DOI: 10.1002/ejic.201100843

Titanium Complexes Stabilized by Bulky Electron-Rich Aminopyridinates and Their Application in Ethylene and Styrene Polymerization

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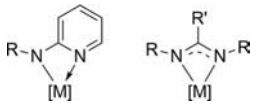
Keywords: Polymerization / Titanium / Amido ligands / N ligands

A series of electron-rich aminopyridines with high electron density at the $N_{pyridine}$ atom (due to an electron-donating mesomeric effect) was prepared by the Ni^0/2,2′-bipyridine-catalyzed arylation of anilines, followed by an uncatalyzed amination reaction. Reacting 2,6-dichloropyridine with 1 equiv. of aniline in the presence of the Ni^0/2,2′-bipyridine catalyst gave exclusively *N*-(6-chloropyridin-2-yl)aniline. Subsequent reaction with secondary alkylamines provided electron-rich aminopyridines in which the lone pair of the RR′N substituent participates in the molecular π-system. These aminopyridines react with [Et_2NTiCl_3] (Et = ethyl) and undergo amine elimination to form simultaneously the corresponding aminopyridinate (Ap) ligand-stabilized titanium trichlorides [$ApTiCl_3$] and Ap (diethylamido)titanium dichlorides [$Ap(Et_2N)TiCl_2$]. The reaction presumably proceeds via the reaction of the initially formed [$ApTiCl_3$] with 2 equiv. of the prereleased diethylamine to give the [$Ap(Et_2N)TiCl_2$] complexes and diethylammonium chloride. Alternative selective synthetic routes for both sorts of complexes are also presented. These compounds were characterized by spectroscopic methods and X-ray diffraction analysis (selected complexes). Furthermore, their behavior in ethylene and styrene polymerization reactions was explored. The complexes show high activity towards ethylene if activated with d-MAO ("dry" methylaluminoxane) but were almost inactive if d-MAO was replaced with conventional MAO. The observed polyethylene (PE) product was analyzed by NMR spectroscopy and found to be fully saturated, indicating a chain transfer reaction to aluminum had occurred. Styrene was polymerized in a highly syndiospecific fashion.

Introduction

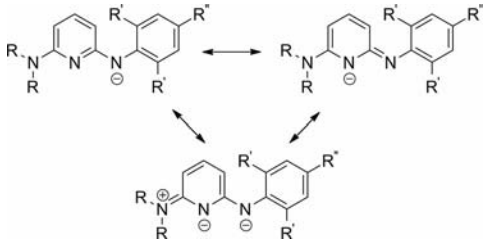
Ap complexes of the group 4 metals are promising alternatives to the widely used metallocenes of these metals for application in homogeneous catalysis, and especially in polymerization catalysis.[1–4] The aminopyridinato ligands mostly show η^2-coordination modes when coordinating with early transition metals (Scheme 1, left) and are related to amidinato ligands (Scheme 1, right).[5] The lower symmetry of the Ap ligands in comparison to the related species provides a higher ligand coordination flexibility that can be advantageous for stabilizing catalytic intermediates.[1–3]



Scheme 1. Binding mode of aminopyridinato (left) and amidinato (right) ligands ([M] = group 4 metal complex; R, R′ = substituent).

Titanium Ap complexes have been a focus of research during the last decade.[6] Most of the ligands reported so far have rather small steric demands and ligand redistribution has been observed frequently. The application of bulky aminopyridinates[7] can solve this problem, and we recently used bulky versions of these ligands to stabilize titanium based polymerization catalysts.[8] These complexes were found to be highly active in ethylene homo- and α-olefin copolymerizations, and also showed a good response towards cyclic olefins when activated with d-MAO, but were almost inactive when MAO that contained free trimethylaluminum (TMA) was used instead. We suspected that ligand transfer to aluminum, as observed earlier for Ap ligands, might be responsible for this inactivity.[9] An increase or decrease in the electron-donating ability of the Ap ligand should significantly alter the rate of ligand transfer, and may lead either to more or less stable catalysts with regard to a transfer to Al.

To increase the electron-donation ability of aminopyridinato ligands one could introduce an amine substituent in 6 position of the pyridine ring. For details of the electron-donating mesomeric effect see Scheme 2. If the lone pair of



Scheme 2. Mesomeric structures of 2,6-diaminopyridinato ligands (R, R′, R″ = alkyl substituents).

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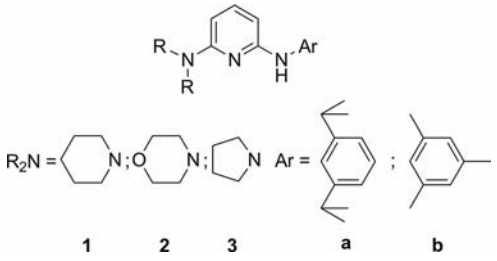
the RR′N-substituent participates in the molecular π-system, the electron density at the pyridine nitrogen atom will increase and the six-electron-donating 4σ,2π Ap ligand may possibly become an eight-electron-donating 4σ,4π ligand.

Herein, we report the synthesis of such Ap ligands (Scheme 3), the synthesis of titanium complexes based on the corresponding aminopyridinato ligands, and the application of selected titanium complexes in ethylene and styrene polymerization reactions. To the best of our knowledge, mono-Ap-titanium complexes have never been employed in the polymerization of styrene before.

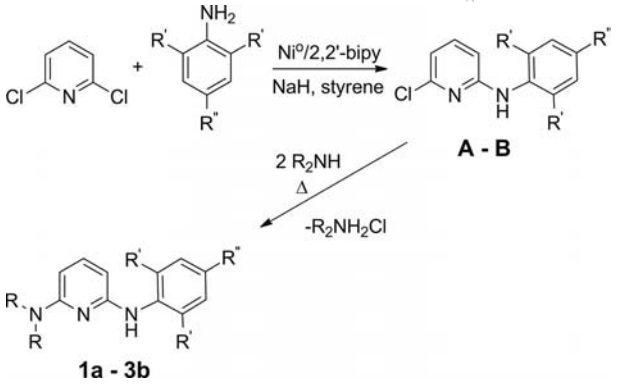


Scheme 3. Aminopyridines **1a**–**3b**.

Results and Discussion

Ligand Synthesis

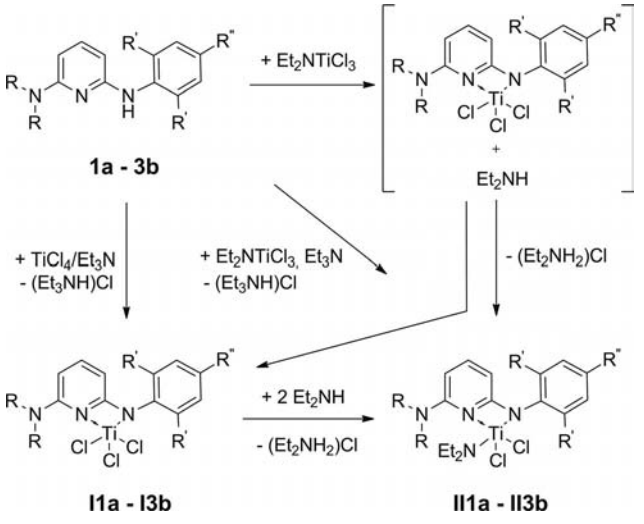
The ligand precursors *N*-(2,6-diisopropylphenyl)-(6-chloropyridin-2-yl)amine (**A**) and *N*-(2,4,6-trimethylphenyl)-(6-chloropyridin-2-yl)amine (**B**) were synthesized in about 45% isolated yield by the reaction of 2,6-dichloropyridine with the respective aniline derivative catalyzed by a Ni^0/2,2′-bipyridine catalyst system – a modified version of the synthesis method developed by Fort and co-workers.[10] Subsequent transition metal free thermal amination reactions[11] of **A** and **B** were carried out successfully with piperidine, morpholine and pyrrolidine in toluene at 160 °C in pressure tubes. After separation of the ammonium chloride salt by filtration and removal of all volatiles from the reaction mixtures, the residues were recrystallized from ethanol to provide the corresponding *N*-(2,6-diisopropylphenyl)-6-(N heterocycle)pyridin-2-amines [N heterocycle: piperidine (**1a**); morpholine (**2a**); pyrrolidine (**3a**)] and *N*-(2,4,6-trimethylphenyl)-6-(N heterocycle)pyridin-2-amines [N heterocycle: piperidine (**1b**); morpholine (**2b**); pyrrolidine (**3b**)] in good yields (Scheme 4).



Scheme 4. Synthesis of aminopyridine ligands, for an explanation of labels **1a**–**3b** refer to Scheme 3 (**A**: R′ = isopropyl and R′′ = H; **B**: R′, R′′ = methyl).

