Octahedral Group 4 Metal Complexes That Contain Amine, Amido, and Aminopyridinato Ligands: Synthesis, Structure, and Application in α-Olefin Oligo- and Polymerization

Hans Fuhrmann, Simon Brenner, Perdita Arndt, and Rhett Kempe*

MPG AG “Komplexkatalyse” an der Universität Rostock, Buchbinderstrasse 5-6,
18055 Rostock, Germany

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The reaction of trimethylsilyl-substituted 2-aminopyridines with mixed chloro(dialkylamido)metal complexes (titanium and zirconium) leads via amine elimination to octahedral group 4 metal complexes that contain amine, amido, and aminopyridinato ligands. The X-ray crystal structure analyses of (4-Me-TMS-APy)(NMe_2)($HNMe_2$)**Ti**Cl_2 (**1**) (crystallographic data: $P2_1/c$ (No. 14), monoclinic, $a = 16.754(2)$ Å, $b = 14.395(2)$ Å, $c = 17.890(3)$ Å, $\beta = 110.28(1)°$, $Z = 8$) and (6-Me-TMS-APy)(NEt_2)($HNEt_2$)**Zr**Cl_2 (**2**) (crystallographic data: $P2_1/n$ (No. 14) monoclinic, $a = 10.125(1)$ Å, $b = 16.331(1)$ Å, $c = 15.276(2)$ Å, $\beta = 93.90(1)$, $Z = 4$) prove the compounds to be mononuclear with a cisoid arrangement of the two chloro ligands embedded in a reactive pocket determined by the steric demand of the three nitrogen containing ligands. Oligo- and polymerization studies with propene and 1-butene reveal the following results. First, **1** is a remarkably active precatalyst in contrast to the very low activity of **2**. Second, MAO, a 1:1 mixture of i-$Bu_3Al/B(C_6F_5)_3$ (homogeneous polymerization) and ethylaluminum sesquichloride (if **1** is incorporated in a $MgCl_2$-matrix) have shown to be the most active cocatalysts. Third, the polymers and oligomers are atactic.

Introduction

Metallocene-catalyzed olefin polymerization[1] is an excellent example of understanding the structure−reactivity relationship in homogeneous catalysis. Thus, new applications, for instance, cycloolefin polymerization,[2] oligomerization of functionalized monomers,[3] and block copolymerization of olefins and esters,[4] could be developed by fine tuning the precatalyst molecular structure and the catalyst activation process. In order to extend Ziegler−Natta-based homogeneous catalytic applications recently activities are focused on non-metallocene systems like alkoxy[5] and amido[6] supporting ligands. Whereas alkoxy-based group 4 metal complexes are reported to be active in polymerization of higher α-olefins, such an activity is rarely observed for amido metal complexes.[7] In the paper presented herein it is reported about synthesis and structure of octahedral group 4 metal complexes that contain amine, amido, and aminopyridinato[8] ligands. Such complexes represent a novel structural type in group 4 metal chemistry and serve as a useful model for systematic investigations of structure−activity relations of an amido-based olefin polymerization catalyst, because they contain a variety of exchangeable supporting ligands and they show interesting activities in α-olefin oligo- or polymerization depending on the precatalyst activation protocols.

Experimental Section

Materials and Procedures. All reagents were obtained commercially and used as supplied. All manipulations of air sensitive materials were performed with rigorous exclusion of oxygen and moisture in dried Schlenk-type glassware on a dual manifold Schlenk line, interfaced to a high-vacuum line, or in an argon-filled Vacuum Atmospheres glovebox (mBraun labmaster 130) with a high-capacity recirculator (<1.5 ppm O_2). Solvents (Aldrich) and NMR solvents (Cambridge Isotope Laboratories all 99 atom% D) were freshly distilled from sodium tetraethylaluminate.

