Novel Group 4 Metal Amido Complexes – Syntheses, Reactivity and Olefin Polymerization Catalysis

DISSERTATION

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Vorgelegt von
M. Sc. Muhammad Hafeez
Geboren in Azad Kashmir, Pakistan

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Dean:	Prof. Dr. Beate Lohnert
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Doctoral Committee:

First referee:	Prof. Dr. Rhett Kempe
Second referee:	Prof. Dr. Brigit Weber
Third referee:	Prof. Dr. Rainer Schobert
Chairman:	Prof. Dr. Peter Strohriegl

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Dedicated to my son Umer Hafeez

Abbreviations

Ar	aryl
Ap	aminopyridine
Å	angstrom
Bn	benzyl
BuLi	butyl lithium
br	broad
^{o}C	degree Celsius
calcd	calculated
d	doublet
d	day
δ	chemical shift (ppm)
DPPP	bis(diphenylphosphino)propane
d- MAO	dry methyl aluminoxane
δ	chemical shift
equiv.	equivalent
Et	ethyl
η	eta
g	gram
GPC	gel permeation chromatography
h	hours
Hz	hertz
K	kelvin
m	multiplet
mg	milligram
M	molar
MHz	mega hertz
min	minutes
$Pd_2(DBA)_3$	tris(dibenzilideneacetone)dipalladium(0)
PE	polyethylene
Π	pi

PS	polystyrene
ppm	parts per million
%	per cent
sept	septet
tert	tertiary
TMA	trimethylaluminum
mL	milliliter
mmol	millimol
μmol	micromol
NMR	nuclear magnetic resonance
q	quartet
σ	sigma
s	singlet
t	triplet

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1. Summary / Zusammenfassung

1.1 Summary

A series of amine functionalized electron rich aminopyridinato ligands was synthesized by the methodology developed by Fort and coworkers and subsequent Ulmann thermal amination. In addition to this some tripodal ligands containing nitrogen donor functionalities were also synthesized. The corresponding titanium and hafnium complexes of these ligands were synthesized using the amine / diethyl-ammonium chloride / toluene elimination and salt metathesis routes. These compl-exes were characterized by NMR and elemental analysis. Many of these complexes have been studied on the basis of structure and their catalytic potential was investigated. The overall evaluation of this work tells about the electrophilicity of the metal centre and the steric and electronic effects of the ligand.

Mono Ap di / trichloride complexes of titanium were synthesized by amine / diethyl-ammonium chloride elimination and salt metathesis routes by reacting the corresponding ligand with diethylamido titanium trichloride or titanium tetrachloride respectively. The structural investigation of these complexes gives insight into the more electron donating capability of the aminopyridinato ligands. These complexes were found moderatly active for ethylene and styrene polymerization when activated with d-MAO giving syndiotactic polystyrene of high molecular weight and aluminum terminated polyethylene. The low activity of these complexes was attributed to the ligand transfer to aluminum during catalysis.

Mono Ap trialkyl hafnium complexes were synthesized by reacting the respective aminopyridinato ligand with tetrabenzyl hafnium at room temperature. Some of these complexes were studied by single crystal X- ray analysis. These complexes have shown very low activity towards ethylene polymerization when activated with d-MAO probably due to very fast ligand transfer to aluminum. The low temperature NMR investigations of these complexes indicate the η^3-coordination of one benzyl with hafnium metal centre.

To overcome the problem of ligand transfer during catalysis, we synthesized the tri-podal ligands containing nitrogen donors either by $Pd_2(DBA)_3$ / DPPP catalysed cross

coupling reactions or by $Ni^{(o)}$ / 2, 2 -bipyridine catalyst system followed by thermal amination. The titanium trichloride complexes of these ligands were synthesized by reacting the respective tripodal ligand with [Et_2NTiCl_3] at room temperature. The titanium complexes containing tripodal ligands were found less active towards ethylene polymerization.

1.2 Zusammenfassung

Eine Reihe aminofunktionalisierter elektronenreicher aminopyridinato Liganden wurde nach der Methode von Fort *et al.* mit nachfolgender thermischer Aminierung nach Ulmann entwickelt. Zusätzlich zu diesen wurden tripodal Liganden mit Stickstoff-Donor-Funktionalitäten synthetisiert. Die entsprechenden Titan und Hafnium-Komplexe wurden über Amin / Diethylammoniumchlorid / Toluol-Eliminierung und Salzmetathese hergestellt und durch NMR und Elementaranalyse charakterisiert. Die meisten Komplexe sind auf Basis ihrer Struktur studiert worden und auf ihr katalytisches Potenzial untersucht worden. Die Thematik dieser Arbeit beschäftigt sich mit der Elektrophilie des Metallzentrums und den sterischen und elektronischen Effekten der Liganden.