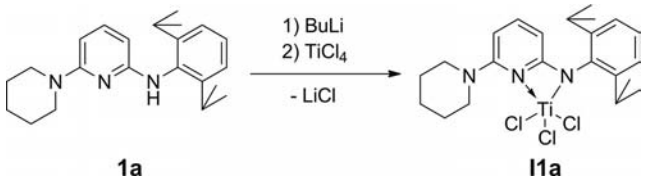
Synthesis and Structure of the Complexes

The *N*-6-(dialkylamino)pyridin-2-amines **1a**–**3b** reacted with [Et_2NTiCl_3] (Et = ethyl) in a 1:1 ratio in *n*-hexane under amine elimination to form simultaneously the corresponding Ap titanium trichlorides **I1a**–**I3b** and Ap-diethylamido-titanium dichlorides **II1a**–**II3b** (Scheme 5). These reactions probably proceed via the reaction of the initially formed [$ApTiCl_3$] with 2 equiv. of the prereleased diethylammonium chloride salts. In a NMR experiment, a nearly one to one ratio of both types of titanium complexes is observed. Reaction of [$ApTiCl_3$] with 2 equiv. of diethylamine gave the exclusive formation of [$Ap(Et_2N)TiCl_2$]. Furthermore, the addition of 1 equiv. of triethylamine to the amine elimination reaction could drive the reaction towards the selective formation of **II1a**–**II3b** (Scheme 5). Such behavior was not observed for the earlier reported bulky aminopyridines[8] that yielded [$Ap(Et_2NH)TiCl_3$] complexes instead.



Scheme 5. Synthetic routes to [$ApTiCl_3$] and [$Ap(Et_2N)TiCl_2$] complexes.

The selective synthesis of the [$ApTiCl_3$] complexes **I1a**–**I3b** were carried out by the treatment of the corresponding aminopyridines with 1 equiv. of $TiCl_4$ and triethylamine in dichloromethane (Scheme 5), also by the alternative reaction of the lithiated aminopyridines with 1 equiv. of $TiCl_4$ in toluene (Scheme 6). For less bulky Ap ligands (electron-poor) the latter synthetic route selectively yielded [Ap_2TiCl_2].[6]



Scheme 6. Synthesis of the Ap titanium trichloride **II1a**.

All complexes were characterized by NMR spectroscopy and elemental analysis. Single crystal structure analysis was carried out for selected complexes. Suitable crystals for X-ray analysis were obtained by slowly cooling saturated *n*-hexane solutions of the complexes to –24 °C. The molecular structures of complexes **I2b**, **II1a**, **II2a** and **II3a** are presented in Figures 1, 2, 3, and 4, respectively. X-ray crystal structure analysis details are given in Table 1. The coordination of all four complexes is best described as a distorted trigonal bipyramid with a pyridine moiety in one of the apical positions.

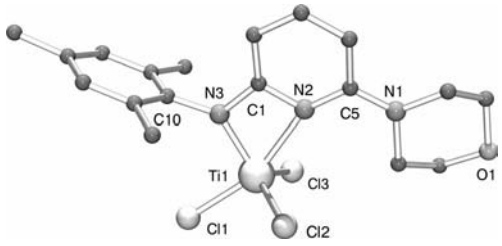


Figure 1. Molecular structure of **I2b**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5–N1 1.358(3), C5–N2 1.360(6), C1–N2 1.393(3), C1–N3 1.392(3), N2–Ti1 2.232(4), N3–Ti1 1.893(2), average Cl–Ti1 2.239(1), N1–C5–N2 119.4(2), N2–C1–N3 107.8(2), N2–Ti1–N3 64.9(1), Σ∠(N1) 357.5.

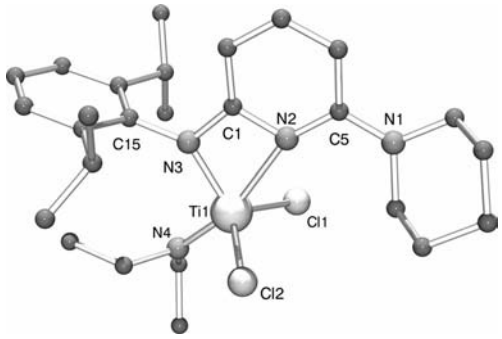


Figure 2. Molecular structure of **II1a**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5–N1 1.369(6), C5–N2 1.349(5), C1–N2 1.380(6), C1–N3 1.401(5), N2–Ti1 2.342(4), N3–Ti1 1.931(4), N4–Ti1 1.864(4), average Cl–Ti1 2.284(2), N1–C5–N2 118.7(4), N2–C1–N3 108.2(4), N2–Ti1–N3 62.78(14), Cl1–Ti1–Cl2 122.66(7), Σ∠(N1) 358.6.

The C5–N1 bond lengths of all four complexes are between 1.34–1.37 Å and are clearly shorter than expected for a Csp^2–Nsp^3 (pyramidal) single bond (ca. 1.416 Å).[12] The calculated sums of all angles around the N1 atoms in these complexes were between 353–360° confirming that these nitrogen atoms have an almost planar environment, which is typical for an sp^2-hybridized N atom. The sp^2 hybridization

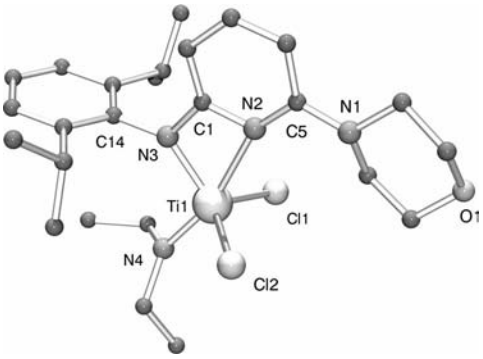


Figure 3. Molecular structure of **II2a**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5–N1 1.356(6), C5–N2 1.3576(6), C1–N2 1.357(6), C1–N3 1.396(6), N2–Ti1 2.365(4), N3–Ti1 1.928(4), N4–Ti1 1.862(4), average Cl–Ti1 2.270(2), N1–C5–N2 117.8(4), N2–C1–N3 109.2(4), N2–Ti1–N3 62.01(2), Cl1–Ti1–Cl2 119.73(6), Σ∠(N1) 353.1.

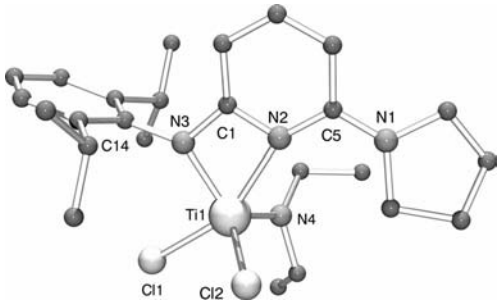


Figure 4. Molecular structure of **II3a**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5–N1 1.343(5), C5–N2 1.356(5), C1–N2 1.360(4), C1–N3 1.387(5), N2–Ti1 2.241(3), N3–Ti1 1.961(3), N4–Ti1 1.858(3), average Cl–Ti1 2.294(2), N1–C5–N2 120.1(3), N2–C1–N3 107.8(3), N2–Ti1–N3 63.37(11), Cl1–Ti1–Cl2 98.05(4), Σ∠(N1) 360.0.

of the N1 atoms together with the short C5–N1 distances clearly indicates that the lone pair of the N1 atoms participate in the π-systems of the ligands. Despite their high electron-donating ability the aminopyridinato ligands discussed herein still coordinate in their amido pyridine form with short Ti–N_{amido} distances within the range of 1.89–1.96 Å, and long Ti–$N_{pyridine}$ distances of 2.24–2.37 Å.[2]

In the ^{1}H NMR spectra of **II1a**–**II3b** the proton resonances for the 3 and 5 position of the pyridine ring appear between 4.6 and 5.6 ppm (Figure 5). These signals are further up field than usually observed for pyridine or aromatic protons, but is typical for olefinic ones. The mesomeric enhancement increases the electron-donating ability of the ligand but weakens the ring current of the pyridine ring. The increased bond order for the C5–N1 bonds were also confirmed by low-temperature experiments that show coalescence of the proton resonances of the piperidine, morpholine and pyrrolidine rings at temperatures between –50 and –40 °C, which is a result of the increase in the rotation barriers.

Table 1. Crystallographic data for the compounds that were investigated by single crystal X-ray structure analysis.