General Oligomerization or Polymerization Protocol. Homopolymerization experiments were carried out in a thermostated 1 L glass autoclave (equipped with a magnetically driven hollow shaft stirrer). The autoclave was evacuated at 90 °C for 2 h prior to use and charged with 200 mL of solvent, 0.1 mmol of the precatalyst, and the corresponding amount of the cocatalyst as well as further additives if

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necessary. The gaseous monomers addition was controlled by a calibrated flow meter. Polymerization experiments were carried out for 4 h if not otherwise mentioned to collect a suitable amount of product for characterization. At the end of the polymerization reaction, the mixture was quenched with acidified methanol. After removal of unreacted monomer, the product layer was separated, dried, and distilled. Waxy oligomers were collected after removing the solvent under vacuum. Polymers were filtered off, washed, and dried in vacuum. Propene (99.95%) and 1-butene (99.3%) (Linde AG) were purified by passing them through a set of multisorb columns (Messer Griesheim), $i\text{-}Bu_3Al$, $Et_3Al_2Cl_3$, and $i\text{-}Bu_2Mg$ hydrocarbon diluted were purchased from Aldrich, and methylalumoxane (MAO) was purchased as a 10 wt % toluene solution from Witko.

Oligomer and Polymer Characterization. Products have been characterized by GC (HP5880A), GC-FTIR on line (HP 5890/2 with IR detector 5965B), GC-MS (HP5890/2 combined with AMD/3 mass spectrometer, Intectra), ^1H and ^{13}C NMR (Bruker AC 250 MHz , FT mode, relaxation delay > 5s, pulse width 60°), preparative GC (HP 5890/2 multi column system, Gerstel(Germany)), and molecular weight and molecular weight distribution with GPC (GPC-100, Waters, USA).

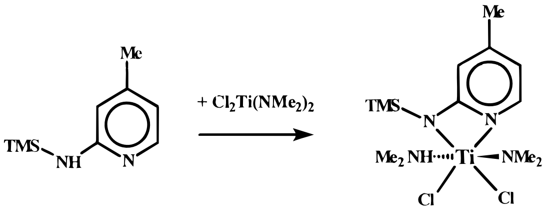
Physical Measurements. NMR spectra were recorded on a Bruker ARX 400 instrument with variable temperature unit. ^1H and ^{13}C chemical shifts were referenced to the solvent resonances and reported relative to TMS. ^{29}Si chemical shifts were reported relative to TMS. Melting points were determined in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were performed with a Leco CHNS-932 elemental analyzer. X-ray diffraction data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The crystals were mounted inside a capillary. The structure was solved by direct methods (SHELXS-86)[9] and refined by full-matrix least-square techniques against F^2 (SHELXL-93).[10] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

(4-Me-TMS-APy)(NMe$_2$)(HNMe$_2$)TiCl$_2$ (1). A slurry of 409 mg (2.00 mmol) of $(Me_2N)_2TiCl_2$ in 50 mL hexane was cooled to −40 °C. 4-Methyl-2-((trimethylsilyl)amino)pyridine (360 μL, 2.00 mmol) was added slowly via syringe. The mixture was allowed to warm to room temperature over a period of 20 min and was stirred for further 3 h. The suspension turned into an almost clear brown solution. The solution was filtered, and the volume was reduced under vacuum to approximately 30 mL. Cooling down to −30 °C over night afforded a brown microcrystalline material. Yield: 491 mg, 1.27 mmol, 64%. ^1H NMR (303 K, C_7D_8): δ 7.99 (d, J = 5.6 Hz, 1H, H-6), 5.96 (s, 1 H, H-3), 5.80 (d, J = 5.6 Hz, 1 H, H-5), 3.62 (s, 6 H; $N(CH_3)_2$), 1.95 (br, 6 H, $N(CH_3)_2H$), 1.85 (s, 1 H, NH), 1.66 (s, 3 H, Me-Ap), 0.43 (s, 9 H, $SiMe_3$). ^1H NMR (230 K, C_7D_8): δ 8.03 (d, J = 5.6 Hz, 1H, H-6), 5.93 (s, 1 H, H-3), 5.71 (d, J = 5.6 Hz, 1 H, H-5), 3.60 (s, 6 H; NMe_2), 1.95, 1.68 (br, 6 H, $N(CH_3)_2H$), 1.84 (s, 1 H, NH), 1.54 (s, 3 H, Me-Ap), 0.38 (s, 9 H, $SiMe_3$). ^{13}C NMR (303 K, C_7D_8): δ 175.0 (C-2), 160.2 (C-4), 151.5 (C-6), 118.3 (C-3), 116.8 (C-5), 54.3 ($N(CH_3)2$), 42.0 ($N(CH_3)_2H$), 21.6 (Me-Ap), 0.7 ($SiMe_3$). ^{13}C NMR (220 K, C_7D_8): δ 164.1 (C-2), 151.1 (C-4), 143.0 (C-6), 112.0 (C-3), 110.5 (C-5), 51.7 ($N(CH_3)_2$), 41.2, 40.2 ($N(CH_3)_2H$), 21.3 (Me-Ap), 1.7 ($SiMe_3$). Anal. Calcd for $C_{13}H_{28}N_4Cl_2SiTi$: C, 40.32; H, 7.29; N, 14.47. Found: C, 39.72; H, 7.08; N, 14.20.