Mono-Ap di/trichlor Titan-Komplexe wurden durch Amin/diethylammoniumchlorid-Eliminierung und Salzmetathese synthetisiert, indem die entsprechenden Liganden entweder mit Diethylamidotitantrichlorid oder mit Titantetrachlorid umgesetzt wurden. Die Strukturuntersuchung dieser Komplexe liefert Einblick in die verstärkte Elektrondonorfähigkeit des Aminopyridinato Liganden. Die Komplexe zeigen nach Aktivierung mit d-MAO mäßige Aktivität in der Ethylen- und Styrolpolymerisation, und liefern syndiotaktisches Polystyrol mit hohem Molekulargewicht sowie Aluminium-terminiertes Polyethylen. Die niedrige Aktivität dieser Komplexe ist auf den Liganden-Transfer zum Aluminium während der Katalyse zurück zu führen.

Mono-AP trialkyl Hafnium-Komplexe wurden durch Umsetzung der jeweiligen Aminopyridinato Liganden mit Tetrabenzyl Hafnium bei Raumtemperatur synthetisiert. Einige dieser Komplexe wurden durch Einkristallröntgenstrukturanalyse untersucht. Die Komplexe zeigten nach Aktivierung mit d-MAO sehr niedrige Aktivität in der Ethylenpolymerisation, wahrscheinlich aufgrund des sehr schnellen Ligandentransfers zum Aluminium. Niedrig NMR Temperaturuntersuchungen dieser Komplexe zeigen die η^3-Koordination eines Benzyls am Hafnium-Metallzentrum. Um das Problem des Ligandentransfers während der Katalyse zu umgehen, entschlossen wir uns, tripodal Liganden mit Stickstoff-Donoren durch $Pd_2(DBA)_3$ / DPPP katalysierte Kreuzkupplungsreaktionen oder mit einem $Ni^{(o)}$ / 2, 2-bipyridine Katalysatorsystem gefolgt von thermischer Aminierung zu synthetisieren. Die Titantrichlorid Komplexe dieser Liganden wurden durch Umsetzung der jeweiligen tridentaten Liganden mit $[Et_2NTiCl_3]$ bei Raumtemperatur synthetisiert. Die Titan

Komplexe mit tripodal Liganden zeigten eine geringere Aktivität in der Ethylenpolymerisation.

2. Introduction

Transition metal catalysts play an important role in the polymerization of olefins, for instance styrene and ethylene. [1] The transition metal catalyzed olefin polymerization at low temperature and low pressure conditions started with the pioneering work of Karl Ziegler in 1953. [2] Ziegler found 1- butene in the autoclave while he was trying to synthesize long chain aluminum alkyls with the insertion of ethylene into the aluminum carbon bond of triethylaluminum. A trace of a nickel compound in the reaction autoclave was responsible for this unexpected product. Based on this fascinating finding, Ziegler started the application of the other transition metal compounds for example zirconium acetylacetonate which gave higher molecular weight polyethylene and he found that the combination of the $TiCl_4$ and $AlEt_3$ was the best catalyst for the ethylene polymerization. [3] Giulio Natta extended Ziegler's work to stereospecific polymerization of the propylene. [4] Both Ziegler and Natta were awarded noble prize in chemistry in 1963 for their excellent inventions.

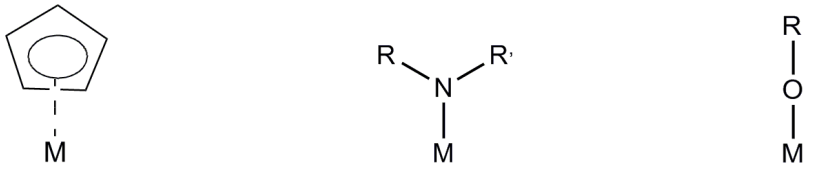
Soon after the discovery and structural characterization of ferrocene, [5,6] Wilkinson and Birmingham, synthesized Cp_2TiCl_2 and Cp_2ZrCl_2 polymerization catalysts. [7] Understanding of metallocene catalyst provided an insight to structural correlation between the catalyst and the polymer obtained from it.

In1970's, a main breakthrough in homogenous catalysis came through the finding that the catalytic activity of the $Cp_2TiCl_2/AlMe_2Cl$ and $Cp_2TiMe_2/AlMe_3$ catalysts could be dramatically increased with the addition of a small amount of water. [8, 9] During this catalytic reaction, trimethylaluminum was hydrolysed to methylaluminoxane (MAO) which enhanced the catalytic activity.

