] Conditions: toluene, 20 °C, 1.5 bar of ethylene, 1.5 h, cocatalyst: methylaluminoxane. The given data are an average of three runs. – [b] Productivity is related to the yield of polyethylene per mole of catalyst, time, and pressure of polymerisation. – [c] number-average degree of molecular mass. – [d] weight-average degree of molecular mass.

precipitating polymers is a further reason for the broad molecular weight distribution.

Conclusion

The results of the present work allow several conclusions to be drawn. First, siloxane-bridged bis(aminopyridines) can be synthesized by a variety of simple nucleophilic substitution reactions. Deprotonated, they act as dianionic tetradentate ligands (*ansa*-aminopyridinato ligands). Second, such *ansa*-aminopyridinato ligands can stabilize a novel type of monomolecular titanium complexes due to the strained η^2-binding mode of the aminopyridinato moieties. Third, the activity of such complexes in ethylene polymerization strongly depends on the nature of the ligand. An increase in ligand basicity and a decrease in the steric demand of the ligand backbone improve the activity. We are continuing to explore the potential utility of *ansa*-aminopyridinato complexes for organometallic chemistry and are currently extending our studies to other early transition metals.

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Experimental

All operations were carried out under argon with standard Schlenk techniques. Prior to use solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. MAO was purchased from Witco/Bergkamen as a 10% solution in toluene. – Mass spectra: AMD 402. – NMR spectra: Bruker ARX 400. Chemical shifts referenced to signals of the used solvents: [D$_8$]THF (β-CH$_2$: δ_H = 1.73, δ_C = 25.2) or C_6D_6 (δ_H = 7.16, δ_C = 128.0). The spectra were assigned with the help of DEPT, NOE, and COSY experiments. – Melting points: sealed capillaries, Büchi 535 apparatus. – Elemental analyses: Leco CHNS-932 elemental analyzer. – GPC: an apparatus from Knaur, suitable for High-Temperature Gel-Permeation Chromatography. Four columns were used, charged with size exclusion polystyrene gels of a pore diameter of 500 Å, 10 E4 Å, 10 E5 Å, and 10 E6 Å, respectively. A flow rate of 1 ml per minute of 1,2,4-Trichlorobenzene at 135 °C was applied in the chromatography. – X-ray diffraction data: STOE-IPDS using graphite-monochromated Mo-K_α radiation. The crystals were sealed inside capillaries. The structures were solved by direct methods (SHELXS-86[17]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[18]). XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Further details of the crystal structure investigations are available upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

Preparation of Sodium 4-Picoline-2-ylamide: In a 100-ml flask, 1.17 g (30.0 mmol) of sodium amide was suspended in 20 ml of THF. The suspension was cooled to 0 °C. A solution of 3.24 g (30.0 mmol) of 2-amino-4-picoline in 10 ml of ether was added within 15 minutes. After stirring for four hours at room temp. the mixture was filtered and the filtrate evaporated to dryness. In order to remove the THF completely the remaining solids were dried in vacuo for 1 hour. The solvent-free solids were washed twice with 10 ml of ether and dried. Yield 3.44 g (26.0 mmol, 87%) of colorless solid. – ^{1}H NMR ([D$_8$]THF): δ = 7.35 (d, 1H, J = 5.3 Hz), 5.71 (s, 1H), 5.50 (dd, 1H, J_1 = 1.3 Hz, J_2 = 5.3 Hz), 5.59 (s, 1H), 1.89 (s, 3H). – ^{13}C NMR ([D$_8$]THF): δ = 174.0, 148.8, 145.2, 112.3, 105.2, 20.9.

Preparation of **1**: A solution of 2.68 g of sodium 4-picoline-2-ylamide (20.6 mmol) in 20 ml of THF was cooled to −78 °C. To this stirred solution 2.95 g (9.4 mmol) of 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane was added via a syringe. The reaction mixture, which forms an orange jelly, was allowed to warm up to room temp. The supernatant yellow solution was filtered off. The residue was extracted three times with 20 ml of ether each. The combined extracts were evaporated to dryness and the crude product was recrystallized from hexane. Yield 3.88 g 8.5 mmol, 90%) of colorless crystals. – ^{1}H NMR (CDCl$_3$): δ = 7.95 (d, 2H, J = 5 Hz), 6.43 (m, 2H), 6.28 (m, 2H), 4.77 (s, 2H), 2.18 (s, 6H), 1.28 (sept, 4H, J = 7.5 Hz), 1.06 (dd, 24H, J_1 = 7.5 Hz, J_2 = 3.5 Hz). – ^{13}C NMR (CDCl$_3$): δ = 159.6, 148.1, 147.5, 114.8, 110.3, 21.0, 17.6, 13.5. – ^{29}Si NMR (CDCl$_3$): δ = 12.1. – $C_{24}H_{42}N_4OSi_2$ (458): calcd. C 62.83, H 9.23, N 12.21; found C 62.77, H 9.34, N 12.22.