(6-Me-TMS-APy)(NEt$_2$)(HNEt$_2$)ZrCl$_2$ (2). To a slurry of 504 mg (2.16 mmol) of $ZrCl_4$ in 30 mL of ether was added slowly via syringe 822 μL (2.16 mmol) of $Zr(Et_2N)_4$. The mixture was stirred and became almost clear. After 30 min, 6-methyl-2-((trimethylsilyl)amino)pyridine (780 μL, 4.33 mmol) was added slowly via syringe. The solution was stirred for further 2 h. The solution was filtered, and the volume was reduced under vacuum to approximately 15 mL. Cooling down to −30 °C afforded overnight a light yellow crystalline material. Yield: 1.285 g, 2.64 mmol, 61%. ^1H NMR (303 K, C_6D_6): δ 6.82 (dd, 1 H, H-4), 6.08, 5.92 (d, 1 H, H-3, H-5), 3.72 (q, 4 H, $N(-CH_2-)_2$), 2.7 (b, 4 H, $N(-CH_2-)_2H$), 2.50 (s, 3 H, Me−Ap), 2.0 (b, 1 H, NH), 0.98 (t, 6 H, $N(-CH_2CH_3)_2$; 0.71 (t, b, 6 H, $HN(-CH_2CH_3)_2$), 0.39 (s, 9H, $SiMe_3$). ^{13}C NMR (303 K, C_6D_6): δ 167.9 (C-2), 155.5 (C-6), 140.9 (C-4), 111.8 (C-3), 109.5 (C-5), 43.5 ($N(-CH_2CH_3)_2$), 42.8 (b, $N(-CH_2CH_3)_2H$), 23.4 (Me−Ap); 13.69 ($N(-CH_2CH_3)_2$), 13.75 (b, $HN(-CH_2CH_3)_2$), (1.5 ($SiMe_3$). Anal. Calcd for $C_{17}H_{36}N_4Cl_2SiZr$: C, 41.95; H, 7.46; N, 11.51. Found: C, 41.09; H, 7.29; N, 10.75.

Results and Discussion

The reaction of 4-methyl-2-((trimethylsilyl)amino)pyridine (4-Me-TMS-APy-H) which is easily prepared in high yield[11] by the method of Phillion[12] with the mixed chloro(dimethylamido) complex $(Me_2N)_2TiCl_2$, which is prepared via a comproportionation reaction between $Ti(NMe_2)_4$ and $TiCl_4$,[13] affords complex **1** in an amine elimination reaction according to eq 1 (64% yield). The room temperature ^1H NMR spectrum shows a single resonance set for a strained coordinated aminopyridinato ligand, a typical dimethylamido singlet, and a further broad peak (seven hydrogens). The latter signal splits into two singlets each covering three hydrogens and a multiplet (one hydrogen) at 230 K. Thus it is indicative of a lone pair coordinated dimethylamine ligand. Elemental analysis is in accordance with the formula in eq 1.