Although the metallocenes are the versatile catalysts, [10] for instance half sandwitch type group (IV) metal complexes producing high molecular weight elastomeric poly-propylene yet they cannot give all the desired properties to the polymers. Polar monomers can bind with the metallocenes and hence cannot be polymerized. Highly patented metallocenes with no capability to polymerize the polar monomers motivated the researchers to search for the nonmetallocene catalysts for example coordination catalysts. The potential of coordination catalysts is their easy convertibi-

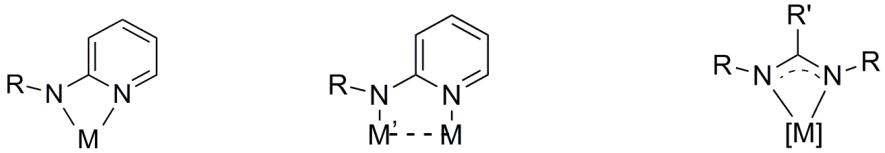
lity and now a days coordination catalysts with comparable activiies to metallocenes have already been synthesized. [11]

The important alternatives to cyclopentadienyl ligand are alkoxy (scheme 1, right) and amido ligands (scheme 1, centre) [12] which stabilize the early, electron deficient transition metal ions in medium or high oxidation states.



Scheme 1: The three most important ligand types for the stabilization of early transition metals in medium to high oxidation states (R, R´ = alkyl, aryl or silyl).

Among others, the amido ligand is more interesting because of the possibility for double substitution at the donor atom and hence a greater variety of ligands and complexes could be synthesized. As compared to closely related amidinates, the ligand “asymmetry” due to two different donor functionalities (the pyridine and the amido function) may be considered as an additional interesting feature. [13]



Scheme 2: Binding modes of aminopyridinato and amidinate ligands (R = aryl, alkyl or silyl; M = transition metal, M´ = late transition metal).

The amidinate $[RC(NR)_2]$ and guanidinate $[R_2NC(NR)_2]$ ligands are capable to sabilize mononuclear main group transition metals and lanthanide complexes, and may act as bridging ligands in di-or poly-nuclear metal complexes.which have the potential application in the olefin and polar monomer polymerization. [14]

Cotton *et al* synthesized first strained η^2-coordinated aminopyridinato complex (scheme 2, left) [15] and before 1996 only a few compounds [16, 17] were investigated. Gambarotta and coworkers published the first early transition metal complex (a vanadium complex) in 1991. [18] Since 1995, aminopyridinato ligands were extensively used to stabilize early transition metals in medium or high oxidation states. The close proximity of the pyridine and amido functions renders unique chemistry to these ligands. [19]

Aminopyridinato complexes of the group (IV) metals are interesting alternatives to the widely used metallocenes of these metals in homogenous catalysis and particularly in polymerization catalysis. [20, 21, 22] The synthesis and reactivity studies of group (IV) metals aminopyridinato complexes started in 1996. [23, 24] The traditional salt metathesis protocol was not useful in the case of titanium as it resulted in very low yield of the complex probably due to the reduction of the titanium metal centre by the lithium salt of the aminopyridinato ligand. Direct synthesis and amine elimination routes were adopted to improve the yield. The direct synthesis approach involves either the reaction of aminopyridine ligand with metal precursor without solvent at higher temperatures (above 100 °C) or in boiling toluene. Polamo *et al* explored the Group (V) metals coordination chemistry by applying the direct synthesis method to synthesize a number of tantalum and niobium complexes in higher oxidation states [25, 26] which were very active for ethylene polymerization when activated with d-MAO. [27] Noor and coworkers reported the trialkyl tantalum complexes through salt metathesis and toluene elimination routes which showed moderate activities for ethylene polymerization. [28] Many group (IV) metals aminopyridinato complexes were synthesized in higher yields under amine elimination synthetic route. [29, 30] which were found highly active for the propene and 1-butene polymerization when activated with MAO, triisobutylaluminum / $B(C_6F_5)_3$ or ethylaluminum sesquichloride cocatalysts. [30,31] In addition to salt metathesis and amine elimination, the direct synthesis has proven to be an efficient synthetic strategy for the synthesis of zirconium aminopyridinates. Metal / ligand stoichiometry was controlled by introduceing sterically demanding alkyl substituents (e.g. adamantyl) on the ligand framework. Scott and coworkers synthesized bis(aminopyridinato) zirconium complexes through amine, alkyl, elimination and salt metathesis protocols [32] however the direct synthesis with hafnium (IV) chloride resulted into the homoleptic complex. [33]

