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Titanium–Imido Complexes with Pendant Groups – Synthesis, Characterization, and Evaluation of Their Role as Precatalysts for Ethylene Polymerization

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The synthesis of several anilines ($Ar^{PG}NH_2$) substituted in the *ortho* position with pendant groups (PGs, terminated by potentially coordinative arene, thienyl, furanyl, or pyridyl functionalities) was accomplished by a two- to five-step synthesis in good yields. The $Ar^{PG}NH_2$ proligands were used for the preparation of titanium complexes starting from $Ti(NMe_2)_4$ in the presence of excess Me_3SiCl. Complexes of the general formula $[Ti(NAr^{PG})Cl_2(NHMe_2)_x]$ ($x = 1, 2$), which are supported by a terminal imido functionality, were obtained in 60–95 % yield. The nature of the pendant group influences the coordination mode of the ligand. Although only monodentate imido linkages have been observed with ligands where PG is arene, thiophene, and furan, ligands with substituted pyridine sidearms lead to chelating imido–donor functionalities. The potential hemilabile behavior of some imido–donor ligands, which results from the reversible coordination of the side arm, was studied by variable-temperature ^1H NMR spectroscopy. These compounds were evaluated as precatalysts for ethylene polymerization with various aluminum cocatalysts. Ultrahigh molecular-weight (UHMW) polyethylenes were obtained. All compounds were fully characterized by spectroscopic methods (^1H and ^{13}C NMR), and elemental analysis and some were also characterized by single-crystal X-ray diffraction.

Introduction

Being isolobal with $[C_5H_5]^-$ (Cp),[1] the dianionic, π-donor terminal imido functional group $[NR]^{2-}$ (R = alkyl or aryl) has emerged as an alternative spectator ligand to Cp ligands (e.g. in alkene metathesis and olefin polymerization).[2–4] Imido complexes have also found application in materials chemistry (organometallic chemical vapor deposition[5] and polyoxometalates)[6] and have been implicated in a number of stoichiometric or catalytic transformations that involve the M=NR linkage itself, such as ammoxidation of propene,[7] metathesis reactions,[8] C–H activation,[9] reactions with unsaturated C–C[10] or C–X bonds,[11] alkyne hydroamination,[12,13] carboamination reaction,[14] and strained-heterocycle opening.[9d,15]

Several groups have probed the interactions of early-metal systems with pendant arenes, thienyl, or ether groups on Cp ligands and reported an enhancement of the catalytic activities in some examples for olefin oligo- or polymerization, which is due to the hemilabile coordination of the pendant fragment at some stage in the catalytic cycle.[16,17] In a somewhat related system, Magna et al. reported aryloxide–titanium complexes with pendant groups, which exhibit interesting catalytic activity for the selective dimerization of ethylene.[18]

Although we[19] and others[4f,20] have shown that early-transition-metal complexes can incorporate functionalities at the periphery of the imido functionality, few complexes are known that incorporate a chelating imido–donor, i.e. with an imido group attached to the same metal center through the N atom of the imido functionality and a second donor atom.[19,20a,20d,20e,20f] To the best of our knowledge, no hemilabile behavior has been demonstrated in such ligand systems (Figure 1).

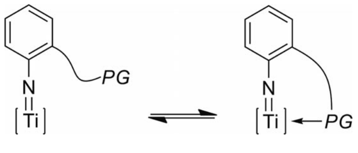

Figure 1. Titanium–imido systems with hemilabile or coordinated pendant groups.

We have previously prepared such imido–titanium complexes with a very short side arm (the distance between the imido N atom and the donor), which lead to bridging imido

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bimetallic complexes (Figure 2).[19,21] The synthesis of aniline proligands substituted in the *ortho* position with pendant groups of longer and varying side-arm lengths and donor functionalities (with potentially coordinative S, O, N, and C atoms) was targeted with the goal of fostering chelation. Synthetic methods to obtain these proligands (Figure 3) and the preparation of the resulting titanium–imido compounds are described in this paper. Preliminary reactivity studies towards ethylene polymerization are also reported.

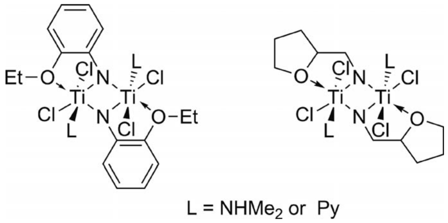


Figure 2. Previously reported titanium complexes with chelating, bridging imido–donor ligands (from ref.[19]).

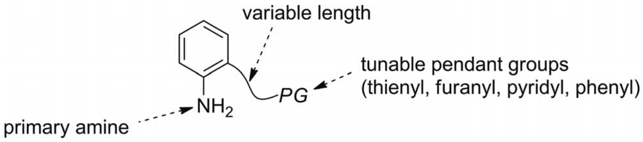


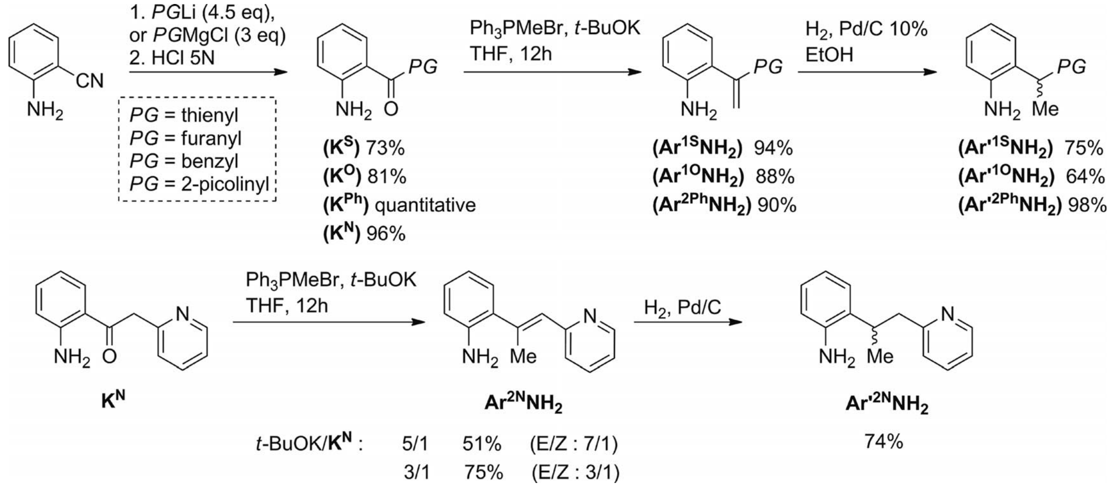
Figure 3. Targeted *ortho*-substituted aniline proligands with a pendant group.

Results and Discussion

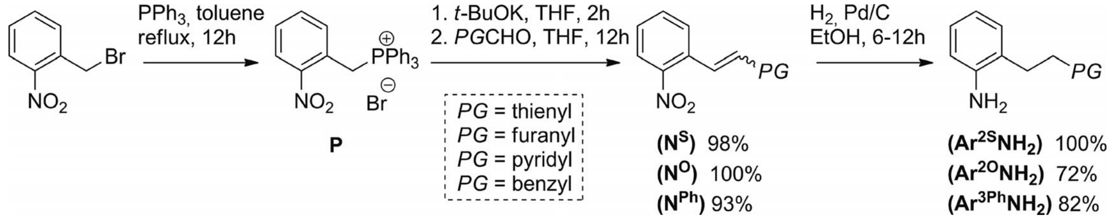
1. Synthesis of the Imido Proligands

Unfortunately, there was no general method for the synthesis of the aniline proligands that were substituted in the *ortho* position with pendant groups of varying side-arm lengths and donor functionalities. Consequently, we developed three different methods (*A*, *B*, and *C*) that depended on the length of the linker between the aniline and the pendant group and the nature of the donor atoms of the pendant group. These three methods used are illustrated in Schemes 1, 2, and 3 and are fully detailed in the Supporting Information. They are based on the use of commercially-available precursors, afford the desired substituted anilines in two to five steps in reasonably good overall yields, and are summarized below.

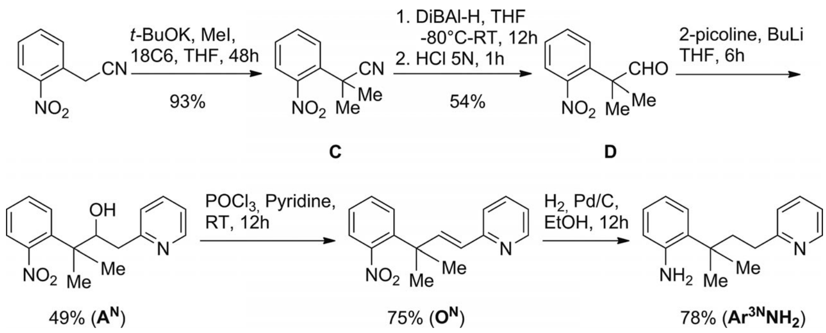
Starting from 2-cyanoaniline, anilines with one (PG = thienyl, furanyl) or two carbon atoms (PG = phenyl, 2-picolinyl) in the linker between the aniline ring and the pendant group were synthesized according to the first route (Method *A*, Scheme 1). Importantly, this method afforded two types of proligand: anilines with an unsaturated methylidene on the linker were obtained in two steps through a



Scheme 1. Method *A* for the synthesis of substituted anilines with one- and two-carbon spacers.



Scheme 2. Method *B* for the synthesis of substituted anilines with two- and three-carbon spacers.



Scheme 3. Method *C* for the synthesis of substituted anilines with three-carbon spacers.

Wittig reaction, and a third reduction step produced anilines with a saturated linker.

The second route (Method *B*, Scheme 2) consists of a three-step synthesis starting from 2-nitrobenzyl bromide, which afforded anilines with two (PG = thienyl, furanyl, pyridyl) or three carbon atoms (PG = phenyl) in the linker between the aniline ring and the pendant group.

The last route (Method *C*, Scheme 3) produced anilines with a more sterically encumbered three-carbon spacer with two methyl groups at the α-position in order to force the coordination of the PG to the metal center. This method was only used for the synthesis of anilines with PG = pyridyl.

The substituted anilines are named $Ar^{nPG}NH_2$ (Figure 4) to take into account the number of carbon atoms (*n*) in the linker chain between the *ortho* position of the aniline and the pendant group, and the nature of the PG (PG = S for thienyl, O for furanyl, N for pyridyl, Ph for phenyl).