Compound	**I2b**	**II1a**	**II2a**	**II3a**	**III1a**
Formula	$C_{18}H_{22}Cl_3N_3OTi$	$C_{26}H_{40}Cl_2N_4Ti$	$C_{25}H_{38}Cl_2N_4OTi$	$C_{25}H_{38}Cl_2N_4Ti$	$C_{24}H_{36}AlN_3$
Formula weight	450.50	527.42	529.39	513.39	393.54
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a [Å]	10.8790(6)	8.454(5)	9.7200(6)	8.6580(5)	9.9850(7)
b [Å]	16.7640(6)	9.986(5)	10.0500(6)	19.0580(11)	14.387(11)
c [Å]	22.7520(7)	16.898(5)	16.7120(10)	16.5830(9)	16.428(11)
α [°]	90	88.275(5)	103.060(5)	90	90
β [°]	90.245(2)	83.266(5)	92.726(5)	104.578(4)	101.556(6)
γ [°]	90	76.726(5)	117.817(4)	90	90
Cell volume [Å^3]	4149.4(3)	1378.9(11)	1384.17(16)	2648.2(3)	2312.1(3)
Z	8	2	2	4	4
Crystal size [mm^3]	$0.55\times0.33\times0.25$	$0.30\times0.17\times0.16$	$0.34\times0.33\times0.24$	$0.41\times0.37\times0.21$	$0.38\times0.35\times0.28$
Habit	block	prism	block	plate	block
Colour	red	orange	red	red	colourless
Density [g cm^{-3}]	1.443	1.270	1.270	1.288	1.131
T [K]	133(2)	133(2)	133(2)	133(2)	133(2)
Theta range	1.51–25.62	1.21–25.69	1.27–25.65	1.27–25.53	1.90–25.75
Unique reflections	7828	5202	5221	5001	4378
Observed reflections [$I > 2\sigma I$]	6203	2814	3169	2931	3020
Parameters	475	298	304	295	255
$wR2$(all data)	0.109	0.123	0.203	0.131	0.107
R value [$I > 2\sigma(I)$]	0.039	0.070	0.074	0.053	0.048

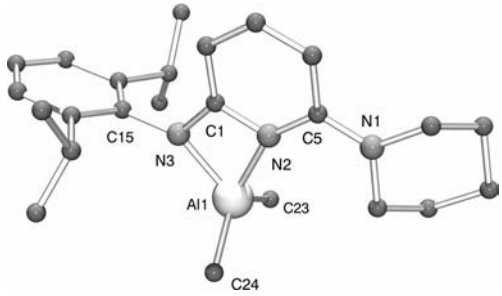
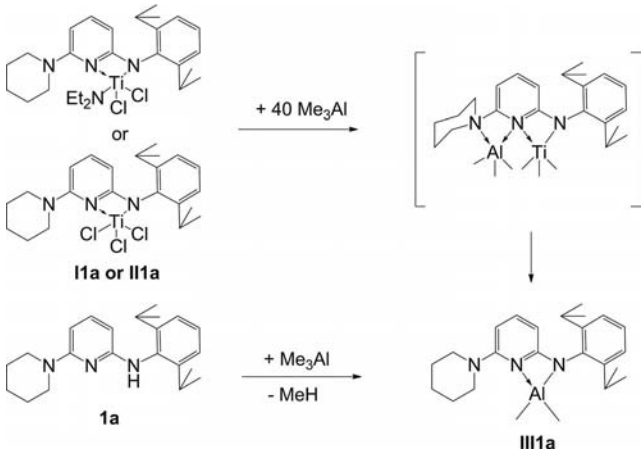


Figure 5. Molecular structure of **III1a**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5–N1 1.363(3), C5–N2 1.356(2), C1–N2 1.378(2), C1–N3 1.354(2), N2–Al1 1.985(2), N3–Al1 1.901(2), average Al1–C 1.956(2), N1–C5–N2 118.45(17), N2–C1–N3 108.09(16), N2–Al1–N3 69.35(7), C23–Al1–C24 121.76(9), Σ∠(N1) 359.6.



Scheme 7. Synthesis of **III1a** and ligand transfer reaction.

Olefin Polymerization and the Formation of ApAl Complexes

Despite their enhanced electron-donating ability and the increased stabilization of their electron-deficient metal centers, the new complexes were found to be sensitive towards trialkylaluminum compounds. When the complexes **I1a**–**II3b** were activated with commercial MAO almost no ethylene polymerization activity was observed. This is presumably due to the fast ligand transfer from titanium to aluminum.[9]

To gain more insight into this behavior, we studied the stability of these complexes with respect to TMA in NMR tube experiments. The NMR tubes were charged with 40 μmol of **I1a** or **II1a** in 0.5 mL of deuterated benzene before 40 equiv. of TMA (160 μmol) was added to each tube. The titanium complexes react fast with TMA forming their corresponding methyl complexes, which after a short period decompose with the release of an NMR detectable amount **III1a**. We believe that this fast ligand transfer is the result of the intermediary formation of a hetero-bimetallic species (Scheme 7). Due to the extra amine function in 6 the position, not only is the electron-donating ability of the aminopyridinato ligand increased but also its tendency to form binuclear complexes, as is known for the dianionic 2,6-diaminopyridines analogues.[13] We independently synthesized the Ap-containing dimethylaluminum complex **III1a** by reacting the aminopyridine **1a** with 1 equiv. of TMA in toluene (Scheme 7). Removal of all volatiles from the reaction mixture under reduced pressure gives the spectroscopically pure product as a colorless solid. Crystallization could be accomplished by very slow cooling of saturated warmed hexane solution of the product. The crystal structure of **III1a** is presented in Figure 5. Experimental details of the X-ray diffraction analysis can be found in Table 1.

The structure of the complex **III1a** is mononuclear and the Ap ligand is in a strained η^2 coordination mode. η^2-Coordinated Ap-aluminum complexes are still rare[14] and the first examples were published by Wang and coworkers.[15] Treatment of **III1a** (40 μmol in 0.5 mL of C_6D_6) with 2, 5, 10, 20, 40 and 100 equivalents of TMA revealed the existence of a second binuclear $ApAl_2$ species in solution (Figure 6, Scheme 8). After the addition of 5 equiv. of TMA to a **III1a** solution, the resonances of a new Al complex (**IV1a**) become visible in the NMR spectrum of the solution, and after the addition of 100 equiv. of TMA this seems to be the only Ap-containing species present. The new complex shows three Al-CH_3 resonances at –0.5 ppm with an intensity ratio of 2:2:1. As a result of the Al coordination to N1, the piperidyl fragment stops rotating around the C5–N1 bond; this is evidenced by the appearance of 10 resonances in the NMR spectrum of the solution that can be assigned to the now diastereotopic protons of the heterocycle. Most likely, such a hetero-binuclear species will also be formed when [$ApTiCl_3$] complexes are reacted with an excess of TMA, allowing fast Ap ligand transfer from titanium to aluminum to take place.

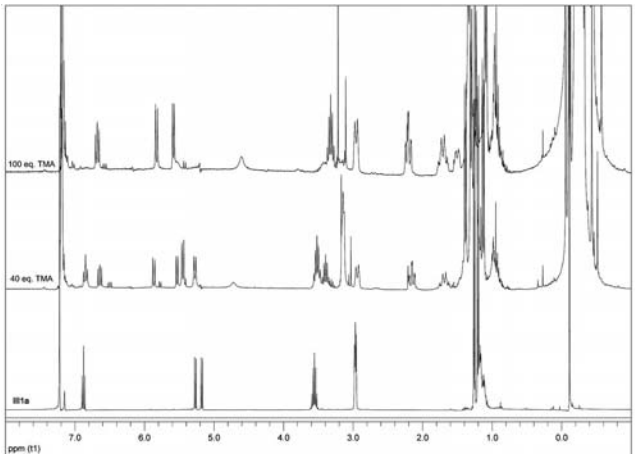


Figure 6. ^{1}H NMR spectra (C_6D_6, 26 °C) of pure **III1a**, **III1a** with 40 equiv. TMA, and **III1a** with 100 equiv. TMA.

Scheme 8. Formation of the bimetallic aluminum complex **IV1a**.

Due to the sensitivity of the new titanium complexes to TMA, we switched the co-catalyst to dry methylaluminoxane (d-MAO). When all the volatiles from the commercially bought MAO are removed, most of the free TMA will also be removed. After activation of complexes **II1a**–**II3b** with d-MAO, high polymerization activities[16] towards ethylene were observed (Table 2). The complexes with the more sterically demanding Ap ligands were found to be more active. Despite the fact that the TMA content in the d-MAO is quite low, ligand transfer may still be taking place. This idea was supported by the observation that the catalysts were active for only a few minutes, and the multimodality of the polymers suggested the existence of several active species in reaction solution. It is notable that the average molecular weight of the polymers is quite high despite of the presence of low molecular weight PE material. The NMR investigation of the low molecular weight material revealed that all polymer chains are fully saturated, and no olefinic proton resonances could be observed in the spectra (Figure 7.). Such material could only emerge if the polymers were terminated with a metal, for example aluminum, before they were hydrolyzed by acidified ethanol. In comparison to the titanium complexes containing very bulky (classic) aminopyridinates,[8] we can say that the new catalysts produce PE with much higher molecular weights.

Table 2. Details of the ethylene polymerizations.[a]

Entry	Precat.[a]	T [°C]	$m_{Pol.}$ [g]	Activity [kg_{PE} mol_{cat}^{-1} h^{-1}]	M_w [kg mol^{-1}]	M_w/M_n
1	**II1a**	80	0.27	540	1275	12.1
2	**II1b**	80	0.19	380	729	12.8
3	**II2a**	80	0.31	620	482	11.6
4	**II2b**	80	0.15	296	1323	11.1
5	**II3a**	80	0.14	280	–	–
6	**II3b**	80	0.12	180	206	7.2

[a] Precatalyst: 2.0 μmol; d-MAO: 1.0 mmol; toluene: 150 mL; p = 2 bar; t = 15 min.