The bis $ApHfCl_2$ and bis $ApZrCl_2$ complexes of bulky aminopyridinato ligands were found highly active (maximum activity 57000 Kg PE/mol_{cat}.h.bar) and selective in ethylene polymerization. [34] The acetylenetitanium complex stabilized by aminopyridinato ligand was prepared by the redcuction of bis (aminopyridinato) titanium dichloride with magnesium and subsequent reaction with equimolar amount of bis(trimethylsilyl)acetylene. The reaction of the acetylenetitanium complex with acetone resulted into titanaoxacyclopentene. [35] The tribenzyl complexes of the Zr / Hf with sterically demanding bulky ligands were synthesized by the toluene elimination route and were

less active for the ethylene polymerization due to benzyl coordination to the metal centre. [36]

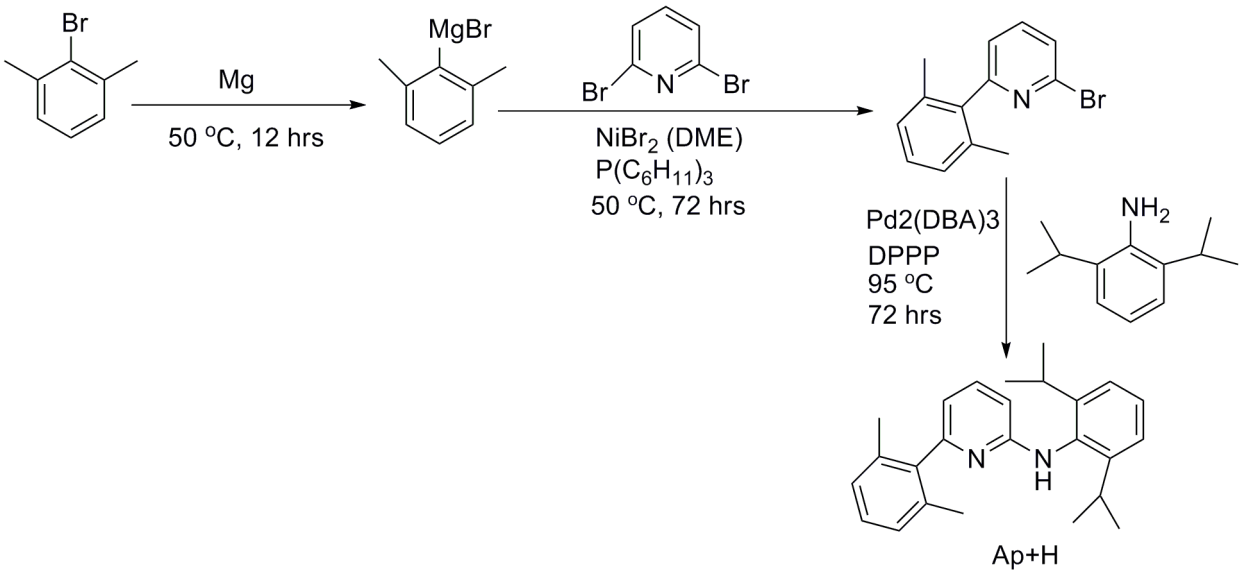
Maraku *et al* has reported the $ApTiCl_3$ and $ApTiCl_2$ complexes with sterically less demanding phenylaminopyridine ligands by HCl elimination. These complexes showed low to moderate activities for ethylene polymerization (65-280 Kg PE/$mol_{Ti.}$ h. bar). [37] The authors also studied the chloro and fluoro substituted aminopyridinato titanium complexes with regard to ethylene polymerization. The mono (2, 6-difluoro-phenylaminopyridinato) titanium catalyst was found to be more active in ethylene polymerization than bis (2, 6-difluorophenylaminopyridinato) and bis (2-chlorophenyl-aminopyridinato) titanium catalysts. These catalysts were of low activities and showed broader molecular weight distribution. [38] They also explored the effect of alkyl group in the phenyl group of the bis (phenylaminopyridinato) titanium dichloride complexes on the catalytic activity and polymer chain length in ethylene polymerization and assumed that electron donating groups on the ligands can increase the chain length of the formed polymer. [39] The titanium complexes bearing bulky aminopyridinato ligands were moderately active for propylene and highly active for ethylene (maximum activity 2840 Kg/mol h bar) and ethylene / propylene copolymerization (maximum activity 33000 Kg/mol h bar). These titanium catalysts were also very active in co and terpolymerization of 2-ethylidenenorbornene (ENB) with ethylene or ethylene – propylene, together with a very good incorporation of ENB. [40]