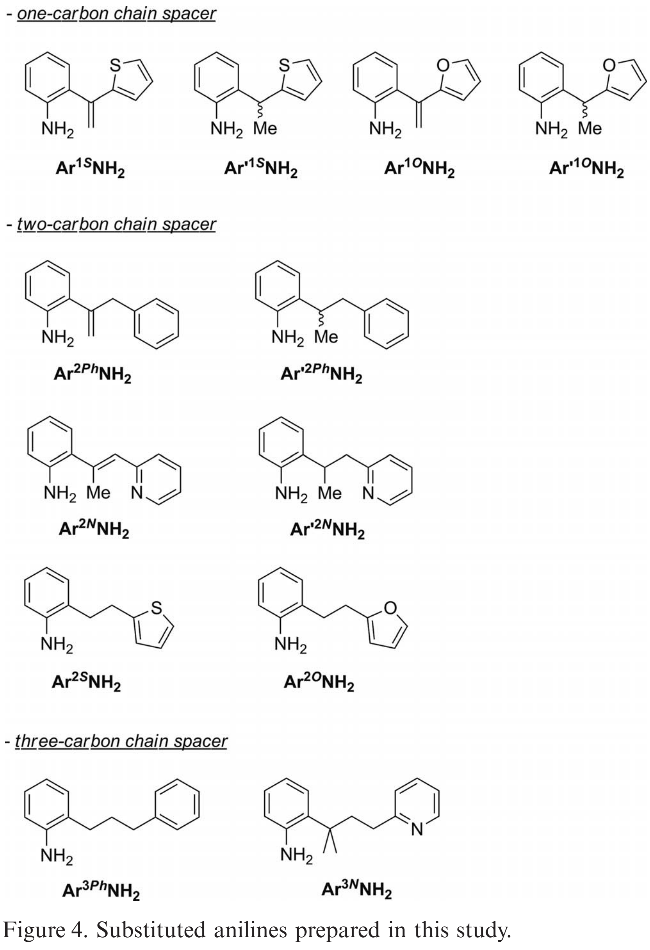
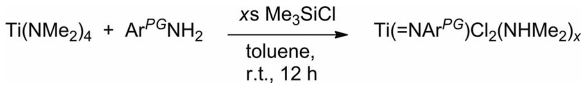


Figure 4. Substituted anilines prepared in this study.

2. Synthesis of the Titanium–Imido Complexes

a) Imido Complexes with PG = Thienyl, Furanyl, and Phenyl

The imido–titanium complexes were prepared according to our general procedure for easy access to various titanium– and vanadium–imido compounds of the type $[M(=NR)Cl_2(NHMe_2)_2]$.[19,22–25] In a one-pot synthesis, a toluene solution of $Ti(NMe_2)_4$ was treated with 1 equiv. of $Ar^{PG}NH_2$ followed by the addition of 6 equiv. of Me_3SiCl (Scheme 4). After suitable workup, the imido complexes were obtained in yields from 59–95% as orange or red solids (Figure 5). Elemental analysis and ^1H and ^{13}C NMR spectra are in agreement with compounds of the general formula $[Ti(=NAr^{PG})Cl_2(NHMe_2)_2]$, i.e. with two dimethylamino ligands coordinated to the metal center.



$$Ti(NMe_2)_4 + Ar^{PG}NH_2 \xrightarrow[\text{toluene, r.t., 12 h}]{xs\ Me_3SiCl} Ti(=NAr^{PG})Cl_2(NHMe_2)_x$$

Scheme 4. General procedure for the synthesis of the titanium–imido complexes.

Single crystals of three of these complexes, **O^1**, **S^1**, and **S^2**, suitable for X-ray diffraction studies were obtained from room temp. toluene or cold toluene/pentane solutions. Thermal ellipsoid plots are presented in Figures 6, 7, and 8, and selected metric parameters are given in Table 1. Two independent molecules are present in the molecular structure of **O^1**, but as the geometric parameters are not significantly different, only one of these molecules (molecule A) is discussed.

In the solid state, the molecular structures of the three bisdimethylamino adducts (**S^1**, **O^1**, and **S^2**) are best described as a distorted trigonal bipyramid for **S^1** with axial dimethylamine ligands ($\tau = 0.58$) or a distorted square pyramid for **O^1** and **S^2** [$\tau = 0.36$ (**O^1**), and 0.37 (**S^2**)].[26] The N_{imido}–Ti–Cl angles are in the range 107–115°, and the N_{imido}–Ti–N_{NHMe_2} angles are in the range 94–100°. The distances and angles associated with the titanium center and the ligands are comparable to those found in other

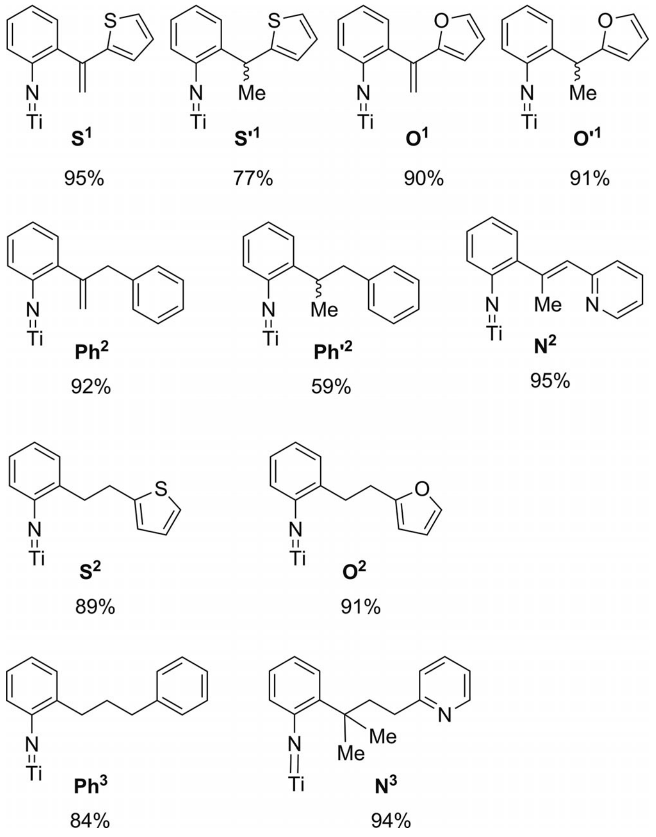


Figure 5. [Ti(=NAr^{PG})Cl$_2$(NHMe$_2$)$_2$] with corresponding yields and labels.

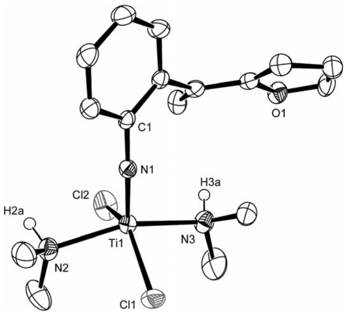


Figure 6. Thermal ellipsoid plot of **O^1** (molecule A) with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

[M(=NR)Cl$_2$(NHMe$_2$)$_2$] complexes (M = Ti,[24,25,27] V[22,23]). The complexes exhibit a short Ti–N$_{imido}$ distance of 1.6979(16) for **O^1**, 1.700(2) for **S^1**, and 1.701(3) Å for **S^2**, and the imido linkage is almost linear [Ti–N$_{imido}$–C$_{ipso}$ 175.72(14), 174.6(2), and 166.9(2)° in **O^1**, **S^1**, and **S^2**, respectively]. This is consistent with the lone pair on nitrogen being donated to an acceptor orbital on titanium, and the imido Ti–N bond can be considered as a triple bond.

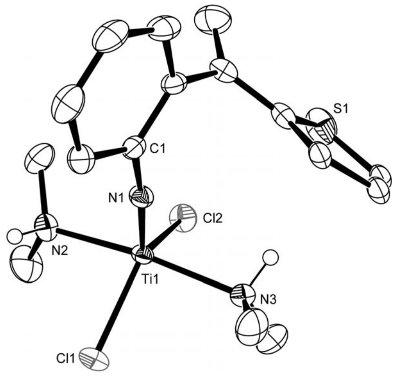


Figure 7. Thermal ellipsoid plot of **S^1** with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

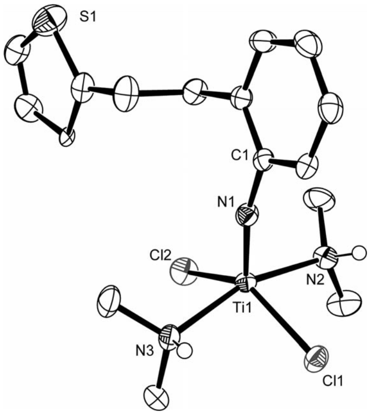


Figure 8. Thermal ellipsoid plot of **S^2** with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

Table 1. Comparison of average interatomic distances [Å] and angles [°] in [Ti(=NAr^{PG})Cl$_2$(NHMe$_2$)$_2$].

	O^1 [a]	**S^1**	**S^2**
Ti–N$_{imido}$	1.6979(16)	1.700(2)	1.701(3)
N$_{imido}$–C$_{ipso}$	1.390(2)	1.389(4)	1.389(4)
Ti–Cl	2.3387(6)	2.3387(10)	2.3652(9)
	2.3441(6)	2.3251(10)	2.3375(9)
Ti–N$_{NHMe_2}$	2.184(16)	2.202(3)	2.214(3)
	2.2088(16)	2.204(3)	2.188(3)
H$_{NHMe_2}$···Cl	2.403	2.482	2.529
Ti–N$_{imido}$–C$_{ipso}$	175.72(14)	174.6(2)	166.9(2)
Cl–Ti–Cl	138.17(3)	131.60(4)	140.39(4)
N$_{NHMe_2}$–Ti–N$_{NHMe_2}$	160.21(7)	170.57(10)	162.55(10)
N$_{imido}$–Ti–N$_{NHMe_2}$	100.20(7)	94.45(11)	100.64(11)
	99.57(7)	94.97(11)	95.62(11)
N–H···Cl	158.4	159.8	148.3
Ti···D^{PG} [b]	5.453	4.511	7.132 [c]
τ	0.36	0.58	0.37

[a] Geometric parameters are given for independent molecule A. [b] D^{PG} is the donor atom in the PG. [c] A shorter (4.566 Å) intermolecular Ti···S distance is found.