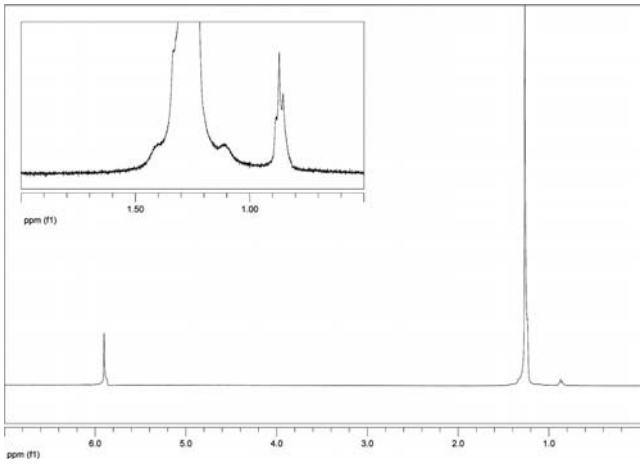


Figure 7. ^{1}H NMR spectrum ($C_2Cl_4D_2$, 120 °C) of PE obtained with the **II1a**/d-MAO catalyst system. The spectrum was recorded after acidic workup of the reaction mixture.

Due to the promising results of amidinate titanium complexes[17,18] in syndiospecific styrene polymerization reactions, we became interested in the polymerization of this monomer when catalyzed by the novel titanium compounds described herein. The polymerization of styrene (2.0 mL) in toluene (10.0 mL) was carried out in sealed glass bottles in a glove box. Subsequently, d-MAO (1.0 mmol) and the catalyst (2.0 μmol) were added, and the solution was stirred and heated to the desired temperature and kept at that temperature for for 90 min. The polystyrene (PS) product from each run was refluxed in acetone. The insoluble fraction

(more than 95%) was separated from solution and dried at 80 °C. The results from these experiments are presented in Table 3.

Table 3. Details of the styrene polymerizations.[a]

Entry	Precat.[a]	T [°C]	$m_{Pol.}$ [g]	Activity [$kg_{PS}\ mol_{cat}^{-1}\ h^{-1}$]	M_w [$g\,mol^{-1}$]	M_w/M_n
9	**II1a**	30	0.02	30	310000	19.0
10		60	0.04	40	141000	11.3
11		90	0.06	110	57800	4.2
12	**II1b**	30	0.01	26	349500	18.0
13		60	0.02	42	137800	9.0
14		90	0.05	100	72700	3.6
15	**II2a**	30	0.03	66	94300	1.5
16		60	0.06	110	101700	1.6
17		90	0.12	240	68800	2.2
18	**II2b**	30	0.01	20	436300	11.2
19		60	0.02	40	109900	6.4
20		90	0.05	90	66100	3.7
21	**II3a**	30	0.02	36	235300	129.5
22		60	0.03	52	2046400	18.2
23		90	0.04	76	68200	2.0
24	**II3b**	30	0.01	24	1136600	27.5
25		60	0.02	32	300600	25.6
26		90	0.03	46	49500	4.0

[a] Precatalyst: 2.0 μmol; d-MAO: 1.0 mmol; toluene: 10 mL; styrene: 2.0 mL; t = 90 min.

The activity of all complexes increases as a function of temperature, with maxima observed at 90 °C. As already observed in the ethylene polymerization runs, complexes containing sterically more demanding Ap ligands are more active. The differences in catalytic activity of the complexes are not as pronounced in styrene polymerizations as they were in the ethylene polymerizations. The molecular weights of the obtained polymers are quite high. However, the high polydispersities of the polymers suggest that once again more than one active species is formed during the reaction. The tacticity of PS was studied by ^1H and ^{13}C NMR spectroscopy. The NMR spectra were collected at 80 °C and the samples were prepared by dissolving 20 mg of the polymer in deuterated tetrachloroethane. Selected spectra are presented in Figure 8. The proton spectrum shows typical resonances[19] for syndiotactic PS with some traces of atactic material, while the ^{13}C spectrum only shows two singlet resonances corresponding to the methylene and methine carbon atoms, which indicates that the PS is a highly syndiotactic material.

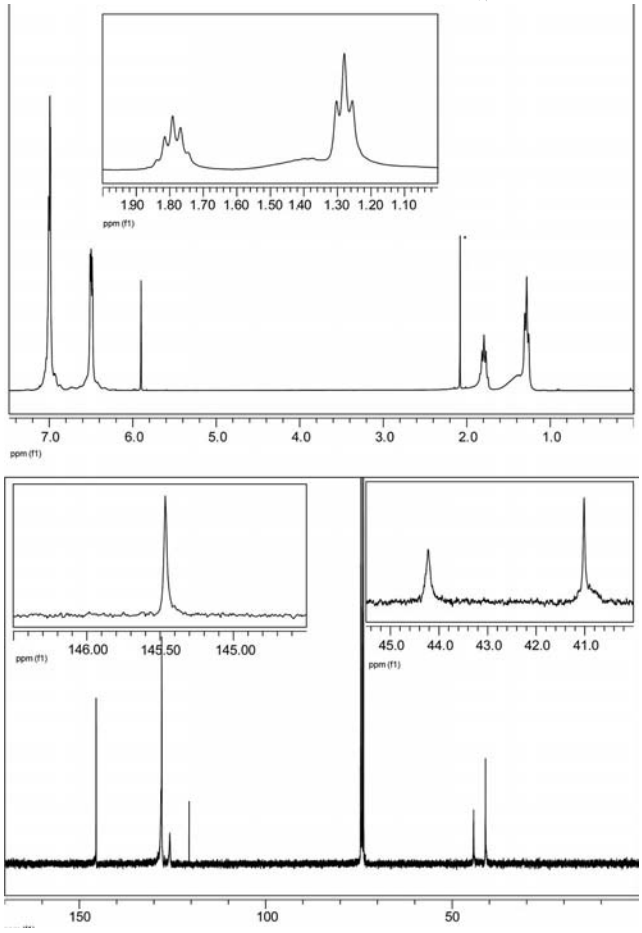


Figure 8. ^1H (above) and ^{13}C (below) NMR spectra ($C_2Cl_4D_2$, 80 °C) of PS obtained with the **II1a**/d-MAO catalyst system.

Conclusions

From the present study a series of conclusions can be drawn; firstly, the novel 6-(N-heterocycle)-substituted aminopyridines can be synthesized (with a large degree of variety) by Ni-catalyzed aryl aminations followed by thermal amination reactions. Secondly, mono Ap titanium trichloride complexes can be synthesized by the reaction of $[TiCl_4]/Et_3N$ with the corresponding aminopyridine. Mixed amido Ap complexes are selectively accessible by amine elimination reactions involving $[Et_2NTiCl_3]$, the aminopyridine, and 1 equiv. of triethylamine. Thirdly, the structures of the titanium complexes confirm the increased electron-donating ability of the novel Ap ligands, but did not show a stronger coordination of these modified ligands to the metal center. The ligands are sensitive to ligand exchange reactions with TMA. Fourthly, the complexes described herein are active in ethylene and styrene polymerizations. Highly syndiotactic PS was produced. In the case of ethylene polymerization, high activities were observed and aluminum terminated PE for the low molecular weight products.

Experimental Section

Synthesis and Structure Analysis: All manipulations were performed with the rigorous exclusion of oxygen and moisture from the systems by use of Schlenk type glassware on a dual manifold Schlenk line, or in an argon filled glove box (Braun 120-G) fitted with a high capacity recirculator (< 0.1 ppm O_2). Nonhalogenated solvents were dried by distillation with a sodium wire/benzophenone system. 2,6-Dichloropyridine, 2,2′-bipyridine, piperidine were purchased from AlfaAesar. Nickel acetate and *tert*-amyl alcohol were purchased from Acros. Morpholine, pyrrolidine and styrene were purchased from Sigma Aldrich. The titanium precursor (Et_2NTiCl_3) was synthesized by a method reported in the literature.[20] Deuterated solvents were obtained from Cambridge Iso-

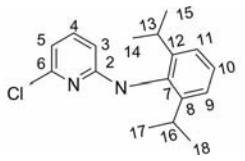
tope Laboratories and were degassed, dried, and distilled prior to use. NMR spectra were recorded with a 400 MHz Varian ARX, or with a 300 MHz Varian ARX, and chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses (CHN) were carried out with a Vario EL III instrument. d-MAO was prepared by removal of volatiles from PMAO (4.9 wt.-% in Al). The polymer samples for NMR spectroscopic measurements were prepared by dissolving 15 mg of the polymer in 0.5 mL of $C_2D_2Cl_4$ for 3 h at 100 °C before measurements were made. Gel permeation chromatography (GPC) analysis was carried out on a PL-GPC 220 (Agilent, Polymer Laboratories) high temperature chromatographic unit equipped with DP and RI detectors and two linear mixed bed columns (Olexis, 13-micron particle size). GPC analysis were performed at 150 °C and with 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.05 wt.-%, c = 1 mg/mL) in the mobile phase solvent in an external oven, and the solutions were run without filtration. The molecular weights of the samples were referenced to PE (M_w = 520–3200000 g mol^{-1}) and PS (M_w = 580–2800000 g mol^{-1}) standards. The reported values are the average of at least two independent determinations. X-ray crystal structure analyses were carried out with a STOE IPDS II diffractometer equipped with an Oxford Cryostream low temperature unit. Structure solution and refinement were accomplished with SIR97,[21] SHELXL-97[22] and WinGX.[23] Selected details of the X-ray crystal structure analyses are listed in Table 1.