The recently reported mixed Cp*/Ap dimethyl complexes of hafnium were applied for the coordinative chain transfer polymerization (CCTP) with a maximum activity for ethylene polymerization 2600 Kg/mol h bar. [41] Scott *et al* has synthesized the aryl substituted aminopyridinato ligands involving three step synthesis. [42] A model scheme (from Scott work) for the synthesis of Ap^+H(N-(2, 6-diisopropylphenyl)-6-(2, 6-dimethylphenyl) pyridin-2-amine) is discussed here:

1. Synthesis of Grignard reagent of 2-bromo-1, 3-dimethylbenzene.
2. Coupling reaction of the dimethylbenzene magnesium bromide with 2,6-dibromop-yridine catalyzed by $NiBr_2$(DME) and $P(C_6H_{11})_3$.
3. Cross coupling reaction of the 2-bromo-6-(2, 6-dimethylphenyl) pyridine with 2, 6-diisopropylaniline catalysed by $Pd_2(DBA)_3$ and DPPP catalyst system.

The main drawbacks associated with this synthesis are:

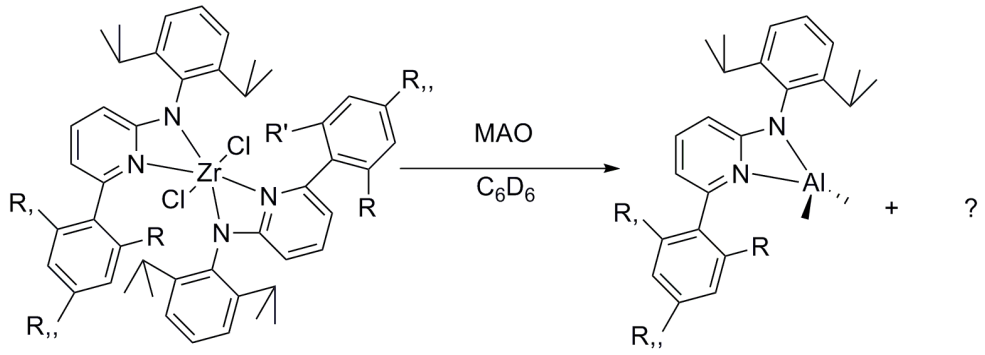
1. Multistep and costly synthesis.



Scheme 3: Synthesis of $AP^{+}H$ (N-(2, 6-diisopropylphenyl)-6-(2, 6-dimethylphenyl) pyridin-2-amine).

2. A transition metal catalyst is required twice for carbon nitrogen bond formation (scheme 3).

3. Owing to the poor electron donating capability of these ligands, their correspond-ding complexes were not stable in the presence of aluminum alkyls during catalysis (scheme 4). [34]



Scheme 4: Ligand transfer to aluminum (R, R' = alkyl, R'' = H or R, R' = R'' = alkyl).

The economic synthesis is valuable in the industry as well as in the laboratory. Keeping it in mind, we tried to synthesize the ligands with the consumption of inexpensive chemicals and *in situ* generated $Ni^{(o)}$ /2, 2-bipyridyl catalyst system which is twenty two times cheaper than the $Pd_2(DBA)_3$ and DPPP. Tables 1 and 2 show the comparison of per mol cost for the synthesis of some of the ligands included in this work with those already reported by our group. The per mol cost reduced four times

with the present synthesis as compared to the previous one (table 1, 2). [43] Moreover only one of the two synthesis steps requires transition metal catalyst for the carbon nitrogen bond formation. The second step goes smoothly by thermal amination.

Table 1: The per mol cost for the synthesis of Ap^pH (N- (N-(2,6-Diisopropylphenyl)-6-(piperidin-1-yl)pyridin-2-amin). The prices of the chemicals are reported from Sigma Aldrich, 2012.

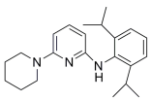
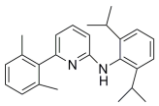
Sr. No	Reactant / Catalyst	Price / g (€)	Ligand	Cost /mol (€)
1	**2, 6-dichloropyridine**	**0.25**		**725.62**
2	2, 6-diisopropylaniline	0.17		
3	**Nickel acetate**	**0.09**		
4	Sodium hydride	0.34		
5	**2, 2-bipyridine**	**2.54**		
6	Styrene	0.20		
7	t-amylalcohol	0.09		
8	Piperidine	0.46		

Table 2: The per mol cost for the synthesis of Ap+H (N-(2, 6-diisopropylphenyl)-6-(2, 6-dimethylphenyl)pyridin-2-amine). The prices of the chemicals are reported from Sigma Aldrich, 2012.