The crystal structure determinations also unambiguously show noninteracting functional thienyl (**S^1**, **S^2**), and furanyl (**O^1**) groups, with normal metric parameters, which are listed in Table 1. Both chlorine atoms occupy equatorial sites in the trigonal bipyramid or square pyramid with Cl1–Ti–Cl2 angles of 138.17(3) (**O^1**), 131.60(16) (**S^1**), and

140.39(4)° (**S^2**) and mean Ti–Cl bond lengths of 2.34 (**O^1**), 2.34 (**S^1**), and 2.35 Å (**S^2**). The two *trans* dimethylamino ligands have mean Ti–N_{NHMe_2} bond lengths of ca. 2.20 Å for the three compounds. The supramolecular structure is characterized by Me_2N–H···Cl intermolecular hydrogen bonds (NH···Cl 2.403–2.529 Å, N–H···Cl 159.8–148.3°), which is a feature that is common to many related compounds.[22,24,27]

Heating solid **O^1** at 60 °C under dynamic vacuum (ca. 5×10^{-2} mbar) resulted in no sign of PG donor atom coordination and left unchanged solids with some degree of decomposition (evidenced by the formation of free aniline ligands and NH_2Me_2Cl). The ammonium salt NH_2Me_2Cl was also detected in substantial amounts after solid **O^2** had been left under dynamic vacuum (ca. 9×10^{-4} mbar) for 12 h at room temp. This suggests that, in the solid state, decomposition of these complexes occurs before the coordination of the O or S atom. However, the compounds are thermally stable in solution: heating a C_6D_6 solution of **O^1** to 80 °C resulted in no sign of decomposition, PG donor atom coordination, or $NHMe_2$ elimination. Furthermore, a variable-temperature ^1H NMR study of **O^2** in [D_8]toluene showed that the proton in the 2-position from the furanyl O atom (α from O) is almost unchanged when lowering the temperature. At low temperature, the only proton that is notably low-field shifted (from 6.35 ppm at 295 K to 6.85 ppm at 195 K, see Supporting Information) is the H atom in the 3-position (β′ from O). This behavior (no line broadening) suggests the presence of a preferred average orientation of the furanyl H or C atoms in the 3-position instead of a dynamic exchange that involves reversible coordination of the oxygen atom.

b) Imido Complexes with PG = Pyridyl

The reaction of the pyridyl-containing PG **$Ar^{2N}NH_2$** with $Ti(NMe_2)_4$ in the presence of Me_3SiCl under similar conditions as described above yields an orange solid in 95% yield. NMR spectroscopy and an X-ray diffraction study clearly show the formation of a bisdimethylamino adduct: $[Ti(=NAr^{2N})Cl_2(NHMe_2)_2]$ (**N^2**).

Figure 9 shows the molecular structure of **N^2**, and selected metric parameters are given in Table 2. The structure of **N^2** resembles that of other five-coordinate $[Ti(=NAr^{PG})Cl_2(NHMe_2)_2]$ complexes described here with comparable metric parameters [Ti–N_{imido} 1.7129(8) Å, Ti–N_{imido}–C1 179.11(8)°, Cl–Ti–Cl 131.857(15)°, mean Ti–Cl 2.351 Å, mean Ti–N_{amine} 2.217 Å]. The main feature in the pentacoordinate titanium center is again the absence of coordination of the PG pyridine nitrogen atom (see below, Ti···N_{Py} 4.931 Å). The molecular structure is characterized by an intramolecular hydrogen bond between the pyridine nitrogen atom and the hydrogen atom of a $NHMe_2$ ligand (N2) [NH···N_{Py} 2.408 Å, N–H···N_{Py} 145.8°].

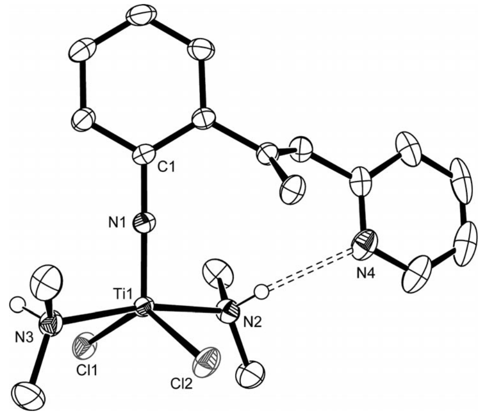


Figure 9. Thermal ellipsoid plot of **N^2** with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

Table 2. Comparison of average interatomic distances [Å] and angles [°] in $[Ti(=NAr^{nPG})Cl_2(NHMe_2)_x]$ complexes containing pyridyl PGs.

	N^2	**N'^2**	**N''^2**	**N'''^2**	**N^3**	**N'^3**
Ti–N_{imido}	1.7129(8)	1.694(3)	1.708(3)	1.7011(15)	1.7107(13)	1.7006(3)
N_{imido}–C_{ipso}	1.3868(12)	1.385(5)	1.375(4)	1.387(2)	1.391(2)	1.389(2)
Ti–Cl	2.3607(4), 2.3347(4)	2.3437(12), 2.3455(12)	2.4029(11), 2.4190(11), 2.4696(10), 2.7771(11)	2.3407(5), 2.3334(6)	2.3465(5), 2.3298(5)	2.3660(5), 2.3349(5)
Ti–N_{NHMe_2}	2.2232(9), 2.2104(9)	2.194(3)	–	2.2100(15), 2.1991(15)	2.2230(14), 2.1924(13)	2.1973(14)
Ti–N_{Py}	–	2.222(3)	2.314(3)	–	–	2.2400(14)
Ti···N_{Py}	4.931	–	–	4.387	4.569	–
H_{NHMe_2}···Cl	2.411	–	–	2.485	–	2.444
Ti–N_{imido}–C_{ipso}	179.11(8)	172.3(3)	172.5(2)	174.86(13)	164.48(12)	167.69(12)
Cl–Ti–Cl	131.857(15)	142.68(5)	84.83(3), 79.32(3), 80.76(3)	128.12(2)	135.42(2)	138.77(2)
N_{NHMe_2}–Ti–N_{NHMe2}	168.74(3)	–	–	173.55(6)	164.76(5)	–
N_{NHMe_2}–Ti–N_{Py}	–	159.14(12)	–	–	–	157.70(6)
N_{imido}–Ti–N_{NHMe_2}	95.31(4), 95.80(4)	98.15(14)	–	94.96(6), 91.35(7)	99.62(6), 95.32(6)	99.46(6)
N_{imido}–Ti–N_{Py}	–	102.55(14)	97.19(11)	–	–	102.68(6)
N–H···Cl	166.0	–	–	162.9	–	155.5
τ	0.61	0.27	–	0.76	0.49	0.32

The noncoordination of the strong donor in the pendant pyridine in $\mathbf{N^2}$ is significant, and might be explained by (i) the weaker donating properties of the N atom due to extended delocalization through the C=C double bond and/or (ii) the rigidity of the unsaturated linker.

In order to test the influence of the length of the side arm on the potential coordination of the pendant pyridine group, we treated the analogous saturated proligand $\mathbf{Ar'^{2N}NH_2}$ with $Ti(NMe_2)_4$ in the presence of Me_3SiCl (Scheme 5). Under identical experimental conditions we observed (by ^1H NMR spectroscopy of an aliquot of the solution) the formation of two compounds: a major species $\mathbf{N'^2}$ and a minor species $\mathbf{N''^2}$. Integration of the ^1H NMR spectrum indicates the presence of only one $NHMe_2$ ligand per imido in $\mathbf{N'^2}$, which is in agreement with a compound of formula $[Ti(=NAr'^{2N})Cl_2(NHMe_2)_1]$, whereas signals assigned to dimethylammonium are present in the spectrum of $\mathbf{N''^2}$. Complex $\mathbf{N''^2}$ was isolated in a very low yield as yellow crystals suitable for an X-ray diffraction study.

The molecular structure of $\mathbf{N''^2}$ is presented in Figure 10, and selected metric parameters are given in Table 2. Complex $\mathbf{N''^2}$ is formulated as the ionic complex $[Ti(=NAr'^{2N})Cl_4][NH_2Me_2]_2$. The chelating imido–pyridine ligand forms an eight-membered ring. The octahedrally coordinated titanium center is surrounded by four chlorine atoms, the nitrogen atom of a linear imido linkage [$Ti–N_{imido}$ 1.708(3) Å, $Ti–N_{imido}–C1$ 172.5(2)°], and the N atom of the pendant pyridine group in the *cis* position with respect to the N_{imido} atom [$Ti–N_{Py}$ 2.314(3) Å, $N_{Imido}–Ti–N_{Py}$ 97.19(11)°]. The Ti–Cl bond length *trans* to the N_{imido} atom is severely elongated [2.7771(11) Å] due to the *trans* influence of the imido ligand.

X-ray quality crystals of neutral $\mathbf{N'^2}$ were also obtained, which allowed us to determine its molecular structure by X-ray diffraction (Figure 11). The most prominent feature of the molecular structure of $\mathbf{N'^2}$ is the coordination of the nitrogen atom of the pendant pyridine group to the titanium center, which forms an eight-membered ring. The pyridine substituent is located *trans* to the remaining dimethylamino ligand [$Ti–N_{NHMe_2}$ 2.194(3) Å, $Ti–N_{Py}$ 2.222(3) Å] within a square pyramidal complex (τ = 0.27). The geometric parameters associated with the titanium center and the ligands are comparable to those found in related $[Ti(=NAr)Cl_2(NHMe_2)_2]$ complexes presented here (see Table 2). The imido functionality exhibits a short $Ti–N_{imido}$

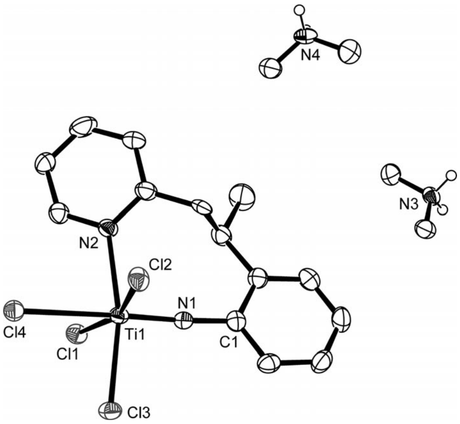


Figure 10. Thermal ellipsoid plot of $\mathbf{N''^2}$ with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