CCDC-838187 (for **I2b**), -838188 (for **II1a**), -838189 (for **II2a**), -838190 (for **II3a**) and -838191 (for **III1a**) 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.

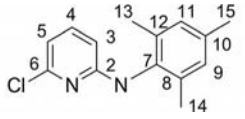
General Description of Ethylene Polymerization Experiments Performed with d-MAO: The catalytic ethylene polymerization reactions were performed in a 250 mL glass autoclave (Buechi) in semi-batch mode (ethylene was added by replenishing the flow to keep the pressure constant). The reactor was temperature and pressure controlled and equipped with separated toluene, catalyst, and co-catalyst injection systems. During a polymerization run the pressure, the ethylene flow, the inner and the outer reactor temperature, and the stirrer speed were monitored continuously. In a typical semi-batch experiment, the autoclave was evacuated and heated for 1 h at 80 °C prior to use. The reactor was then brought to the desired temperature, stirred at 1000 rpm and charged with 150 mL of toluene together with d-MAO (54 mg, 1 mmol), unless mentioned different in the following text. After pressurizing with ethylene to reach 2 bar total pressure, the autoclave was equilibrated for 5 min. Subsequently, 0.002 M catalyst stock solution in toluene (1 mL) was injected into the autoclave to start the reaction. During the run the ethylene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing the gas flow. After a 15 min reaction time the reactor was vented and the residual aluminum alkyls were destroyed by addition of 50 mL of ethanol to the reactor. The polymeric product was collected, stirred for 30 min in acidified ethanol, and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and then in vacuo at 80 °C.

Styrene Polymerizations: Styrene polymerizations were performed in sealed glass bottles in a glove box. Styrene (2.0 mL) and d-MAO (1 mmol) were added to a glass bottle containing toluene (7.0 mL). The mixture was stirred for 10 min followed by the addition of 2.0 μmol of the desired catalyst. The temperature of the solution was raised to 30 °C, 60 °C or 90 °C and then kept at this temperature for 90.0 min. The polymerization reaction was quenched by the addition of ethanol (10.0 mL) acidified with HCl. The resultant polymers were washed with ethanol and the atactic fraction of each polymer was removed by heating the polymer sample in acetone at 60 °C for 2 h. The insoluble syndiotactic fraction was separated for the mixture, and dried first at room temperature and then in an oven at 80 °C for 12 h.

Synthesis of the Ligand Precursors



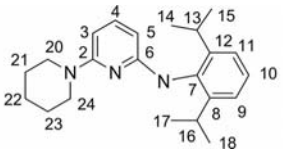
***N*-(2,6-Diisopropylphenyl)-(6-chloropyridin-2-yl)amine (A):** 2,6-Diisopropylaniline (5.31 g, 5.70 mL, 30. 0 mmol) and *tert*-amyl alcohol (0.352 g, 0.45 mL, 4.0 mmol) in THF (20.0 mL) were added to a THF suspension of NaH (0.624 g, 26.0 mmol). The resulting mixture was heated at 65 °C for 2 h and then cooled. 2,2-Bipyridyl (0.94 g, 6.0 mmol) was added to the cool mixture followed by dried $Ni(OAc)_2$ (0.352 g, 2.0 mmol). The reaction mixture was heated for a further 2 h then cooled. To the cool mixture 2,6-dichloropyridine (2.96 g, 20.0 mmol) was added, and the reaction mixture was refluxed for 2 h. After cooling, water (2.0 mL) and dichloromethane (100.0 mL) were added to the mixture. The reaction mixture was filtered through sodium sulfate and the volatiles were removed from the filtrate. The resultant yellow oil was purified by silica gel column chromatography and recrystallized from *n*-hexane; yield 2.30 g (40%). $C_{17}H_{21}N_2Cl$ (288.62): calcd. C 70.68, H 7.33, N 9.70; found C 70.67, H 6.85, N 9.48. ^{1}H NMR (C_6D_6, 298 K): δ = 1.04 (d, 12 H, $H^{14,15,17,18}$), 3.16 (sept, 2 H, $H^{13,16}$), 5.61 (d, 1 H, 1 H^3), 6.33 (d, 1 H, H^5), 6.62 (t, 1 H, H^4), 6.91 (br. s, 1 H, NH), 7.01–7.21 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 23.73 ($C^{14,15,17,18}$), 28.67 ($C^{13,16}$), 103.76 (C^3), 112.02 (C^5), 124.22 ($C^{9,11}$), 128.63 (C^{10}), 133.71(C^7), 135.12 ($C^{8,12}$), 140.50 (C^4), 148.18 (C^2), 160.49 (C^6) ppm.



***N*-(2,4,6-Trimethylphenyl)-(6-chloropyridin-2-yl)amine (B):** 2,4,6-Trimethylaniline (4.05 g, 4.20 mL, 30.0 mmol) and *tert*-amyl alcohol (0.352 g, 0.45 mL, 4.0 mmol) in THF (20.0 mL) were added to a THF suspension of NaH (0.624 g, 26 mmol). The resulting mixture was heated at 65 °C for 2 h then cooled. 2,2-Bipyridyl (0.94 g, 6.0 mmol) was added to the cool mixture followed by dried $Ni(OAc)_2$ (0.35 g, 2.0 mmol). The reaction mixture was heated for a further 2 h then cooled. To the cool mixture 2,6-dichloropyridine (2.96 g, 20.0 mmol) was added, and the reaction mixture was refluxed for 2 h. After cooling, water (2.0 mL) and dichloromethane (120.0 mL) were added to the mixture. The reaction mixture was filtered through sodium sulfate and volatiles were removed from the filtrate. The resultant yellow oil was purified by silica gel column chromatography with dichloromethane as the eluent. Volatiles were removed under vacuum and the product was recrystallized from *n*-hexane at –24 °C; yield 2.0 g (41%). $C_{14}H_{15}N_2Cl$ (246.73): calcd. C 68.13, H 6.13, N 11.36; found C 67.77, H 5.98, N 10.95. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.02 (s, 6 H, $H^{13,14}$), 2.15 (s, 3 H, H^{15}), 5.61 (d, 1 H, H^3), 6.15 (br. s, 1 H, NH), 6.33 (d, 1 H, H^5), 6.65 (t, 1 H, H^4), 6.73 (s, 2 H, $H^{9,11}$) ppm. ^{13}C NMR

(100 MHz, C_6D_6, 298 K): δ = 17.60 ($C^{13,14}$), 20.38 (C^{15}), 102.69 (C^3), 111.65 (C^5), 128.92 ($C^{9,11}$), 135.36 (C^{10}), 136.41 ($C^{8,12}$), 139.13 (C^7), 139.61 (C^4), 149.51 (C^2), 158.51 (C^6) ppm.

Synthesis of Ligands and Complexes

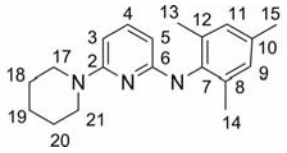


***N*-(2,6-Diisopropylphenyl)-6-(piperidin-1-yl)pyridin-2-amine (1a):** Ligand precursor (6-chloropyridin-2-yl)-(2,6-diisopropylphenyl)-amine (1.44 g, 5.0 mmol) and piperidine (0.85 g, 1.0 mL, 10.0 mmol) in toluene (10 mL) were heated for 3 d at 170 °C in a pressure tube. The solution was filtered and volatiles were removed under vacuum. The yellow oil thus obtained was purified by silica gel column chromatography. After removing the volatiles the yellow oil was then recrystallized from *n*-pentane at –80 °C; yield 1.5 g (89%). $C_{22}H_{31}N_3$ (337.25): calcd. C 78.28, H 9.26, N 12.46; found C 77.93, H 9.79, N 12.16. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.04 (d, 12 H, $H^{14,15,17,18}$), 1.36 (m, 6 H, $H^{21,22,23}$), 3.30 (sept, 2 H, $H^{13,16}$), 3.37 (t, 4 H, $H^{20,24}$), 5.48 (d, 1 H, H^3), 5.80 (d, 1 H, H^5), 7.10 (t, 1 H, H^4), 7.12–7.20 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.30 ($C^{14,15,17,18}$), 24.81 (C^{22}), 25.62 ($C^{21,23}$), 28.67 ($C^{13,16}$), 45.63 ($C^{20,24}$), 95.21 (C^3), 96.24 (C^5), 124.03 ($C^{9,11}$), 128.20 (C^{10}), 134.40 (C^7), 139.15 (C^4), 148.13 ($C^{8,12}$), 158.89 (C^2), 159.34 (C^6) ppm.