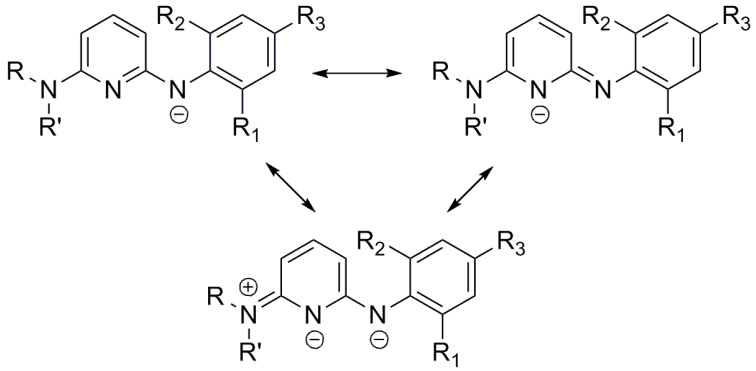
Sr. No	Reactant / Catalyst	Price /g (€)	Ligand	Cost /mol (€)
1	**2, 6-dibromopyridine**	**1.45**		**2946.00**
2	2, 6-diisopropylaniline	0.17		
3	2-bromo-1, 3-dimethylbenzene	2.36		
4	Magnesium turnings	0.91		
5	$NiBr_2$.DME	22.70		
6	Tricyclohexylphosphane	18.40		
7	**$Pd_2(DBA)_3$**	**54.00**		
8	**DPPP**	**13.30**		
9	Sodium tert-butoxide	0.32		

We thought that amine functionalized ligands may solve the problem of instability of the complexes containing less electron donating ligands (scheme 5) towards aluminum alkyls by increasing the electron donation from pyridine nitrogen and thus making this bond more stable in the presence of aluminum alkyls during olefin polymerization.

(a) (b)

Scheme 5: a) Aryl and b) Amine substituted aminopyridines, Ar = aryl, R = alkyl.

The ligands containing an additional amine function are more electron donating as it is indicative from the resonance contributing structures (scheme 6).



Scheme 6: Resonance contributing structures of amine functionalized electron rich ligands (R_1, R_2, R_3, R, R' = alkyl).

The structural investigation of the titanium complexes containing electron rich ligands indicates the more electron donating capability of the ligands. To give the structural proof that the ligands containing an additional amine function (scheme 6) are more electron donating, the crystal structure of a titanium complex containing a more electron donating amine functionalized ligand is compared with a titanium complex containing an aryl substituted less electron donating ligand (Figure 1, 2 and 3 below). In first structure (figure 1), the bond length between N1 (morpholine nitrogen) and C5 is 1.358 Å which is shorter than a carbon nitrogen single bond (1.48 Å) but clearly longer than a carbon nitrogen double bond (1.29 Å). The sum of the angles around N1 is 357.83°, indicating that this nitrogen is planar with sp^2 hybridization. The lone pair on the nitrogen 2p orbital is overlapping with the carbon 2p orbital and increasing the bond order between the carbon and nitrogen more than one (around 1½).

The electronic contribution from N1 to the pyridine ring enhances the electron density on the pyridine ring thus making the pyridine nitrogen more electron donating. Due to more electron donation from the N1, the bond lengths between C5-N2 and C1-N2 (1.393 and 1.360 Å respectively) increase as compared to similar bond lengths in figure 2 (1.344 and 1.344 Å respectively). The pyridine nitrogen titanium bond length

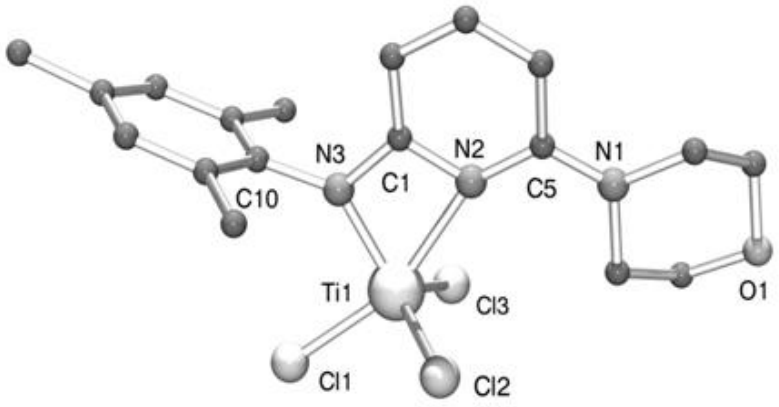


Figure 1: Molecular structure of a Ap titanium trichloride complex containing an electron rich aminopyridinato ligand.