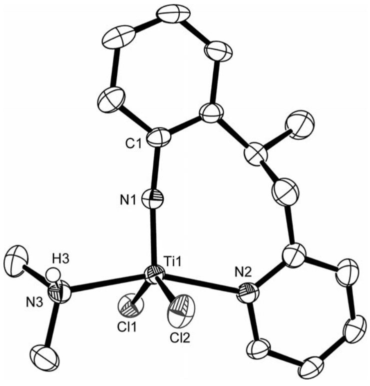
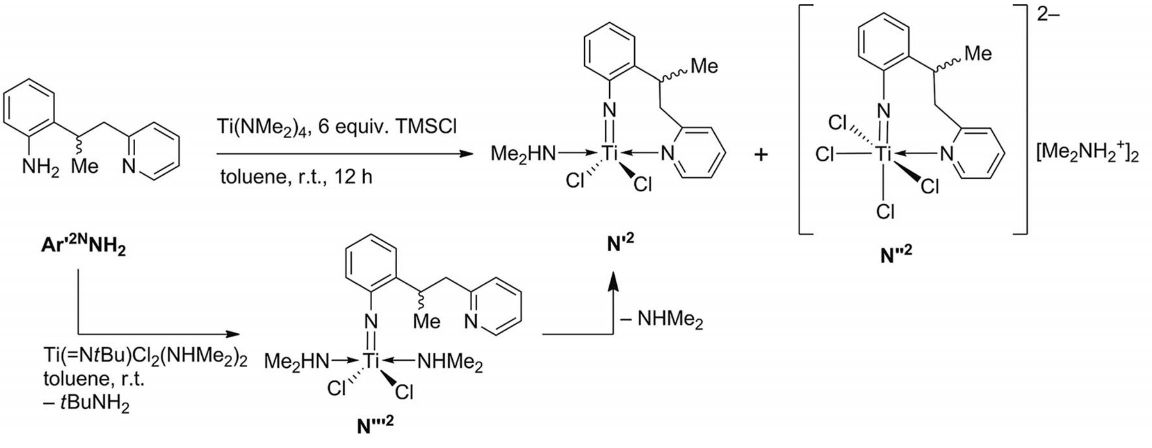


Figure 11. Thermal ellipsoid plot of $\mathbf{N'^2}$ with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C and toluene solvate molecule omitted. H atoms bonded to N drawn as spheres of arbitrary radius.



Scheme 5. Synthesis of chelating imido–pyridine complexes from $\mathbf{Ar'^{2N}NH_2}$.

distance of 1.694(3) Å and an almost linear imido linkage [Ti–N_{imido}–C_{ipso} 172.3(3)°]. The respective *trans*-located chlorine atoms occupy basal sites in the square pyramid with a Cl1–Ti–Cl2 angle of 142.68(5)° and mean Ti–Cl bond lengths of 2.34 Å.

Formation of the ionic $\mathbf{N''^{2}}$ might result from the reaction with in situ generated Me_2NH_2Cl [i.e. from a reaction between liberated $NHMe_2$ and Me_3SiCl,[28] Equation (1)]. The factors that govern the formation of such an ammonium salt are still under scrutiny. Nevertheless, in seeking an alternative synthetic strategy to $\mathbf{N'^{2}}$ free of ionic $\mathbf{N''^{2}}$, the transimination reaction of [Ti(=N*t*Bu)$Cl_2(NHMe_2)_2$] with an equimolar amount of $\mathbf{Ar'^{2N}NH_2}$ was considered (Scheme 5). This mild exchange reaction afforded a high yield of pure $\mathbf{N'^{2}}$.[29] Interestingly, small amounts of the intermediate bis(dimethylamino) adduct ($\mathbf{N'''^{2}}$) were crystallized from the pentane washings from this reaction. As $\mathbf{N'''^{2}}$ is very similar to $\mathbf{N^{2}}$, it will not be discussed (Figure 12 and Table 2), but the isolation of both complexes with and without coordination of the N atom of the pyridine strongly support the potential hemilabile character of the pyridine PG in these ligands.

$$2\ Me_2NH + Me_3SiCl \rightleftharpoons 2\ Me_2NH_2Cl + Me_3SiNMe_2 \qquad (1)$$

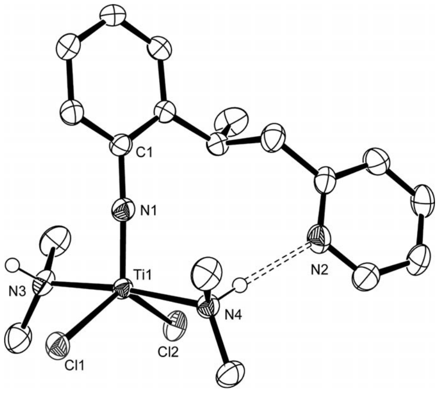


Figure 12. Thermal ellipsoid plot of $\mathbf{N'''^{2}}$ with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

Further proof of the intramolecular coordination of such pyridine PGs comes from our studies with $\mathbf{Ar^{3N}NH_2}$, which possesses a longer, three-carbon linker (Scheme 6).

Treatment of a toluene solution of $Ti(NMe_2)_4$ with $\mathbf{Ar^{3N}NH_2}$ in the presence of 6 equiv. of Me_3SiCl at room temp. for 12 h afforded orange $\mathbf{N^{3}}$. The formation of the bis-$NHMe_2$ adduct was further confirmed by the ^1H NMR spectrum of $\mathbf{N^{3}}$ and X-ray structure determination. A thermal ellipsoid plot is presented in Figure 13, and selected metric parameters are given in Table 2. The structure is similar to the other five-coordinate bis(dimethylamino) adducts presented here and is not detailed further.

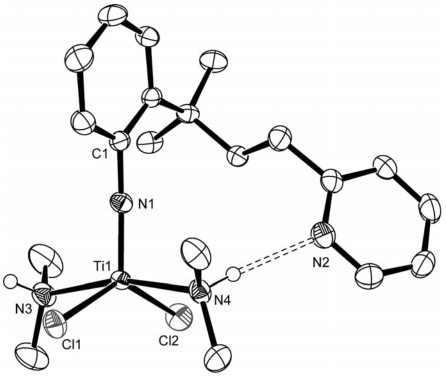
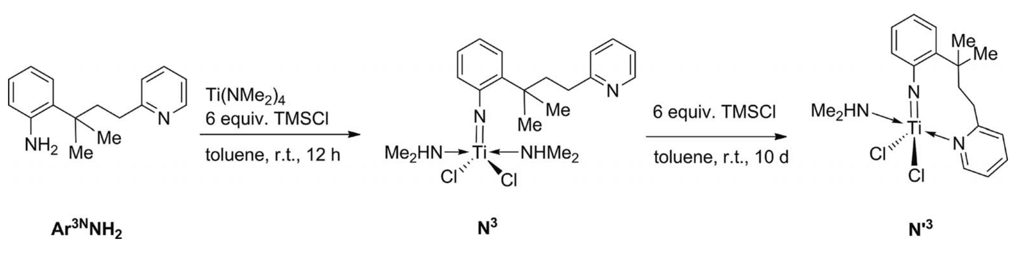
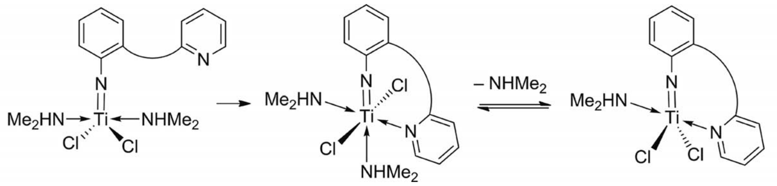


Figure 13. Thermal ellipsoid plot of $\mathbf{N^{3}}$ with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

However, with longer reaction time, we noted a slow evolution of the NMR spectrum of the above reaction mixture [$Ti(NMe_2)_4$, $\mathbf{Ar^{3N}NH_2}$, Me_3SiCl]. After 10 d of reaction in the presence of Me_3SiCl, a new complex, $\mathbf{N'^{3}}$, was obtained as the unique species (Scheme 6). We later found it more convenient and reproducible to prepare $\mathbf{N'^{3}}$ from isolated $\mathbf{N^{3}}$ and Me_3SiCl in toluene. The exact role of the excess Me_3SiCl in this transformation is presently unknown. Me_3SiCl might help the decoordination of the dimethylamine through silylation of the coordinated $NHMe_2$ (see above). Furthermore, in the absence of Me_3SiCl, repeated dissolution of $\mathbf{N^{3}}$ in toluene followed by vacuum treatment (repeated five times) led to dimethylamine elimination with concomitant formation of $\mathbf{N'^{3}}$ (although complete transformation was not achieved, as about 10% of $\mathbf{N^{3}}$ was still present after five repetitions of this treatment). This suggests that vacuum treatment also plays an important role in displacing the equilibrium of $NHMe_2$ decoordination. Hence, the chelate complex $\mathbf{N'^{3}}$ seems more difficult to obtain than the parent $\mathbf{N'^{2}}$, which we attribute to the length of the donor side arm: the eight-membered metallacycle in $\mathbf{N'^{2}}$ is probably more favorable than the nine-membered ring in $\mathbf{N'^{3}}$.



Scheme 6. Synthesis of monodentate and chelating imido–pyridine complexes from $\mathbf{Ar^{3N}NH_2}$.



Scheme 7. From monodentate to chelating imido–pyridine complexes.

A thermal ellipsoid plot of the solid-state structure of **N′3** is presented in Figure 14, and selected metric parameters are given in Table 2. The molecular structure of **N′3** clearly indicates the coordination of the nitrogen atom of the pendant pyridine group to the metal center, which forms a nine-membered ring. The pyridine substituent is *trans* to the remaining dimethylamino ligand. The geometry of the metal center is a distorted trigonal bipyramid (τ = 0.77). The distances and angles associated with the titanium center and the ligands are comparable to those found in related $[Ti(=NAr)Cl_2(NHMe_2)_2]$ complexes presented here (Table 2). The complex exhibits a short $Ti–N_{imido}$ distance of 1.7006(3) Å and an almost linear imido linkage $[Ti–N_{imido}–C_{ipso}$ 167.69(12)°]. The chlorine atoms occupy equatorial sites in the trigonal bipyramid with a Cl1–Ti–Cl2 angle of 138.77(2)° and mean Ti–Cl bond lengths of 2.35 Å. The *trans* dimethylamino and pyridine ligands have similar Ti–N bond lengths $[Ti–N_{NHMe_2}$ 2.1973(14) Å, $Ti–N_{Py}$ 2.2400(14) Å]. Molecules of **N′3** are also associated by a network of $Me_2N–H\cdots Cl$ hydrogen bonds.