Synthesis of the Dichloride II1a: Ligand **1a** (0.337 g, 1.0 mmol) was dissolved in *n*-hexane (15.0 mL). The ligand solution was added to a light green *n*-hexane (15 mL) solution of $(Et_2N)TiCl_3$ (0.226 g, 1.0 mmol) at room temperature. The solution's color changed from light green to dark red. The resulting solution was stirred overnight. The solution was filtered and the filtrate volume was reduced, and the product was crystallized from the solution at –24 °C; yield 0.240 g (45%). $C_{26}H_{40}Cl_2N_4Ti$ (527.10): calcd. C 59.19, H 7.65, N 10.63; found C 59.67, H 7.40, N 10.17. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.79 (t, 6 H, $H^{CH3–CH2–N–}$), 1.02–1.20 (m, 12 H, $H^{14,15,17,18,21,22,23}$), 1.39 (d, 6 H, $H^{14,15,17,18}$), 3.33 (t, 4 H, $H^{20,24}$), 3.46 (sept, 2 H, $H^{13,16}$), 4.05 (q, 4 H, $H^{CH3–CH2–N–}$), 4.87 (d, 1 H, H^3), 5.66 (d, 1 H, H^5), 6.80 (t, 1 H, H^4), 7.14–7.27 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 12.23 ($C^{CH3–CH2–N–}$), 24.40 ($C^{14,15,17,18}$), 24.75 ($C^{14,15,17,18}$), 25.53 (C^{22}), 25.75 ($C^{21,23}$), 28.20 ($C^{13,16}$), 42.31 ($C^{CH3–CH2–N–}$), 47.13 ($C^{20,24}$), 101.47 (C^3), 106.33 (C^5), 123.70 ($C^{9,11}$), 128.10 (C^{10}), 140.74 ($C^{8,12}$), 142.73 (C^4), 147.88 (C^7), 155.38 (C^2), 158.55 (C^6) ppm.

Synthesis of the Trichloride I1a: Ligand **1a** (0.337 g, 1.0 mmol) was dissolved in toluene (15.0 mL). *n*BuLi (0.625 mL, 1.0 mmol) was added drop wise to the ligand solution at 0 °C, which was stirred at room temperature for 2 h. The resultant mixture was added drop wise to a toluene (15.0 mL) solution of titanium tetrachloride (0.189 g, 1.0 mmol) at 0 °C. The resultant dark red solution was stirred overnight. The solution was filtered, and the solution volume was reduced to 10.0 mL. The product was recrystallized from toluene at –24 0 °C; yield 0.370 g (75%). $C_{22}H_{30}Cl_3N_3Ti$ (490.47): calcd. C 53.83, H 6.16, N 8.57; found C 53.45, H 5.86, N 8.40. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.20 (d, 6 H, $H^{14,15,17,18}$), 1.35 (m, 6 H, $H^{21,22,23}$), 1.64 (d, 6 H, $H^{14,15,17,18}$), 3.43 (t, 4 H, $H^{20,24}$), 3.60 (sept, 2 H, $H^{13,16}$), 4.75 (d, 1 H, H^3), 5.75 (d, 1 H, H^5), 6.91 (t, 1 H, H^4), 7.14–7.27 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.60 (C^{22}), 24.04 ($C^{14,15,17,18}$), 24.60 ($C^{14,15,17,18}$), 25.60 ($C^{21,23}$), 28.72 ($C^{13,16}$), 47.88 ($C^{20,24}$), 86.64 (C^3), 106.69 (C^5), 124.07 ($C^{9,11}$), 129.19 (C^{10}), 141.22 ($C^{8,12}$), 141.89 (C^4), 150.35 (C^7), 153.03 (C^2), 157.48 (C^6) ppm.

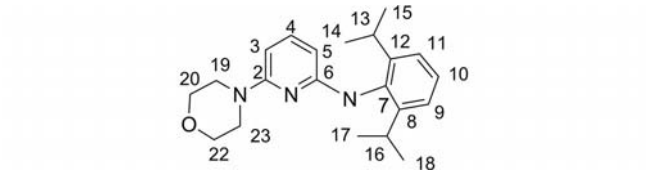
Synthesis of the Aluminum Complex III1a: Ligand **1a** (0.337 g, 1.0 mmol) was dissolved in toluene (10.0 mL) before Me_3Al (0.14 g, 2.0 mmol) was added. The solution was stirred at room temperature for 15 min, after which time all volatiles were removed under reduced pressure. The remaining white solid was dissolved in boiling hexane (10.0 mL), which was then slowly cooled to room temperature over a period of 2 d. Colorless crystals were separated from solution and dried in vacuo; yield 0.30 g (76%). $C_{24}H_{36}AlN_3$ (393.54): calcd. C 73.25, H 9.22, N 10.68; found C 72.91, H 9.20, N 10.70. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = –0.11 (s, 6 H, H^{CH3-Al}), 1.07–1.23 (m, 7 H, $H^{14,15,17,18,21,22,23}$), 1.25–1.27 (d, 12 H, $H^{14,15,17,18}$), 2.97 (m, 4 H, $H^{20,24}$), 3.55 (sept, 2 H, $H^{13,16}$), 5.18 (d, 1 H, H^3), 5.27 (d, 1 H, H^5), 6.88 (t, 1 H, H^4), 7.15 27 (t, 1 H, H^{10}), 7.22 (d, 2 H, $H^{9,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = –8.76 (C^{CH3-Al}), 24.22 ($C^{14,15,17,18}$), 24.56 ($C^{14,15,17,18}$), 24.83 (C^{22}), 25.26 ($C^{21,23}$), 28.40 ($C^{13,16}$), 46.84 ($C^{20,24}$), 92.46 (C^3), 92.85 (C^5), 124.13 ($C^{9,11}$), 126.11 (C^{10}), 143.06 ($C^{8,12}$), 143.15 (C^4), 146.15 (C^7), 155.97 (C^2), 165.99 (C^6) ppm.



***N*-(2,4,6-Trimethylphenyl)-6-(piperidin-1-yl)pyridin-2-amine (1b):** Ligand precursor 6-chloro-*N*-mesitylpyridin-2-amine (1.23 g, 5.0 mmol) and piperidine (0.86 g, 1.0 mL, 10.0 mmol) in toluene (10.0 mL) were heated for 3 d at 160 °C in a pressure tube. The solution was filtered and volatiles were removed under vacuum. The yellow oil thus obtained was purified by silica gel chromatography with dichloromethane as the eluant. The volatiles were removed under vacuum, and resultant yellow oil was recrystallized from *n*-pentane at –80 °C; yield 1.30 g (88%). $C_{19}H_{25}N_3$ (295.20): calcd. C 77.23, H 8.53, N 14.23; found C 77.12, H 8.48, N 14.01. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.30–1.40 (m, 6 H, $H^{18,19,20}$), 2.14 (s, 3 H, H^{15}), 2.23 (s, 6 H, $H^{13,14}$), 3.44 (t, 4 H, $H^{17,21}$), 5.47 (d, 1 H, H^3), 5.61 (br. s, 1 H, NH), 5.93 (d, 1 H, H^5), 6.79 (s, 2 H, $H^{9,11}$), 7.03 (t, 1 H, H^4) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 18.10 ($C^{13,14}$), 20.64 (C^{15}), 24.85 (C^{19}), 25.53 ($C^{18,20}$), 45.82 ($C^{17,21}$), 93.61 (C^3), 96.23 (C^5), 129.03 ($C^{9,11}$), 134.93 (C^7), 135.32 (C^{10}), 136.39 ($C^{8,12}$), 138.91 (C^4), 157.08 (C^2), 159.17 (C^6) ppm.

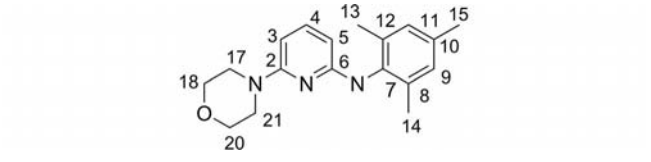
Synthesis of the Dichloride II1b: Ligand **1b** (0.148 g, 0.5 mmol) was dissolved in *n*-hexane (10.0 mL). The ligand solution was added drop wise to a light green *n*-hexane (10 mL) solution of (Et_2N)-$TiCl_3$ (0.113 g, 0.5 mmol) at room temperature. The color of the solution changed from light green to dark red. The resulting solution was stirred overnight. The solution was filtered, and the filtrate volume was reduced, and the product was crystallized from the solution at –24 °C; yield 0.215 g (47%). $C_{23}H_{34}Cl_2N_4Ti$ (485.32): calcd. C 56.90, H 7.06, N 11.55; found C 56.62, H 6.90, N 11.42. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.80 (t, 6 H, $H^{CH3–CH2–N–}$), 1.10–1.25 (m, 6 H, $H^{18,19,20}$), 2.14 (s, 3 H, H^{15}), 2.24 (s, 6 H, $H^{13,14}$), 3.38 (t, 4 H, $H^{17,21}$), 3.98 (q, 4 H, $H^{CH3–CH2–N–}$), 4.88 (d, 1 H, H^3), 5.62 (d, 1 H, H^5), 6.80 (t, 1 H, H^4), 7.13–7.25 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 12.58 ($C^{CH3–CH2–N–}$), 18.48 ($C^{13,14}$), 20.90 (C^{15}), 25.90 (C^{19}), 28.20 ($C^{18,20}$), 47.39 ($C^{CH3–CH2–N–}$), 49.11 ($C^{17,21}$), 87.70 (C^3), 102.04 (C^5), 122.40

($C^{9,11}$), 128.10 (C^{10}), 134.88 ($C^{8,12}$), 138.74 (C^4), 141.30 (C^7), 157.10 (C^2), 159.48 (C^6) ppm.