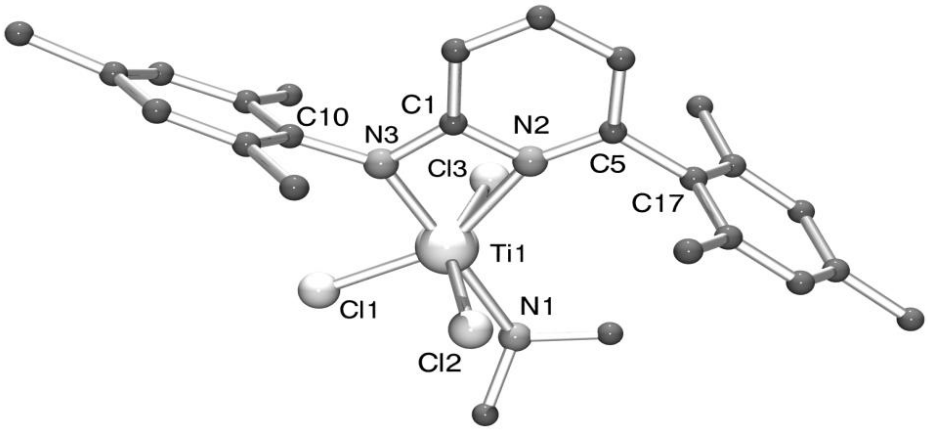


Figure 2: Moleculer structure of a Ap amido titanium trichloride complex containing an aryl substituted aminopyridine ligand.

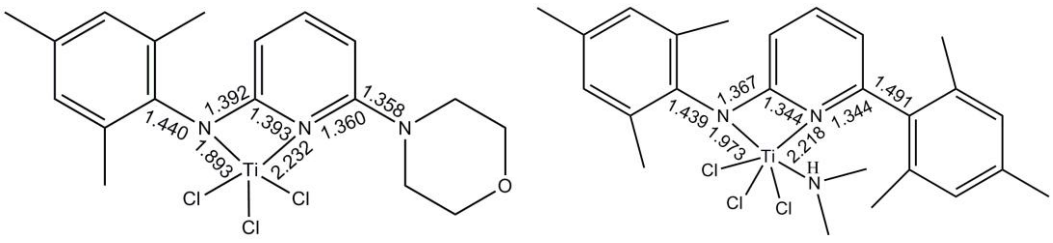


Figure 3: The comparison of bond lengths of compounds in figure 1 and 2.

in the figure 1 (1.893 Å) is shorter as compared to the similar bond length (1.973 Å) in the figure 2, indicating more electron donation from pyridine nitrogen to titanium metal centre.

The electron rich ligands (scheme 6) were used to synthesize Ap amido titanium dichloride, Ap titanium trichloride and $ApHf(Bn)_3$ type hafnium complexes. Owing to high yield and clean synthesis (volatile by products), [29, 30] we preferred the amine and toluene elimination routes for the synthesis of these complexes. Salt metathesis route was adopted to synthesize some titanium complexes. Selective titanium complexes were employed for ethylene and styrene polymerization using d-MAO as cocatalyst. The catalytic potential of hafnium complexes was tested for ethylene polymerization. In addition to this some tripodal ligands containing nitrogen donors were synthesized either by $Pd_2(DBA)_3$ / DPPP catalysed cross coupling reactions or by $Ni^{(o)}$ / 2, 2 -bipyridine catalyst system followed by thermal amination. The tripodal ligands were reacted with $[Et_2NTiCl_3]$ to synthesize titanium trichloride complexes. Some of these complexes were applied for ethylene polymerization. In short this work covers the synthesis of unique aminopyridinate chemistry not only in terms of synthetic and structural aspects of many of the synthesized complexes but also in terms of olefin catalytic reactivity.

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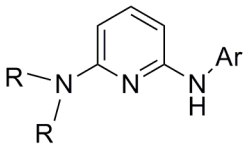
3. Overview of Thesis Results