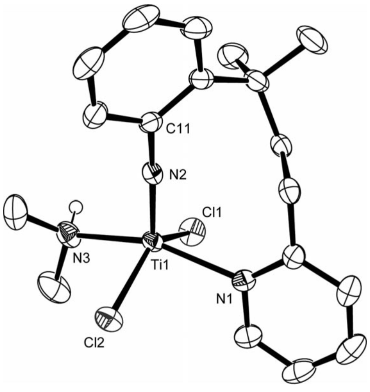


Figure 14. Thermal ellipsoid plot of **N′3** with partial atom labeling. Displacement ellipsoids drawn at the 50% level. H atoms bonded to C omitted. H atoms bonded to N drawn as spheres of arbitrary radius.

A variable-temperature ^1H NMR study was conducted on a [D8]toluene solution of **N3** (Supporting Information). At high temperatures (318–358 K), the broadening of several signals is observed, in particular those assigned to pyridine and aryl *ortho*-H. This fluxional behavior indicates a dynamic equilibrium between two species. At lower temperatures, different behavior is evidenced with broadening and splitting of the signals of $NHMe_2$ (both NH and Me), the methyl groups on the sidearm, and the methylene protons (attached to the pyridyl substituent) of the sidearm. The 2D ^1H-^{15}N NMR and NOESY experiments, show a correlation between the NH proton (^1H δ = 7.37 ppm) of one $NHMe_2$ (^{15}N δ = –339 ppm) with the nitrogen atom of the pyridine (^{15}N δ = –78 ppm) at 183 K. This behavior results from the presence of only one compound at low temperature, which has a hydrogen bond between the N atom of the pyridine and the NH of one dimethylamine ligand, as observed in the solid-state structure of **N3**.

The fact that we have not been able to establish hemilability in complexes supported by ligands with a pyridine PG most probably arises from the stability of pentacoordinate bis(dimethylamine) complexes (possibly enhanced by H bonding with pyridine N donors), as well as facile and irreversible $NHMe_2$ displacement in hypothetical octahedral bis(dimethylamine) intermediates through coordination of the pyridine PG (and elimination of the $NHMe_2$ *trans* to the imido function), which leads to pentacoordinate mono-$NHMe_2$ chelate complexes (Scheme 7).

3. Preliminary Catalytic Ethylene Polymerization Studies

Several precatalysts have been evaluated in the polymerization reaction of ethylene with various cocatalysts [methylaluminoxane (MAO) and triethylaluminum (TEA)] and under different conditions. The results are summarized in Table 3, with reference to $[Ti(=N\text{-}2,6\text{-}iPr_2–C_6H_3)Cl_2(NHMe_2)_2]$ as a precatalyst.[19]

Whatever the precatalyst, low to moderate activities were observed (Table 3, Entries 1–12). No significant influence on the activity is observed whether the pendant group is a thiophenyl, a phenyl, a furanyl, or a pyridyl group. An increase of activity is observed with **S1** and **Ph′2** when activated with MAO compared to TEA. Decreasing the temperature from 60 to 25 °C led to a slight decrease in activity for **N′2** (Entries 9 and 10). Optimization of the titanium concentration led to an increase in activity of up to 24000 g/(mol_{Ti} h bar) (Entries 6, 7, and 11). However, no clear benefit to the polymerization activity could be evidenced by the presence of the PG compared to $[Ti(=N\text{-}2,6\text{-}iPr_2–C_6H_3)Cl_2(NHMe_2)_2]$ (Entry 12). Furthermore, the activities of these precatalysts remain largely inferior to the some of the most productive imido–titanium precatalysts.[2c,4g,30] One explanation for the relatively poor activity of our systems is the presence of donor ligands in the precatalysts that could interact with the aluminum cocatalyst.

Size exclusion chromatography could not be carried out on the polymer samples as gels were obtained. Accordingly, we conclude that the polymers were UHMW polyethylenes with M_w above 10^6 g mol^{-1}. The presence of an additional side arm might therefore favor propagation over termination.

Table 3. Ethylene polymerization with different titanium–imido precatalysts.[a]

Entry	Precatalyst (mmol)	Cocatalyst	Al/Ti	Polymer yield [g]	Activity [g/(mol$_{Ti}$ h bar)][b]
1	**S**^{1} (0.15)	MAO	200	5.6	1866
2	**S**^{1} (0.15)	TEA	3	0.7	233
3	**Ph′**^{2} (0.15)	MAO	200	6.3	2100
4	**Ph′**^{2} (0.15)	TEA	3	0.5	167
5	**N**^{2} (0.15)	MAO	200	8.7	2900
6	**O**^{2} (0.0125)	MAO	500	5.6	22400
7	**Ph**^{3} (0.0125)	MAO	500	6.1	24400
8	**N**^{3} (0.15)	MAO	200	9.3	3100
9	**N′**^{2} (0.15)	MAO	200	9.5	3167
10 [c]	**N′**^{2} (0.15)	MAO	200	6.1	2033
11	**N′**^{2} (0.0125)	MAO	500	6.0	24000
12	**N′**^{2} (0.0125)	TEA	3	0.26	104
13	[Ti(=NAr)Cl$_2$(NHMe$_2$)$_2$][d]	MAO	500	7.6	30400

[a] Conditions: toluene (25 mL), 60 °C, ethylene (20 bar), 1 h. [b] Calculated from isolated polymer. [c] T = 25 °C instead of 60 °C. [d] With Ar = 2,6-C$_6$H$_3$ (synthesis according to ref.[19]).

Conclusions

New imido proligands that possess a potentially coordinating functional PG have been synthesized. The corresponding imido complexes were prepared by reaction with Ti(NMe$_2$)$_4$ in the presence of Me$_3$SiCl or by transamination from [Ti(NtBu)Cl$_2$(NHMe$_2$)$_2$]. The O-, S-, and Ph-based ligands afforded five-coordinate complexes [Ti(NAr^{PG})Cl$_2$(NHMe$_2$)$_2$] with no sign of PG coordination, whereas ligands that bear a pyridyl substituent, which is a better coordinating group, associated with a longer and more flexible side arm led to the formation of chelated imido–pyridine complexes [Ti(NAr^{PG})Cl$_2$(NHMe$_2$)$_1$]. However, the hemilabile behavior of these ligands could not be firmly established. When associated with various aluminum activators, some of these complexes are precatalysts for ethylene polymerization, which produced UHMW polyethylenes. Contrary to that reported occasionally in the literature, the presence and/or the nature of the PG seems to favor propagation over termination. Another detrimental consequence of these PG-functionalized imido compounds could be direct interaction with the cocatalyst. Further studies are necessary to fully understand these catalytic systems and probe the effects of the various PGs.

Experimental Section

General Methods and Instrumentation: All manipulations were carried out using standard Schlenk or dry box techniques under an atmosphere of argon. Solvents were dried with appropriate drying agents under an atmosphere of argon and collected by distillation. NMR spectra were recorded with Bruker ARX250, DPX300, Avance300, and Avance500 spectrometers and referenced internally to residual protiosolvent (^{1}H) resonances and are reported relative to tetramethylsilane. Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France). IR spectra were recorded with a Perkin–Elmer Spectrum GX FT-IR spectrometer. Samples were prepared under an argon atmosphere in a glove box as nujol mulls between NaCl plates. Gel permeation chromatography was conducted with a Waters Alliance GPCV 2000 chromatograph equipped with three columns (two Styragel HT6E and one Styragel HT2). Samples (1 mg mL^{-1}) were eluted with 1,2,4-trichlorobenzene with a flow rate of 1 mL min^{-1} at 150 °C. Ti(NMe$_2$)$_4$ was purchased from Aldrich. [Ti(=N-2,6-iPr$_2$–C$_6$H$_3$)Cl$_2$(NHMe$_2$)$_2$] was prepared according to our published procedure.[19] MAO (10 wt.-% toluene solution) and TEA were purchased from Chemtura.

Crystal Structure Determination: The structures of nine compounds were determined. Crystal data collection and processing parameters are given in Tables 4 and 5. The selected crystals, which were sensitive to air and moisture, were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 180 K in a stream of cold N$_2$. For all the structures, data were collected at low temperature (T = 180 K) either with a Stoe Imaging Plate Diffraction System, an Oxford Diffraction Kappa CCD Excalibur diffractometer, or a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well measured reflections. Crystal decay was monitored during data collection by measuring 200 reflections by image and no significant fluctuation of the intensities was observed. Structures were solved by direct methods using the program SIR92[31] and subsequent difference Fourier maps, models were refined by least-squares procedures on a F^2 with SHELXL-97[32] integrated in WINGX version 1.64,[33] and empirical absorption corrections were applied to the data.[34] For **N′′**^{2} and **N′**^{3}, it was not possible to solve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON[35] resulted in a smooth refinement. As a few low-order reflections were missing from the data set, the electron count is underestimated. Thus, the values given for D(calc), F(000), and the molecular weight are only valid for the ordered part of the structure. Details of the structure solution and refinements are given in the Supporting Information (CIF files), together with a full list of atomic coordinates, bond lengths and angles, and displacement parameters for all structures.

CCDC-836637 (for **O**^{1}), -836638 (for **S**^{1}), -836639 (for **N′′**^{2}), -836640 (for **N**^{2}), -836641 (for **N′**^{2}), -836642 (for **N′**^{3}), -836643 (for **N**^{3}), -836644 (for **S**^{2}), and -836645 (for **N′′′**^{3}) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Proligands: A full description of the synthesis of the proligands is given in the Supporting Information.

Table 4. Crystallographic data, data collection, and refinement parameters for **O**^{1}, **S**^{1}, **S**^{2}, and **N**^{2}.