***N*-(2,6-Diisopropylphenyl)-6-(morpholino)pyridin-2-amine (2a):** (6-Chloropyridin-2-yl)-(2,6-diisopropylphenyl)amine (1.44 g, 5.0 mmol) and morpholine (0.87 g, 10.0 mmol) in toluene (15.0 mL) were heated at 160 °C for 3 d in a pressure tube. The solution was filtered and volatiles were removed under vacuum. The yellow oil thus obtained was purified by silica gel column chromatography with dichloromethane as the eluent. The volatiles were removed under vacuum and the resultant yellow oil was recrystallized from *n*-hexane at –24 °C; yield 1.45 g (85%). $C_{21}H_{29}N_3O$ (339.23): calcd. C 74.29, H 8.62, N 12.38; found C 73.82, H 8.96, N 11.88. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.09 (d, 12 H, $H^{14,15,17,18}$), 3.34 (t, 4 H, $H^{19,23}$), 3.38 (sept, 2 H, $H^{13,16}$), 3.48 (t, 4 H, $H^{20,22}$), 5.48 (d, 1 H, H^3), 5.74 (br. s, 1 H, NH), 5.80 (d, 1 H, H^5), 7.10 (t, 1 H, H^4), 7.12–7.20 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.92 ($C^{14,15,17,18}$), 28.54 ($C^{13,16}$), 45.63 ($C^{19,23}$), 66.76 ($C^{20,22}$), 94.95 (C^3), 96.24 (C^5), 124.03 ($C^{9,11}$), 128.20 (C^{10}), 134.52 ($C^{8,12}$), 139.15 (C^4), 148.13 (C^7), 158.59 (C^2), 159.34 (C^6) ppm.

Synthesis of the Dichloride II2a: Ligand **2a** (0.170 g, 0.5 mmol) was dissolved in *n*-hexane (10.0 mL). The ligand solution was added drop wise to a light green *n*-hexane (10.0 mL) solution of $(Et_2N)TiCl_3$ (0.113 g, 0.50 mmol) at room temperature. The solution's color changed from light green to dark red. The resulting solution was stirred overnight. The solution was filtered, and the filtrate volume was reduced, and the product was crystallized from the solution at –24 °C; yield 0.125 g (47%). $C_{25}H_{38}Cl_2N_4OTi$ (529.08): calcd. C 56.70, H 7.24, N 10.59; found C 56.36, H 7.10, N 10.72. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.80 (t, 6 H, $H^{CH3–CH2–N–}$), 1.20 (d, 6 H, $H^{14,15,17,18}$), 1.36 (d, 6 H, $H^{14,15,17,18}$), 3.23 (t, 4 H, $H^{19,23}$), 3.43 (sept, 2 H, $H^{13,16}$), 3.50 (t, 4 H, $H^{20,24}$), 3.96 (q, 4 H, $H^{CH3–CH2–N–}$), 4.88 (d, 1 H, H^3), 5.54 (d, 1 H, H^5), 6.80 (t, 1 H, H^4), 7.14–7.24 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 10.99 ($C^{CH3–CH2–N–}$), 25.01 ($C^{14,15,17,18}$), 25.42 ($C^{14,15,17,18}$), 28.41 ($C^{13,16}$), 42.60 ($C^{CH3–CH2–N–}$), 47.37 ($C^{19,23}$), 66.58 ($C^{20,22}$), 92.20 (C^3), 105.86 (C^5), 124.32 ($C^{9,11}$), 138.74 (C^4), 140.24 (C^7), 140.82 (C^{10}), 143.65 ($C^{8,12}$), 153.74 (C^2), 159.69 (C^6) ppm.



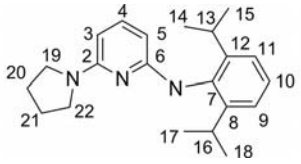
***N*-(2,4,6-Trimethylphenyl)-6-(morpholino)pyridin-2-amine (2b):** Ligand precursor 6-chloro-*N*-mesitylpyridin-2-amine (1.47 g, 6.0 mmol) and morpholine (1.04 g, 12.0 mmol) in toluene (10.0 mL) were heated at 170 °C in a pressure tube. The solution was filtered and volatiles were removed under vacuum. The yellow oil thus obtained was purified by silica gel column chromatography with dichloromethane as the eluent. The volatiles were removed under vacuum and the resultant yellow oil was recrystallized from *n*-hexane at –24 °C; yield 1.50 g (85%). $C_{18}H_{23}N_3O$ (297.18): calcd. C 72.68, H 7.80, N 14.14; found C 72.28, H 8.16, N 13.86. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.16 (s, 6 H, $H^{13,14}$), 2.23 (s, 3 H, H^{15}), 3.37 (t, 4 H, $H^{18,20}$), 3.61 (t, 4 H, $H^{17,21}$), 5.47 (d, 1 H, H^3), 5.74 (br. s, 1 H, NH), 5.93 (d, 1 H, H^5), 6.79 (s, 2 H, $H^{9,11}$), 7.03 (t, 1 H, H^4) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 18.38 ($C^{13,14}$), 20.40 (C^{15}), 45.86 ($C^{17,21}$), 66.96 ($C^{18,20}$), 95.03 (C^3), 96.33 (C^5), 122.40 ($C^{9,11}$), 135.08 (C^{10}), 136.64 ($C^{8,12}$), 139.16 (C^4), 141.50 (C^7), 157.70 (C^2), 159.48 (C^6) ppm.

Synthesis of the Dichloride II2b: Ligand **2b** (0.148 g, 0.5 mmol) was dissolved in *n*-hexane (10.0 mL). The ligand solution was added drop wise to a light green *n*-hexane (10.0 mL) solution of $(Et_2N)TiCl_3$ (0.113 g, 0.5 mmol) at room temperature. The solution's color changed from light green to dark red. The resulting solution was stirred overnight. The solution was filtered, the filtrate volume was reduced, and the product was crystallized from solution at –24 °C; yield 0.110 g (45%).

Alternative Procedure for the Synthesis of II2b: Titanium tetrachloride (0.189 g, 1.0 mmol) was added to a Schlenk tube containing dichloromethane (10.0 mL). Ligand **2b** (0.297 g, 1.0 mmol) was dissolved in dichloromethane (10.0 mL). The ligand solution was added drop wise to the titanium tetrachloride solution. The solution color changed from colorless to pink. Triethylamine (0.145 g, 0.20 mL, 1.40 mmol) was added to the solution, and changed the color of the solution to dark red. The solution was stirred for 2 h. Diethyamine (0.146 g, 0.22 mL, 2.20 mmol) was added to the solution. The resultant solution was stirred overnight. The solution was filtered, the solvent was removed under vacuum, and the product was extracted with, and recrystallized at –24 °C from, toluene; yield 0.110 g (45%). $C_{22}H_{32}Cl_2N_4OTi$ (487.03): calcd. C 54.21, H 6.62, N 11.50; found C 53.82, H 6.53, N 11.13. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.19 (t, 6 H, $H^{CH3–CH2–N–}$), 2.10 (s, 6 H, $H^{13,14}$), 2.20 (s, 3 H, H^{15}), 3.38 (t, 4 H, $H^{17,21}$), 3.64 (t, 4 H, $H^{18,20}$), 3.96 (q, 4 H, $H^{CH3–CH2–N–}$), 4.86 (d, 1 H, H^3), 5.56 (d,1 H, H^5), 6.80 (t, 1 H, H^4), 6.86 (s, 2 H, $H^{9,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 11.10 ($C^{CH3–CH2–N–}$), 18.42 ($C^{13,14}$), 20.95 (C^{15}), 25.53 ($C^{17,21}$), 46.56 ($C^{CH3–CH2–N–}$), 66.98 ($C^{18,20}$), 92.76 (C^3), 96.30 (C^5), 122.40 ($C^{9,11}$), 128.10 (C^{10}), 134.88 ($C^{8,12}$), 138.74 (C^4), 141.30 (C^7), 157.12 (C^2), 159.48 (C^6) ppm.

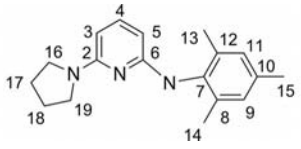
Synthesis of the Trichloride I2b: Titanium tetrachloride (0.189 g, 1.0 mmol) was added to a Schlenk tube containing dichloromethane (10.0 mL). Ligand **2b** (0.297 g, 1.0 mmol) was dissolved in dichloromethane (10.0 mL). The ligand solution was added drop wise to the titanium tetrachloride solution. The color of the solution changed from colorless to pink. Triethylamine (0.141 g, 0.20 mL, 1.40 mmol) was added to the solution, and changed the color of the solution to dark red. The resultant solution was stirred overnight. The solution was filtered, the solvent was removed under vacuum, and the product was extracted with, and recrystallized at –24 °C from, toluene; yield 0.270 g (62%). $C_{18}H_{22}Cl_3N_3OTi$ (450.40): calcd. C 47.96, H 4.92, N 9.33; found C 47.70, H 4.85, N 9.14. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.10 (s, 3 H, H^{15}), 2.33 (s, 6 H, $H^{13,14}$), 3.25 (t, 4 H, $H^{17,21}$), 3.42 (t, 4 H, $H^{18,20}$), 4.68 (d, 1 H, H^3), 5.49 (d, 1 H, H^5), 6.67 (t, 1 H, H^3), 6.73 (s, 2 H, $H^{9,11}$). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 17.98 (C^{15}), 20.96 ($C^{13,14}$), 47.05 ($C^{17,21}$), 66.10 ($C^{18,20}$), 87.34 (C^3), 106.06 (C^5), 128.02 (C^{10}), 128.26 ($C^{9,11}$), 129.61 (C^{10}), 137.59 ($C^{8,12}$), 142.19 (C^7), 151.52 (C^2), 153.57 (C^6) ppm.