Preparation of **2**: A solution of 5.00 g (46.0 mmol) of 2-amino-4-picoline in 20 ml of THF was diluted with ether up to 150 ml. To this solution 9.0 ml (64.0 mmol) of triethylamine and with vigorous stirring 4.1 ml (21.3 mmol) of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane were added. The reaction mixture was stirred overnight. After filtration and washing of the residue with hexane the combined filtrates were evaporated to dryness. The remainder, a colorless highly viscous syrup, was dried at 100 °C/1 mbar for several hours until all traces of residual solvent had been removed. Yield 7.20 g (20.8 mmol, 98%) of colorless viscous product. – ^{1}H NMR (CDCl$_3$): δ = 7.96–7.94 (m, 2H), 6.46–6.44 (m, 2H), 6.30 (m, 2H), 4.61 (s, 2H), 2.18 (s, 6H), 0.31 (s, 12H). – ^{13}C NMR (CDCl$_3$): δ = 160.1, 148.1, 147.9, 115.1, 110.8, 20.8, 0.4. – ^{29}Si NMR (CDCl$_3$): δ = −11.5. – $C_{16}H_{26}N_4OSi_2$ (346): calcd. C 55.45, H 7.56, N 16.17; found C 55.63, H 7.09, N 16.28.

Preparation of **3**: In a 100-ml flask 4.18 g (44.0 mmol) of 2-aminopyrimidine was dissolved in 50 ml of THF. To this solution 8.3 ml (60 mmol) of triethylamine and 3.9 ml (4.10 g, 20.0 mmol) of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane were added via a syringe. The reaction mixture was stirred overnight, then evaporated to dryness. The residue was suspended in a mixture of ether (30 ml) and THF (10 ml). The suspension was filtered, the residue was washed with 10 ml of ether. The combined filtrates were evaporated to dryness and the crude product was recrystallized from boiling hexane. Yield 4.30 g (13.4 mmol, 67%) of colorless needles, m.p. 71.3 °C. – ^{1}H NMR (CDCl$_3$): δ = 8.31–8.27 (m, 4H), 6.59–6.56 (m, 2H), 5.72 (s, 2H, H-N), 0.32 (m, 12H). – ^{13}C NMR (CDCl$_3$): δ = 163.8, 158.2, 157.9, 111.3, 0.3. – ^{29}Si NMR (CDCl$_3$): δ =

−10.20. − $C_{12}H_{20}N_6OSi_2$ (320): calcd. C 44.97, H 6.29, N 26.22; found C 45.69, H 6.28, N 27.43.

Preparation of **5**: A solution of 0.60 g (2.7 mmol) of $Ti[N(CH_3)_2]_3Cl$ (**4**)[10] in 30 ml of hexane was added to a solution of 1.27 g (2.7 mmol) of **1** in 30 ml of hexane. The resulting dark red oily liquid was kept overnight at +4 °C. After the formation of some crystals the mixture was kept for some days at −30 °C. The supernatant solution was decanted, the crystals were collected and dried in vacuo. Yield 1.26 g (2.0 mmol, 72%) of light brown crystals, m.p. 175 °C (dec.). − ^1H NMR (C_6D_6): δ = 8.79 [s, broad, 2H, C(6)py], 6.10 [s, 2H, C(3)py], 6.00 [m, 1H, C(5)py], 5.99 [m, 1H, C(5)py], 3.64 (s, 6H, CH_3-N-Ti), 2.03 [s, broad, 6H, $(CH_3)_2$N-H], 1.82 (s, 6H, CH_3-py), 1.37 [s, 14H, *i*-Pr(β)], 1.26 (m, 6H, CH_3-C-Si), 1.23 [m, 8H, CH_3-CH-Si(α)]. − ^{13}C NMR (C_6D_6): δ = 150.8 [C(2)-py], 143.9 [C(6+4)-py], 111.9 [C(5)-py], 111.4 [C(3)-py], 52.3 (C-N-Ti), 39.7 (C-N-H), 21.6 (C-py), 19.2 [*C*-C-Si(α)], 18.8 [*C*-C-Si(α)], 16.9 [C-Si(α)], 16.5 [C-Si(α)]. − ^{29}Si NMR (C_6D_6): δ = −10.8. − $C_{28}H_{53}ClN_6OSi_2Ti$ (629): calcd. C 53.44, H 8.49, N 13.36; found C 53.43, H 8.49, N 13.15.