	O^{1}	**S**^{1}	**S**^{2}	**N**^{2}
Chemical formula	$C_{16}H_{23}Cl_2N_3OTi$	$C_{16}H_{23}Cl_2N_3STi$	$C_{16}H_{25}Cl_2N_3STi$	$C_{18}H_{26}Cl_2N_4Ti$
Formula weight	392.14	408.21	410.25	417.23
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	17.7630(6)	8.5177(18)	13.5942(3)	17.576(3)
b [Å]	14.8830(3)	27.216(5)	7.2519(2)	10.2796(15)
c [Å]	16.2330(5)	8.943(2)	20.4286(5)	12.3180(19)
α [°]	90	90	90	90
β [°]	115.862(4)	101.761(6)	93.011(2)	103.577(9)
γ [°]	90	90	90	90
V [Å^3]	3861.7(2)	2029.8(7)	2011.15(9)	2163.3(6)
Z	8	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.349	1.336	1.355	1.281
μ (Mo-K_α) [mm^{-1}]	0.726	0.789	0.797	0.65
F(000)	1632	848	856	872
θ range [°]	3.08 to 26.37	2.55 to 25.68	3.36 to 26.37	2.61 to 38.69
Measured reflections	40093	18475	17088	55082
Unique reflections/Rint	7886/0.0574	3855/0.0316	4088/0.0361	12212/0.0309
Parameters/restraints	435/6	206/3	212/0	231/0
Final R indices [$I > \sigma 2(I)$]	$R1$ = 0.0312, $wR2$ = 0.058	$R1$ = 0.0463, $wR2$ = 0.1251	$R1$ = 0.0459, $wR2$ = 0.1300	$R1$ = 0.0383, $wR2$ = 0.0874
Final R indices (all data)	$R1$ = 0.061, $wR2$ = 0.0624	$R1$ = 0.0585, $wR2$ = 0.1346	$R1$ = 0.0560, $wR2$ = 0.1377	$R1$ = 0.0739, $wR2$ = 0.1019
Goodness of fit	0.876	1.032	1.039	1.004
$\Delta\rho_{max.} - \Delta\rho_{min.}$	0.293 and –0.28	1.904 and –0.795	1.057 and –0.802	0.592 and –0.286

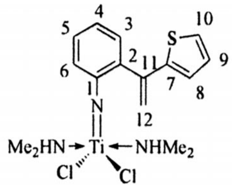
Table 5. Crystallographic data, data collection, and refinement parameters for **N**$''^{2}$, **N**$'''^{2}$, **N**^{3}, and **N**$'^{3}$.

	N$'^{2}$	**N**$''^{2}$	**N**$'''^{2}$	**N**^{3}	**N**$'^{3}$
Chemical formula	$C_{16}H_{21}Cl_2N_3Ti$, C_7H_8	$C_{18}H_{30}Cl_4N_4Ti$	$C_{18}H_{28}Cl_2N_4Ti$	$C_{20}H_{32}Cl_2N_4Ti$	$C_{18}H_{25}Cl_2N_3Ti$
Formula weight	466.29	492.16	419.24	447.30	402.21
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_12_12_1$	$P\bar{1}$
a [Å]	7.5496(7)	7.9478(6)	29.7027(18)	10.02920(10)	8.5768(5)
b [Å]	10.7460(10)	12.1653(11)	16.5297(10)	10.81580(10)	10.2656(6)
c [Å]	28.686(3)	16.5930(11)	9.1432(7)	21.4911(2)	13.8592(7)
α [°]	90	76.999(7)	90	90	81.360(2)
β [°]	94.007(6)	81.157(6)	106.421(2)	90	74.808(2)
γ [°]	90	88.214(7)	90	90	86.146(2)
V [Å^3]	2321.6(4)	1544.6(2)	4306.0(5)	2331.22(4)	1163.74(11)
Z	4	2	8	4	2
$D_{calcd.}$ [g cm^{-3}]	1.334	1.058	1.293	1.274	1.148
μ (Mo-K_α) [mm^{-1}]	0.613	0.631	0.654	0.608	0.601
F(000)	976	512	1760	944	420
θ range [°]	1.42 to 26.37	3.35 to 24.71	2.46 to 27.86	3.36 to 26.37	1.54 to 26.37
Measured reflections	21076	17091	19825	48330	20142
Unique reflections/Rint	4743/R(int) = 0.0483	5269/0.0605	5111/0.0387	4767/0.0413	4746/0.0243
Parameters/restraints	266/0	249/0	231/0	250/0	221/0
Final R indices [$I > \sigma 2(I)$]	$R1$ = 0.0603, $wR2$ = 0.1356	$R1$ = 0.0374, $wR2$ = 0.0919	$R1$ = 0.0339, $wR2$ = 0.0772	$R1$ = 0.0226, $wR2$ = 0.0568	$R1$ = 0.0327, $wR2$ = 0.0881
Final R indices (all data)	$R1$ = 0.1039, $wR2$ = 0.1530	$R1$ = 0.0729, $wR2$ = 0.0961	$R1$ = 0.0584, $wR2$ = 0.0872	$R1$ = 0.0248, $wR2$ = 0.0584	$R1$ = 0.0425, $wR2$ = 0.0923
Goodness of fit	1.045	0.842	1.014	1.065	1.076
$\Delta\rho_{max.} - \Delta\rho_{min.}$	1.098 and –0.400	0.284 and –0.234	0.281 and –0.220	0.235 and –0.131	0.280 and –0.202

Syntheses of Titanium–Imido Complexes

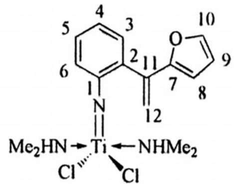
General Procedure:[19] To a toluene solution (2 mL) of $Ti(NMe_2)_4$ (300 mg, 1.34 mmol) was slowly added the aniline $ArNH_2$ (1–1.1 equiv.) at room temperature. After slow addition of trimethylsilyl chloride (TMSCl, 1.1 mL), the solution was stirred overnight at room temperature. The volatiles were removed under reduced pressure, the residue was washed with pentane (3 × 6 mL), and dried under vacuum to afford the pure material.

Synthesis of S^1



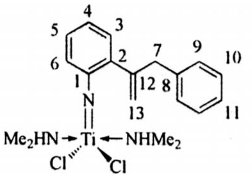
This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (100 mg, 0.45 mmol), toluene (2 mL), $\mathbf{Ar^{1S}NH_2}$ (100 mg, 0.5 mmol), and TMSCl (0.35 mL, 2.68 mmol). $\mathbf{S^1}$ (175 mg, 0.43 mmol, 95%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at –35 °C. ^1H NMR (250 MHz, C_6D_6): δ = 7.05–7.15 (m, 2 H, H^3 + H^5), 7.02 (dt, J = 1.5, 7.7 Hz, 1 H, H^{10}), 6.81 (dd, J = 0.7, 5.1 Hz, 1 H, H^9), 6.70–6.78 (m, 2 H, H^4 + H^8), 6.64 (dd, J = 3.7, 5.1 Hz, 1 H, H^6), 5.94 (s, 1 H, H^{12a}), 5.31 (s, 1 H, H^{12b}), 2.60 (m, 2 H, H_{NH}), 2.26 (d, J = 6.1 Hz, 12 H, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (62.5 MHz, C_6D_6): δ = 144.20 (C^1), 143.91 (C^{11}), 141.49 (C^7), 134.73 (C^2), 129.53 (C^3), 128.07 (C^5), 126.91 (C^9), 126.18 (C^8), 125.83 (C^{10}), 124.67 (C^4), 122.21 (C^6), 114.59 (C^{12}), 40.51 (C_{Me}) ppm. $C_{16}H_{23}Cl_2N_3STi$ (408.21): calcd. C 47.08, H 5.68, N 10.29; found C 46.81, H 5.61, N 10.03.

Synthesis of O^1



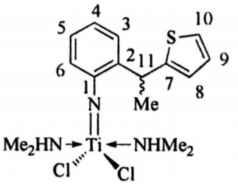
This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), $\mathbf{Ar^{1O}NH_2}$ (270 mg, 1.46 mmol), and TMSCl (1.0 mL, 7.88 mmol). $\mathbf{O^1}$ (470 mg, 1.20 mmol, 90%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at –35 °C. ^1H NMR (250 MHz, C_6D_6): δ = 6.97–7.15 (m, 4 H, H^3 + H^4 + H^5 + H^{10}), 6.73 (dt, J = 1.0, 7.4 Hz, 1 H, H^6), 6.16 (d, J = 1.0 Hz, 1 H, H^{12a}), 6.09 (dd, J = 1.8, 3.1 Hz, 1 H, H^9), 5.93 (d, J = 3.1 Hz, 1 H, H^8), 5.38 (d, J = 1.0 Hz, 1 H, H^{12b}), 2.80 (m, 2 H, H_{NH}), 2.29 (d, J = 6.1 Hz, 12 H, H_{NMe_2}) ppm. $^{13}C\{^1H\}$ NMR (62.5 MHz, C_6D_6): δ = 158.30 (C^1), 155.54 (C^7), 142.28 (C^{10}), 137.20 (C^{11}), 132.72 (C^2), 129.60 (C^3), 128.01 (C^5), 125.99 (C^4), 122.15 (C^6), 113.51 (C^{12}), 110.94 (C^9), 108.34 (C^8), 40.17 (C_{Me}) ppm. $C_{16}H_{23}Cl_2N_3OTi$ (392.15): calcd. C 49.00, H 5.91, N 10.72; found C 48.89, H 5.95, N 10.58.

Synthesis of Ph^2



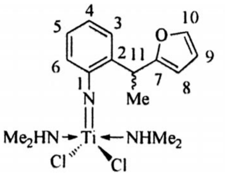
This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (200 mg, 0.89 mmol), toluene (2 mL), $\mathbf{Ar^{2Ph}NH_2}$ (208 mg, 1.00 mmol), and TMSCl (0.7 mL, 5.5 mmol). $\mathbf{Ph^2}$ (340 mg, 0.82 mmol, 92%) was obtained as an orange solid. ^1H NMR (250 MHz, C_6D_6): δ = 7.46–7.52 (m, 2 H, H^{10}), 7.36 (dd, J = 1.1, 8.2 Hz, 1 H, H^{11}), 7.14–7.24 (m, 2 H, H^9), 7.04–7.11 (m, 1 H, H^3), 6.96–7.04 (m, 2 H, H^4 + H^5), 6.69 (dt, J = 1.3, 7.5 Hz, 1 H, H^6), 5.15–5.25 (m, 2 H, H^{13}), 4.35 (s, 2 H, H^7), 2.77 (m, 2 H, H_{NH}), 2.29 (d, J = 6.1 Hz, 12 H, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (62.5 MHz, C_6D_6): δ = 158.21 (C^1), 150.50 (C^{12}), 140.25 (C^8), 134.24 (C^2), 129.77 (C^9), 129.10 (C^5), 128.31 (C^{10}), 128.20 (C^3), 127.50 (C^{11}), 126.09 (C^4), 122.61 (C^{13}), 115.29 (C^6), 43.83 (C^7), 40.47 (C_{Me}) ppm. $C_{19}H_{27}Cl_2N_3Ti$ (416.21): calcd. C 54.83, H 6.54, N 10.10; found C 54.77, H 6.58, N, 9.97.