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(1)

In order to prove the fact that **1** is mononuclear and has the expected cisoid arrangement of the two chloro ligands an X-ray crystal structure analysis was carried out. A perspective ORTEP drawing of the molecular structure of **1** is shown in Figure 1 including key bond distances and angles. Selected crystallographic data are listed in Table 1. The coordination geometry of **1** is described best as disturbed octahedral. Due to the strained η^2-coordination mode of the aminopyridinato ligand the ideal octahedral arrangement cannot be accomplished. The bond angles between the chloro and the amido ligands (N(3)−Ti(1)−Cl(2) = 93.90(11)°, N(3)−Ti(1)−Cl(1) = 98.02(10)°) are significant larger than the corresponding angles between the chloro and the amine ligand (Cl(1)-Ti(1)-N(4) = 84.02(8)°, Cl(2)−Ti(1)−N(4) = 81.50(9)°). This fact might by explained by steric reasons. Steric repulsion is furthermore an important condition for the cisoid arrangement of the chloro ligands. The steric demand of the amine and the amido ligand causes their transoid arrangement which is in combination with the bidentate binding mode of the aminopyridinato ligand the reason for the desired cisoid arrangement of the chloro ligand.

Attempts to synthesize a zirconium complex analogous to **1** failed. Only $(4\text{-}Me\text{-}TMS\text{-}APy)_3ZrCl$ was obtained as a main product.[14] In order to keep the sterically determined cisoid arrangement of the chloro ligands steric more demanding amine, amido and aminopyridinato ligands are needed if analogous complexes of the larger group 4 metals are desired. The reaction of 2 equiv of 6-methyl-2-((trimethylsilyl)amino)pyridine[15] (6-

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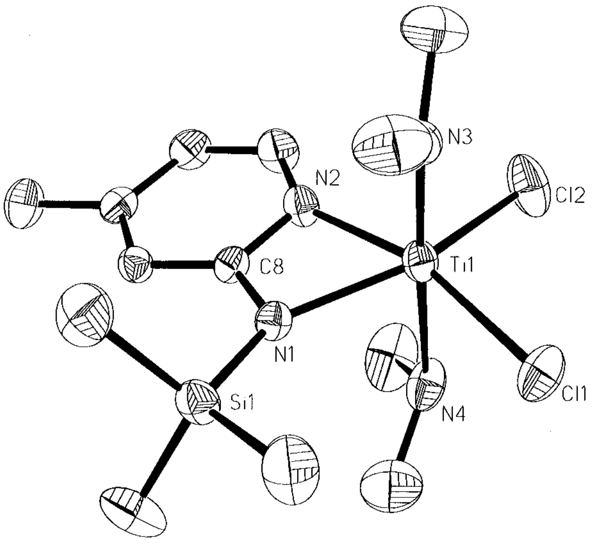
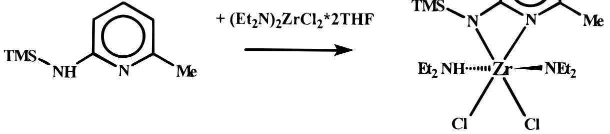


Figure 1. Perspective ORTEP drawing of the molecular structure of **1**. The asymmetric unit contains two symmetry independent molecules; only one is shown. All non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 30% probability. Selected bond lengths (Å) and angles (deg): C(8)−N(2) 1.355(4), C(8)−N(1) 1.368(4), N(1)−Ti(1) 2.073(3), N(2)−Ti(1) 2.107(3), N(3)−Ti(1) 1.872(3), N(4)−Ti(1) 2.355(3), Cl(1)−Ti(1) 2.3172(11), Cl(2)−Ti(1) 2.3347(12); N(6)−C(2)−N(5) 108.9(3), N(3)−Ti(1)−N(1) 97.60(12), N(3)−Ti(1)−N(2) 93.96(12), N(1)−Ti(1)−N(2) 64.36(10), N(3)−Ti(1)−Cl(1) 98.02(10), N(1)−Ti(1)−Cl(1) 103.94(8), N(3)−Ti(1)−Cl(2) 93.90(11), N(2)−Ti(1)−Cl(2) 89.21(8), Cl(1)−Ti(1)−Cl(2) 99.88(5), N(1)−Ti(1)−N(4) 86.03(11), N(2)−Ti(1)−N(4) 84.82(11), Cl(1)−Ti(1)−N(4) 84.02(8), Cl(2)−Ti(1)−N(4) 81.50(9).