Preparation of **6**: A solution of 4.95 g (14.3 mmol) of **2** in 40 ml of hexane was added to a solution of 3.08 g (14.3 mmol) of $Ti[N(CH_3)_2]_3Cl$ (**4**)[10] in 60 ml of hexane at room temp. The resulting yellow-brown suspension was refluxed until all solids had dissolved. By slowly cooling down from +69 °C to −30 °C a crystalline product was obtained. The reaction afforded 7.07 g (12.6 mmol, 88%) of brown crystals. − ^1H NMR (C_6D_6): δ = 9.10 (s, 2H), 6.01 (d, 2H, *J* = 5.6 Hz), 5.98 (d, 2H, *J* = 0.5 Hz), 3.67 (s, 6H), 2.05−1.85 (m, 7H), 1.79 (s, 6H), 1.23 (m, 4H, 1/2 hexane), 0.88 (t, 3H, *J* = 4.5 Hz, 1/2 hexane), 0.57 (s, 6H), 0.37 (s, 6H). − ^{13}C NMR (C_6D_6): δ = 168.9, 150.7, 144.7, 111.2, 109.5, 53.3, 39.9, 31.9, 23.0, 21.5, 14.3, 2.7, 1.5. − ^{29}Si NMR (C_6D_6): δ = −10.2. − $C_{23}H_{44}ClN_6OSi_2Ti$: calcd. C 49.32, H 7.92, N 15.00; found C 48.17, H 7.50, N 14.45.

Preparation of **7**: In a 100-ml flask a solution of 1.25 g (3.9 mmol) of **3** in 30 ml of hexane was added to a solution of 0.84 g (3.9 mmol) of **4**[10] in 30 ml of hexane. After stirring for 30 minutes the solids were allowed to settle down. The supernatant solution was filtered and concentrated to half of its volume. A slow decrease of the temperature from +40 °C to +4 °C overnight resulted in 0.77 g (1.6 mmol, 40%) of yellow-brown crystals, which were collected and dried in vacuo. − ^1H NMR (C_6D_6): δ = 8.93 (m, 2H), 7.91 (m, 2H), 5.71 (t, 2H, *J* = 4.95 Hz), 3.59 (s, 6H), 1.98 (s, 1H), 1.72 (s, 6H), 0.80 (s, 6H), 0.61 (s, 6H). − ^{13}C NMR (C_6D_6): δ = 169.4, 161.1, 153.2, 107.5, 53.6, 39.9, 2.6, 1.7. − ^{29}Si NMR (C_6D_6): δ = −7.2. − $C_{16}H_{31}ClN_8OSi_2Ti$: calcd. C 39.14, H 6.36, N 22.82; found C 39.17, H 6.45, N 22.62.

Polymerization of ethylene: In a typical polymerization experiment a 100-ml flask was charged with 25 ml (40 mmol) of a MAO solution in toluene. This solution was magnetically stirred and degassed in vacuo. It was saturated with ethylene at 20 °C and 1 bar. Then 20 µmol of the corresponding catalyst (0.02 M solution in toluene) was injected. The pressure of ethylene was adjusted to 1.5 bar and the mixture was stirred at 20 °C for 1.5 hours. The reaction was quenched by slowly pouring it into a vigorously stirred mixture of 50 ml methanol and 25 ml of concentrated aquous hydrogen chloride. The resulting suspension was boiled for 1 h. After addition of 50 ml of water it was boiled for another hour to remove the toluene and to dissolve residual aluminium compounds. After filtration the product was washed several times with water, ethanol, acetone and dried in air. The polyethylene was characterised by IR {$\tilde{\nu}$ [cm^{-1}] = 3059 (terminal olefinic groups), 2918, 2850 (saturated CH), 1640 (olefin), 1473, 1463, 730, 719}, elemental analyses, and High-Temperature GPC.

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