***N*-(2,6-Diisopropylphenyl)-6-(pyrrolidin-1-yl)pyridin-2-amine (3a):** Ligand precursor (6-chloro-pyridin-2-yl)-(2,6-diisopropylphenyl)-amine (1.44 g, 5.0 mmol) and pyrrolidine (0.71 g, 0.82 mL, 10.0 mmol) in toluene (10.0 mL) were heated at 160 °C in a pressure tube. The solution was filtered and volatiles were removed un-



der vacuum. The yellow oil thus obtained was purified by silica gel column chromatography. The volatiles were removed under vacuum and resultant yellow oil was recrystallized from *n*-pentane at –80 °C; yield 1.35 g (83%). $C_{21}H_{29}N_3$ (323.24): calcd. C 77.96, H 9.04, N 13.00; found C 77.42, H 8.96, N 12.78. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.10 (d, 12 H, $H^{14,15,17,18}$), 1.49 (t, 4 H, $H^{20,21}$), 3.31 (t, 4 H, $H^{19,22}$), 3.41 (sept, 2 H, $H^{13,16}$), 5.42 (d,1 H, H^3), 5.70 (d, 1 H, H^5), 5.84 (t, 1 H, H^3), 7.02–7.22 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 24.03 ($C^{14,15,17,18}$), 25.22 ($C^{20,21}$), 28.25 ($C^{13,16}$), 46.29 ($C^{19,22}$), 92.65 (C^3), 96.04 (C^5), 123.67 ($C^{9,11}$), 128.20 (C^{10}), 134.66 (C^7), 138.36 (C^4), 147.92 ($C^{8,12}$), 157.15(C^2), 158.73 (C^6) ppm.

Synthesis of the Dichloride II3a: Ligand **3a** (0.323 g, 1.0 mmol) was dissolved in *n*-hexane (15.0 mL). The ligand solution was added drop wise to a light green *n*-hexane (15 mL) solution of (Et_2N)-$TiCl_3$ (0.226 g, 1.0 mmol) at room temperature. The color of the solution changed from light green to dark red. The resulting solution was stirred overnight. The solution was filtered, the filtrate volume was reduced, and the product crystallized from solution at –24 °C; yield 0.245 g (48%). $C_{25}H_{38}Cl_2N_4Ti$ (513.08): calcd. C 58.47, H 7.46, N 10.92; found C 58.45, H 7.80, N 10.41. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.79 (t, 6 H, $H^{CH3–CH2–N–}$), 1.10 (d, 6 H, $H^{14,15,17,18}$), 1.18 (d, 6 H, $H^{14,15,17,18}$), 1.34 (t, 4 H, $H^{20,21}$), 3.32 (t, 4 H, $H^{19,22}$), 3.40 (sept, 2 H, $H^{13,16}$), 4.06 (q, 4 H, $H^{CH3–CH2–N–}$), 4.86 (d, 1 H, H^3), 5.51 (d, 1 H, H^5), 6.80 (t, 1 H, H^4), 7.14–7.27 (m, 3 H, $H^{9,10,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 12.62 ($C^{CH3–CH2–N–}$), 24.16 ($C^{14,15,17,18}$), 24.58 ($C^{14,15,17,18}$), 25.28 ($C^{20,21}$), 28.45 ($C^{13,16}$), 46.57 ($C^{CH3–CH2–N–}$), 47.73 ($C^{19,22}$), 92.42 (C^3), 95.92 (C^5), 123.53 ($C^{9,11}$), 128.10 (C^{10}), 134.52 ($C^{8,12}$), 138.17 (C^4), 147.77(C^7), 157.00 (C^2), 158.56 (C^6) ppm.



***N*-(2,4,6-Trimethylphenyl)-6-(pyrrolidin-1-yl)pyridin-2-amine (3b):** Ligand precursor 6-chloro-*N*-mesitylpyridin-2-amine (1.47 g, 6.0 mmol) and pyrrolidine (0.710 g, 0.81 mL, 10. 0 mmol) in toluene (15.0 mL) were heated at 160 °C in a pressure tube for 3 d. The solution was filtered and volatiles were removed under vacuum. The yellow oil thus obtained was purified by silica gel column chromatography. The volatiles were removed under vacuum and the resultant yellow oil was recrystallized from *n*-pentane at –80 °C; yield 1.50 g (89%). $C_{18}H_{23}N_3$ (281.19): calcd. C 76.82, H 8.24, N 14.94; found C 76.63, H 8.10, N 14.73. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.10 (t, 4 H, $H^{17,18}$), 2.15 (s, 3 H, H^{15}), 2.18 (s, 6 H, $H^{13,14}$), 3.30 (t, 4 H, $H^{16,19}$), 5.70 (d, 1 H, H^5), 5.81 (d, 1 H, H^3), 6.79 (s, 2 H, $H^{9,11}$), 7.12 (t, 1 H, H^4) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 18.02 ($C^{13,14}$), 20.55 (C^{15}), 25.15 ($C^{17,18}$), 46.17 ($C^{16,19}$), 92.38 (C^3), 95.95 (C^5), 128.94 ($C^{9,11}$), 135.17 (C^7), 135.37 (C^{10}), 136.33 ($C^{8,12}$), 138.35 (C^4), 157.10 (C^2), 157.48 (C^6) ppm.

Synthesis of the Dichloride II3b: Ligand **3b** (0.281 g, 1.0 mmol) was dissolved in *n*-hexane (15.0 mL). The ligand solution was added drop wise to a light green *n*-hexane (15.0 mL) solution of (Et_2N)-$TiCl_3$ (0.226 g, 1.0 mmol) at room temperature. The color of the solution changed from light green to dark red. The resulting solution was stirred overnight. The solution was filtered, the filtrate volume was reduced, and the product was crystallized from solution at –24 °C; yield 0.220 g (46%). $C_{22}H_{32}Cl_2N_4Ti$ (471.03): calcd. C 56.05, H 6.85, N 11.89; found, C 56.13, H 7.36, N 11.65. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.78 (t, 6 H, $H^{CH3–CH2–N–}$), 1.36–1.38 (t, 4 H, $H^{17,18}$), 2.14 (s, 3 H, H^{15}), 2.17 (s, 6 H, $H^{13,14}$), 3.32 (t, 4 H, $H^{16,19}$), 3.90 (q, 4 H, $H^{CH3–CH2–N–}$), 5.49 (d, 1 H, H^3), 5.64 (t, 1 H, H^4), 5.74 (d, 1 H, H^5), 6.79 (s, 2 H, $H^{9,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 11.12 ($C^{CH3–CH2–N–}$), 18.42 ($C^{13,14}$), 20.95 (C^{15}), 28.20 ($C^{17,18}$), 42.50 ($C^{CH3–CH2–N–}$), 46.26 ($C^{16,19}$), 92.76 (C^3), 96.30 (C^5), 122.40 ($C^{9,11}$), 128.10 (C^{10}), 134.88 ($C^{8,12}$), 138.74 (C^4), 141.30 (C^7), 157.10 (C^2), 159.48 (C^6) ppm.

Reactions in NMR Tubes of the Complexes with TMA

(a) An NMR tube was charged with **II1a** (20 mg, 0.04 mmol), deuteriobromobenzene (0.5 mL) and TMA (115 mg, 1.60 mmol). Afterwards, the tube was sealed, shaken for 5 min, and then an NMR spectrum was recorded. (b) An NMR tube was charged with **II1a** (21 mg, 0.04 mmol), deuterio-bromobenzene (0.5 mL) and TMA (115 mg, 1.60 mmol). Afterwards, the tube was sealed, shaken for 5 min, and then an NMR spectrum recorded. (c) NMR tubes were charged with **III1a** (0.016 g, 40 μmol) and deuterio-bromobenzene (0.5 mL) before TMA (6, 14, 29, 58, 115, and 289 mg, 0.08, 0.20, 0.40, 0.80, 1.60, and 4.0 mmol, respectively) was added. Afterwards, the tube was sealed, shaken for 5 min, and the NMR spectra recorded (Figure 7).

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG), SFB 840 for supporting this work. M. H. thanks the University of Azad Jammu & Kashmir and the Higher Education Commission, Pakistan for a scholarship. We thank I. Haas, Dr. Ch. Döring, and T. Bauer for their help in the X-ray laboratory.

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Received: August 11, 2011
Published Online: November 10, 2011