Me-TMS-APy-H) with $(Et_2N)_2ZrCl_2 \cdot 2THF$[16] affords according to eq 2 a yellow crystalline material (6-Me-TMS-APy)Zr-



(2)

$(Et_2N)(Et_2NH)Cl_2$ **2** in 61% yield. ^1H and ^{13}C NMR spectra as well as elemental analysis are consistent with the formula in eq 2. The single-crystal X-ray structure analysis of **2** established its monomeric structure and the desired cisoid arrangement of the chloro ligands as shown in Figure 2 including principal bond distances and angles. Selected crystallographic data are listed in Table 1. Coordination geometry and the general arrangement are similar to the findings of the molecular structure of **1**. Thus it is shown that the concept to create a sterically determined cisoid arrangement of the chloro ligand works also for the larger group 4 metals. Furthermore, **1** and **2** might be considered as similar to the well-known benzamidinato,[17] porphyrin,[18] and tetraaza macrocyclic[19] group 4 complexes, and a structural analogy can be drawn.

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
chem formula	$C_{13}H_{28}ClN_4SiTi$	$C_{17}H_{36}Cl_2N_4SiZr$
fw	387.3	486.7
space group (No.)	$P2_1/c$ (14)	$P2_1/n$ (14)
temp (°C)	20	20
λ (Å)	0.71069	0.71069
ρ (g cm^{-3})	1.27	1.28
a (Å)	16.754(2)	10.125(1)
b (Å)	14.395(2)	16.331(1)
c (Å)	17.890(3)	15.276(2)
β (deg)	110.28(1)	93.90(1)
V (Å^3)	4044.5(9)	2520.1(4)
Z	8	4
μ (mm^{-1})	0.746	0.704
$R_1{}^a$ ($I > 2\sigma(I)$)	0.041	0.054
wR2^b (all data)	0.113	0.157

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b \mathrm{wR2} = \{\sum[w(F_o^2 - F_c^2)]^2/\sum[w(F_o^2)]^2\}^{1/2}$.

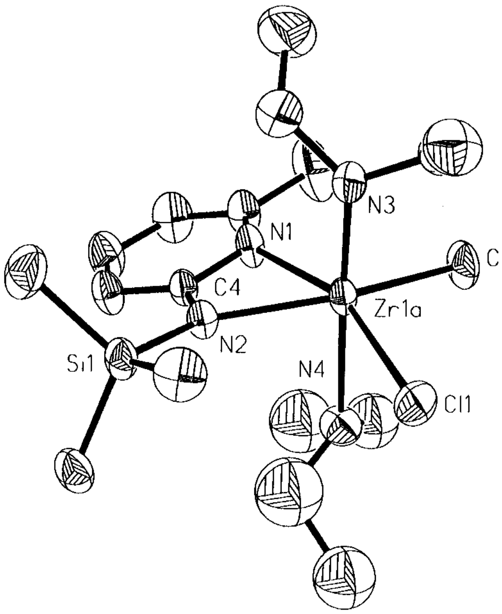


Figure 2. Structural representation of **2**. Hydrogen atoms and one part of the disordered atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C(4)−N(2) 1.341(6), C(4)−N(1) 1.373(6), N(1)−Zr(1A) 2.329(4), N(2)−Zr(1A) 2.172(4), N(3)−Zr(1A) 2.003(5), N(4)−Zr(1A) 2.490(5), Cl(1)−Zr(1A) 2.443(2), Cl(2)−Zr(1A) 2.461(2); N(2)−C(4)−N(1) 112.5(4), N(3)−Zr(1A)−N(2) 96.7(2), N(3)−Zr(1A)−N(1) 97.6(2), N(2)−Zr(1A)−N(1) 60.07(13), N(3)−Zr(1A)−Cl(1) 97.20(14), N(2)−Zr(1A)−Cl(1) 104.58(11), N(3)−Zr(1A)−Cl(2) 97.5(2), N(1)−Zr(1A)−Cl(2) 91.38(11), Cl(1)−Zr(1A)−Cl(2) 100.18(7), N(2)−Zr(1A)−N(4) 85.4(2), N(1)−Zr(1A)−N(4) 82.9(2), Cl(1)−Zr(1A)−N(4) 82.75(14), Cl(2)−Zr(1A)−N(4) 80.41(13).