Synthesis of S'^1



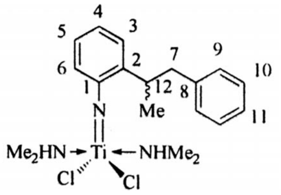
This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (100 mg, 0.45 mmol), toluene (2 mL), $\mathbf{Ar'^{1S}NH_2}$ (100 mg, 0.5 mmol), and TMSCl (0.35 mL, 2.68 mmol). $\mathbf{S'^1}$ (140 mg, 0.34 mmol, 77%) was obtained as an orange solid. ^1H NMR (250 MHz, C_6D_6): δ = 6.70 (dd, J = 1.4, 7.9 Hz, 1 H, H^3), 7.13 (dd, J = 1.4, 7.7 Hz, 1 H, H^4), 6.92–6.99 (m, 2 H, H^5 + H^{10}), 6.81 (dd, J = 1.2, 5.1 Hz, 1 H, H^9), 6.76 (dt, J = 1.3, 7.5 Hz, 1 H, H^6), 6.70 (dd, J = 3.4, 5.1 Hz, 1 H, H^8), 5.73 (q, J = 7.2 Hz, 1 H, H^{11}), 2.69 (m, 2 H, H_{NH}), 2.23 (t, J = 6.4 Hz, 12 H, $H_{Me(NH)}$), 1.68 (d, J = 7.2 Hz, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (62.5 MHz, C_6D_6): δ = 158.84 (C^1), 152.86 (C^7), 138.57 (C^2), 127.65 (C^{10}), 126.71 (C^3), 126.30 (C^5), 126.22 (C^6), 124.08 (C^4), 123.27 (C^9), 122.99 (C^8), 40.64 ($C_{Me(NH)}$), 40.11 ($C_{Me(NH)}$), 34.81 (C^{11}), 23.27 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3239 (ν_{NH}) cm^{-1}. $C_{16}H_{25}Cl_2N_3STi$ (410.23): calcd. C 46.84, H 6.14, N 10.24, found C 46.92, H 6.43, N 10.14.

Synthesis of O'^1



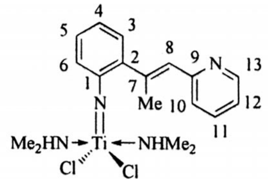
This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (100 mg, 0.45 mmol), toluene (2 mL), $\mathbf{Ar^{1O}NH_2}$ (94 mg, 0.5 mmol), and TMSCl (0.35 mL, 2.68 mmol). $\mathbf{O'^1}$ (160 mg, 0.41 mmol, 91%) was obtained as an orange solid. ^1H NMR (250 MHz, C_6D_6): δ = 7.24 (dd, J = 1.0, 7.9 Hz, 1 H, H^{10}), 7.09–7.12 (m, 1 H, H^3), 7.04 (dd, J = 1.1, 7.7 Hz, 1 H, H^5), 6.94 (dt, J = 1.4, 7.7 Hz, 1 H, H^4), 6.73 (dt, J = 1.1, 7.6 Hz, 1 H, H^6), 6.05–6.15 (m, 2 H, H^8 + H^9), 5.53 (q, J = 7.1 Hz, 1 H, H^{11}), 2.79 (m, 2 H, H_{NH}), 2.29 (d, J = 6.1 Hz, 12 H, $H_{Me(NH)}$), 1.77 (d, J = 7.1 Hz, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (62.5 MHz, C_6D_6): δ = 160.32 (C^1), 158.84 (C^7), 141.05 (C^{10}), 136.91 (C^2), 126.80 (C^3), 126.63 (C^5), 126.51 (C^4), 123.08 (C^6), 109.90 (C^9), 105.14 (C^8), 40.48 ($C_{Me(NH)}$), 40.27 ($C_{Me(NH)}$), 33.40 (C^{11}), 20.30 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3280, 3251 (ν_{NH}) cm^{-1}. $C_{16}H_{25}Cl_2N_3OTi$ (394.16): calcd. C 48.75, H 6.39, N 10.66; found C 48.63, H 6.62, N 10.83.

Synthesis of Ph′²



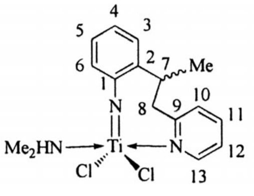
This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), **$Ar'^{2Ph}NH_2$** (300 mg, 1.42 mmol), and TMSCl (1.1 mL, 8.7 mmol). **Ph′²** (330 mg, 0.79 mmol, 59%) was obtained as an orange solid. ^1H NMR (300 MHz, C_6D_6): δ = 7.28–7.34 (m, 2 H, H^{10}), 7.18–7.24 (m, 1 H, H^{11}), 7.02–7.15 (m, 3 H, H^5 + H^9), 6.95–7.00 (m, 1 H, H^3), 6.91 (dt, J = 1.6, 7.5 Hz, 1 H, H^4), 6.80 (dt, J = 1.3, 7.5 Hz, 1 H, H^6), 4.49 (m, 1 H, H^{12}), 2.87 (m, 2 H, H^7), 2.61 (m, 2 H, H_{NH}), 2.23 (t, J = 5.9 Hz, 12 H, $H_{Me(NH)}$), 1.29 (d, J = 7.0 Hz, 3 H, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 159.16 (C^1), 141.57 (C^8), 129.20 (C^2), 127.86 (C^{10}), 127.06 (C^9), 125.90 (C^3), 125.85 (C^5), 125.58 (C^4), 123.06 (C^6), 44.90 (C^7), 40.72 ($C_{Me(NH)}$), 39.97 ($C_{Me(NH)}$), 34.33 (C^{12}), 22.13 (C_{Me}) (C^{11} signal not observed; probably obscured by C_6D_6 signals) ppm. $C_{19}H_{29}Cl_2N_3Ti$ (418.23): calcd. C 54.56, H 6.99, N 10.05; found C 54.59, H 6.76, N 9.95.

Synthesis of N²



This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), **$Ar^{2N}NH_2$** (280 mg, 1.42 mmol), and TMSCl (1.1 mL, 8.7 mmol). **N²** (515 mg, 1.28 mmol, 95%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at –35 °C. ^1H NMR (300 MHz, C_6D_6): δ = 8.36–8.44 (m, 1 H, H^{13}), 7.15–7.22 (m, 2 H, H^{10} + H^{12}), 6.95–7.10 (m, 3 H, H^3 + H^4 + H^5), 6.90–6.95 (m, 1 H, H^8), 6.77 (dt, J = 1.5, 7.4 Hz, 1 H, H^6), 6.59–6.67 (m, 1 H, H^{11}), 3.68–3.84 (m, 2 H, H_{NH}), 2.60 (d, J = 1.4 Hz, 3 H, H_{Me}), 2.40 (d, J = 6.1 Hz, 12 H, $H_{Me(NH)}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 158.12 (C^9), 157.60 (C^1), 149.24 (C^{13}), 142.69 (C^7), 138.74 (C^2), 135.78 (C^{11}), 129.34 (C^8), 127.46 (C^4), 127.16 (C^3), 125.62 (C^5), 124.02 (C^{10}), 122.10 (C^6), 120.85 (C^{12}), 40.44 ($C_{Me(NH)}$), 20.64 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3228 (ν_{NH}) cm⁻¹. $C_{18}H_{26}Cl_2N_4Ti$ (417.20): calcd. C 51.82, H 6.28, N 13.43; found C 51.65, H 6.58, N 13.39.

Synthesis of N′²



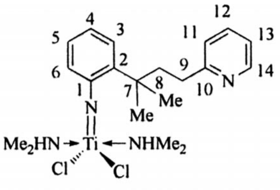
Method 1 (general procedure): This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), **$Ar'^{2N}NH_2$** (280 mg, 1.42 mmol), and TMSCl (1.1 mL, 8.7 mmol). A grey solid was obtained, which was shown by NMR to contain a mixture of **N′²** and **N′′²** (4:1) (515 mg). The complexes were separated by selective crystallization (toluene, –35 °C). Yield for **N′²:** 385 mg (77%).

Method 2: $Ar'^{2N}NH_2$ (227 mg, 1.07 mmol) was added at room temperature to a toluene solution (6 mL) of $[Ti(=N\mathit{t}Bu)Cl_2(NHMe_2)_2]$ (300 mg, 1.07 mmol). After stirring overnight, the volatiles were removed under reduced pressure, the residue was washed with pentane/toluene (9:1) (3 × 2 mL), and concentrated under vacuum to afford **N′²** (390 mg, 1.05 mmol, 98%) as a tan solid. ^1H NMR (400 MHz, C_6D_6): δ = 8.65–8.70 (m, 1 H, H^{13}), 7.01–7.10 (m, 2 H, H^3 + H^5), 6.89 (t, J = 7.4 Hz, 1 H, H^4), 6.77 (t, J = 7.4 Hz, 1 H, H^{11}), 6.71 (d, J = 7.6 Hz, 1 H, H^6), 6.43 (d, J = 7.6 Hz, 1 H, H^{10}), 6.40 (t, J = 6.4 Hz, 1 H, H^{12}), 4.10 (d, J = 13.3 Hz, 1 H, H^8), 3.83–3.92 (m, 1 H, H^7), 3.06–3.18 (m, 1 H, H_{NH}), 2.53 (t, J = 6.0 Hz, 6 H, $H_{Me(NH)}$), 2.13 (dd, J = 8.2, 13.3 Hz, 1 H, H^8), 0.98 (d, J = 6.9 Hz, 3 H, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 162.38 (C^9), 161.12 (C^1), 149.74 (C^{13}), 143.74 (C^2), 138.81 (C^{11}), 125.80 (C^3), 125.30 (C^{10}), 124.03 (C^5), 121.72 (C^4), 120.85 (C^{12}), 118.92 (C^6), 48.15 (C^8), 41.33 ($C_{Me(NH)}$), 41.05 ($C_{Me(NH)}$), 37.48 (C^7), 16.15 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3217 (ν_{NH}) cm⁻¹. $C_{16}H_{21}Cl_2N_3Ti$ (374.13): calcd. C 51.36, H 5.66, N 11.23; found C 51.40, H, 5.91, N, 11.46.

Synthesis of N′′²: N′′² was obtained as a minor product in the synthesis of complex **N′²** (see Method 1, above). Crystals suitable for an X-ray diffraction study were obtained from recrystallization of a mixture of **N′²** and **N′′²** from $C_6D_6/CDCl_3$ (9:1) at –35 °C.