Beside the reactivity of **1** and **2** in organometallic chemistry, which is under investigation, our interest is focused on catalytic applications. For this purpose polymerization studies with propene and 1-butene were carried out. Surprisingly, the zirconium complex **2** demonstrates a significantly lower or even absent polymerization activity compared to the related titanium complex **1**. This observation was made for all polymerization protocols listed in Table 2. This is in contrast to a general experience in metallocene-catalyzed olefin polymerization where zirconocenes are known to be much more active than the corresponding titanocenes.[20] Table 2 summarizes propene and 1-butene oligo- and polymerization results using **1** as precatalyst

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Table 2. Propene and 1-Butene Oligomerization with **1** as Precatalyst under Various Conditions (Run Time 1 h [precatalyst 0.5 mmol/L])

run	cocatalyst	Al/Ti	temp (°C)	activity (kg_{oligo}/(g_{Ti} h))	$\bar{M}_n$[a] (g/mol)	olefins[b] (%)
	Oligo- and Polypropenes					
1	*i*-Bu_3Al	38	50	1.9	2150	traces
2[c]	MAO	500	25	59.5	388	18
3	*i*-$Bu_3Al/B(C_6F_5)_3$[e]	75	5	10.0	2800	no
	Oligo- and Polybutenes					
4	*i*-Bu_3Al	50	50	3.9	143	11
5	*i*-$Bu_3Al/B(C_6F_5)_3$	38	10	33.6	3100[g]	no
6[d]	$Et_3Al_2Cl_3$	40	70	45.2	850[f]	no

[a] By vapor pressure osmometry. [b] By GC-FTIR and ^{1}H-NMR. [c] In toluene (all other experiments in hexane). [d] The titanium complex was incorporated in a $MgCl_2$ matrix by coprecipitation from a mixture of *i*-Bu_2Mg and CCl_4 in hexane. [e] Modified with $B(C_6F_5)_3$ (molar ratio Ti/B = 1:1). [f] About 40-50% of the saturated oligomers in the C_{10}−C_{22} fraction are products of carbometalation. [g] After 20 h, 6−8 g of a rubber-like polybutene were isolated ($\bar{M}_n$ 8580 by GPC) with an unusual broad molecular mass distribution of $\bar{M}_w/\bar{M}_n = 125$).

and various activation procedures. MAO, a 1:1 mixture of *i*-$Bu_3Al/B(C_6F_5)_3$ (homogeneous polymerization) and ethylaluminum sesquichloride (if **1** is incorporated in the $MgCl_2$-matrix) have shown to be the most active cocatalysts. Although the polymerization parameters varied considerably, the poly- and oligomers exhibit similar features. They are saturated for the most part. Thus chain termination process by β-hydrogen transfer is only of marginal significance. ^{13}C NMR spectra of the oligo- and polymers are indicative that chain transfer to the alkylaluminum cocatalyst should be the prevailing chain termination process. The possible transfer to vinylidene end groups is less probable because an adequate appearance of oligomers with trisubstituted double bonds has not been observed. A further result which follows from the ^{13}C NMR spectra is the low content of m = meso = isotactic dyads. Compound **1** produces atactic oligomers or polymers with a slight preponderance of r = racemic dyads. It is proposed that the flexible nature of the ligand set might allow for a high degree of freedom, randomness and thus an atactic polymer is produced under a presumed chain-end control regime. The nature of the active titanium species is not clear also because amido as well as amine ligands might be replaced by MAO or $B(C_6F_5)_3$. Furthermore, carboalumination of the lower oligomers caused by the strong lewis acidic $Et_3Al_2Cl_3$ (run 6 in Table 2) takes place. It competes with oligomer growth and is known to be observed for titanium catalysts under such conditions.[21]

Conclusions

Several conclusions can be drawn from this study. First, group 4 amido metal complexes that contain a novel ligand core like in **1** and **2** can be synthesized easily via amine elimination up to a large scale. Second, the desired cisoid arrangement of the chloro ligands in such complexes is predominantly caused by the steric demand of the amine and the amido ligands. Third, such titanium complexes seem to have a better activity in polymerization and/or oligomerization of higher olefins. Fourth, atactic oligomers and polymers are produced which might be explained by the bulk and the flexibility of the ligand set.

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Supporting Information Available: Tables of crystal data, positional parameters, thermal parameters, and complete bond distances and angles and complete ORTEP drawings (18 pages). X-ray crystallographic files, in CIF format, are also available. Ordering and access information is given on any current masthead page.

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