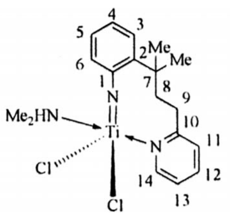
Synthesis of Complex N′′′²: N′′′² was obtained in low amount as an intermediate in the synthesis of **N²** (see Method 2, above). Crystals suitable for X-ray diffraction were obtained from recrystallization from a mixture of toluene/pentane (–35 °C).

Synthesis of N³



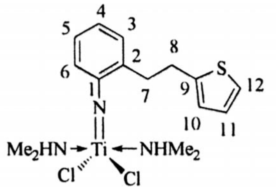
This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (300 mg, 1.34 mmol), toluene (6 mL), **$Ar^{3N}NH_2$** (320 mg, 1.34 mmol), and TMSCl (1.0 mL, 7.9 mmol). **N³** (560 mg, 1.26 mmol, 94%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at –35 °C. ^1H NMR (300 MHz, C_6D_6): δ = 8.11 (d, J = 4.3 Hz, 1 H, H^{14}), 7.84 (d, J = 7.8 Hz, 1 H, H^3), 6.98–7.16 (m, 3 H, H^4 + H^5 + H^{13}), 6.76 (m, 1 H, H^{11}), 6.69 (d, J = 7.8 Hz, 1 H, H^6), 6.57 (dd, J = 5.3, 6.7 Hz, 1 H, H^{12}), 4.66–4.85 (m, 2 H, H_{NH}), 2.88–3.00 (m, 2 H, H^9), 2.52 (d, J = 6.0 Hz, H_{MeNH}), 2.40–2.48 (m, 2 H, H^8), 1.61 (s, 6 H, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 163.49 (C^{10}), 159.85 (C^1), 148.82 (C^{14}), 136.98 (C^2), 136.27 (C^{12}), 132.99 (C^3), 126.75 (C^5), 126.26 (C^4), 123.11 (C^{11}), 122.63 (C^6), 120.54 (C^{13}), 42.25 (C^9), 40.36 (C_{MeNH}), 38.46 (C^7), 35.03 (C^8), 29.09 (C_{Me}) ppm. ^{15}N NMR (50.71 MHz, $C_6D_5CD_3$): δ = 298 K –75.5 (N_{Py}), –343.0 ($NHMe_2$); 183 K –77.6 (N_{Py}), –339 ($NH\cdots N_{Py}$), –342 ($NHMe_2$) ppm. IR: $\tilde{\nu}$ = 3285 (ν_{NH}) cm⁻¹. $C_{20}H_{32}Cl_2N_4Ti$ (447.27): calcd. C 53.71, H 7.21, N 12.53; found C 53.69, H 7.39, N 12.34.

Synthesis of N'^3



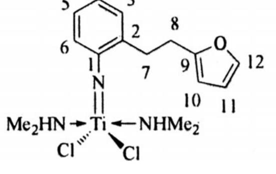
A of toluene solution (6 mL) of $\mathbf{N^3}$ (205 mg, 0.46 mmol) and TMSCl (0.7 mL, 5.5 mL) was left for 10 d at room temp. Removing the volatiles under vacuum and washing with pentane afforded $\mathbf{N'^3}$ (160 mg, 0.40 mmol, 87%) as a yellow solid. Recrystallization from toluene/pentane at –35 °C gave crystals suitable for X-ray diffraction. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.37–8.40 (m, 1 H, H^{14}), 7.17–7.24 (m, 2 H, $H^3 + H^5$), 7.01–7.08 (m, 1 H, H^4), 6.84–6.89 (m, 1 H, H^6), 6.77 (dt, J = 1.6, 7.8 Hz, 1 H, H^{12}), 6.47 (d, J = 7.8 Hz, 1 H, H^{11}), 6.34–6.39 (m, 1 H, H^{13}), 3.18–3.28 (m, 1 H, H_{NH}), 2.54 (d, J = 6.1 Hz, 6 H, H_{MeNH}), 1.37 (s, 6 H, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 162.87 (C^{10}), 159.85 (C^1), 149.31 (C^{14}), 138.99 (C^{12}), 138.15 (C^2), 128.73 (C^3), 127.63 (C^5), 126.23 (C^4), 125.19 (C^{11}), 122.91 (C^6), 120.42 (C^{13}), 44.95 ($C_{Me\text{-}NH}$), 40.64 (C^7), 39.44 ($C^8 + C^9$), 35.95 (C_{Me}) ppm. IR: $\tilde{\nu}$ = 3226 (ν_{NH}) cm^{-1}. $C_{18}H_{25}Cl_2N_3Ti$ (402.18): calcd. C 53.75, H 6.27, N 10.45; found C 53.70, H 6.22, N 10.39.

Synthesis of S^2



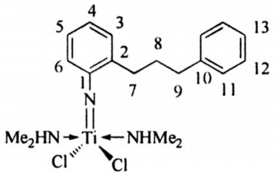
This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), $\mathbf{Ar^{2S}NH_2}$ (272 mg, 1.34 mmol), and TMSCl (1 mL, 8.03 mmol). $\mathbf{S^2}$ (490 mg, 1.20 mmol, 89%) was obtained as an orange solid and was recrystallized from toluene/pentane (9:1) at –35 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.28 (dd, J = 1.0, 7.7 Hz, 1 H, H^3), 7.10–7.19 (m, 1 H, H^4), 6.96 (dt, J = 1.5, 7.7 Hz, 1 H, H^6), 6.87–6.92 (m, 1 H, H^{12}), 6.78–6.86 (m, 2 H, $H^5 + H^{11}$), 6.73 (dt, J = 1.2, 7.5 Hz, 1 H, H^{10}), 3.36–3.45 (m, 2 H, H^8), 3.24–3.33 (m, 2 H, H^7), 2.66–2.82 (m, 2 H, H_{NH}), 2.25 (d, J = 6.1 Hz, 12 H, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 159.83 (C^1), 144.87 (C^9), 133.77 (C^2), 129.00 (C^{12}), 126.97 (C^3), 126.80 (C^5), 126.45 (C^6), 125.06 (C^4), 123.07 (C^{11}), 122.91 (C^{10}), 40.39 (C_{Me}), 34.09 (C^7), 31.49 (C^8) ppm. IR: $\tilde{\nu}$ = 3288, 3253 (ν_{NH}) cm^{-1}. $C_{16}H_{25}Cl_2N_3STi$ (410.23): calcd. C 46.84, H 6.14, N 10.24; found C 46.63, H 6.25, N 10.21.

Synthesis of O^2



This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), $\mathbf{Ar^{2O}NH_2}$ (250 mg, 1.34 mmol), and TMSCl (1 mL, 8.03 mmol). $\mathbf{O^2}$ (480 mg, 1.22 mmol, 91%) was obtained as an orange solid. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.28 (dd, J = 0.9, 7.7 Hz, 1 H, H^3), 7.16–7.20 (m, 1 H, H^{12}), 6.96 (dt, J = 1.4, 7.7 Hz, 1 H, H^5), 6.89–6.93 (m, 1 H, H^4), 6.73 (dt, J = 1.2, 7.5 Hz, 1 H, H^6), 6.40 (dd, J = 0.7, 3.1 Hz, 1 H, H^{10}), 6.19 (dd, J = 1.9, 3.0 Hz, 1 H, H^{11}), 3.40–3.47 (m, 2 H, H^8), 3.15–3.22 (m, 2 H, H^7), 2.69–2.82 (m, 2 H, H_{NH}), 2.24 (d, J = 6.2 Hz, 12 H, H_{Me}) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 159.82 (C^1), 156.22 (C^9), 140.85 (C^{12}), 134.05 (C^2), 128.77 (C^3), 126.76 (C^5), 126.38 (C^6), 122.92 (C^4), 110.45 (C^{11}), 105.73 (C^{10}), 40.34 (C_{Me}), 30.77 (C^7), 29.62 (C^8) ppm. IR: $\tilde{\nu}$ = 3262, 3227 (ν_{NH}) cm^{-1}. $C_{16}H_{25}Cl_2N_3OTi$ (394.16): calcd. C 48.75, H 6.39, N 10.66; found C 48.65, H 6.48, N 10.68.

Synthesis of Ph^3



This compound was prepared using the general procedure starting from $Ti(NMe_2)_4$ (300 mg, 1.34 mmol), toluene (2 mL), $\mathbf{Ar^{3Ph}NH_2}$ (283 mg, 1.34 mmol), and TMSCl (1 mL, 8.0 mmol). $\mathbf{Ph^3}$ (470 mg, 1.13 mmol, 84%) was obtained as an orange solid. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.30–7.34 (m, 2 H, H^{12}), 7.16–7.28 (m, 3 H, $H^3 + H^{11}$), 7.04–7.10 (m, 1 H, H^4), 6.94–7.00 (m, 2 H, $H^5 + H^{13}$), 6.79 (dt, J = 1.3, 7.5 Hz, 1 H, H^6), 3.07–3.13 (m, 2 H, H^9), 2.89–3.96 (m, 2 H, H^7), 2.66–2.76 (m, 2 H, H_{NH}), 2.24 (d, J = 6.1 Hz, 12 H, H_{Me}), 2.05–2.15 (m, 2 H, H^8) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 159.94 (C^1), 142.94 (C^{10}), 135.51 (C^2), 128.80 (C^{12}), 128.65 (C^{13}), 128.45 (C^{11}), 126.53 (C^3), 126.04 (C^5), 125.78 (C^4), 122.88 (C^6), 40.34 (C_{Me}), 36.27 (C^9), 33.51 (C^7), 30.71 (C^8) ppm. IR: $\tilde{\nu}$ = 3262 (ν_{NH}) cm^{-1}. $C_{19}H_{29}Cl_2N_3Ti$ (418.23): calcd. C 54.56, H 6.99, N 10.05; found C 54.31, H 7.16, N 10.08.

Ethylene Polymerization Studies: All catalytic reactions were carried out in a 110 mL stainless steel autoclave equipped with a mechanical stirrer. A toluene solution of the complex was introduced under an ethylene atmosphere, and the cocatalyst was added. The reactor was sealed and fed with ethylene up to 10 bar. The reactor was heated to the desired temperature with stirring and the pressure adjusted to 20 bar. After 1 h at constant pressure, the reactor was cooled to room temperature and depressurized. The catalyst and the cocatalyst were quenched by addition of 10% HCl in MeOH. The polymer formed was collected by filtration, washed with methanol, and dried in vacuo at 60 °C.

Supporting Information (see footnote on the first page of this article): VT NMR experiments and synthetic details for all compounds prepared in this article.

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