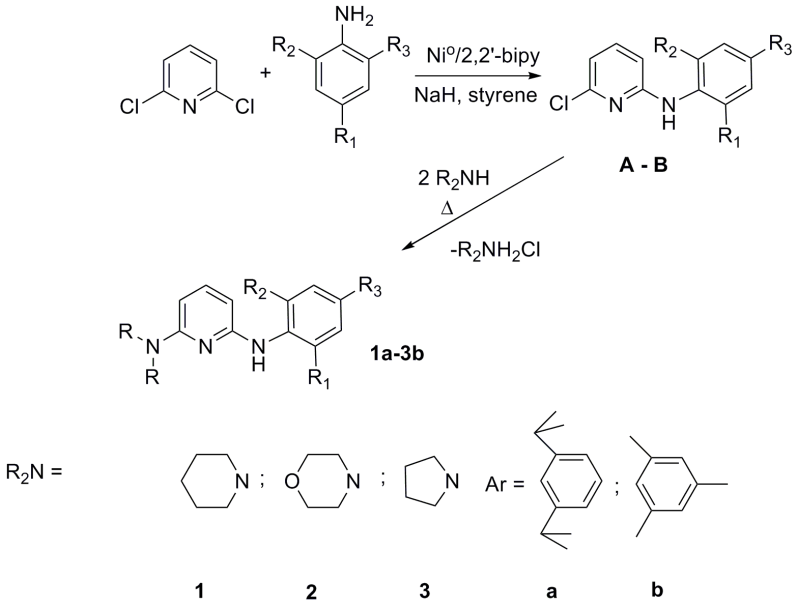
3.1 Titanium Complexes Stabilized by Bulky, Electron-Rich Aminopyridinates and their Application in Ethylene and Styrene Polymerization

Recently, we became interested in the synthesis of more electron donating ligands containing an additional amine function (scheme 1). We assumed that the complexes of these electron rich ligands could be more stable in the presence of aluminum alkyls during catalysis.



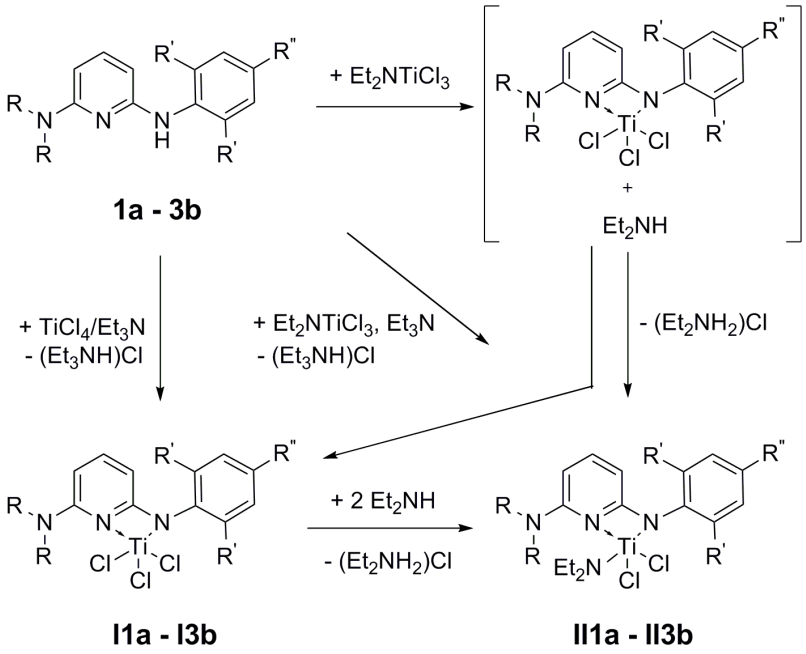
Scheme 1: Amine substituted aminopyridine; Ar = Aryl, $R_2 = (-CH_2-)_5$

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 45 % yield by the reaction of 2,6-dichloropyridine with the respective aniline, catalysed by Ni^o / 2,2'-bipyridine catalyst system which is selective for monoamination of the 2,6-dichloropyridine.



Scheme 2: Synthesis of aminopyridine ligands **1a** - **3b** (**A**; R_1, R_2 = isopropyl and R_3= H; **B**: R_1, R_2, R_3 = methyl; R, R' = alkyl).

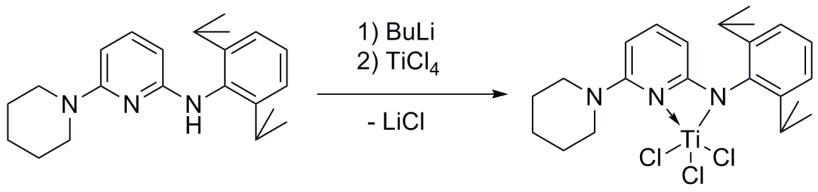
The one equiv. of each N-[6-(dialkylamino)-pyridin-2-yl]-anilines (**1a – 3b**) react with one equiv. of $[(CH_3CH_2)_2NTiCl_3]$ at room temperature in *n*-hexane through amine elimination route to form the corresponding Ap titanium trichlorides ($ApTiCl_3$), and Ap diethylamido titanium dichlorides [$Ap(Et_2N)TiCl_2$ complexes. The reaction proceeds to the final products with the further conversion of the initially formed $ApTiCl_3$ with two equivalents of the released diethylamine towards the $Ap(Et_2N)TiCl_2$ complexes and diethylammonium chloride salt. To support this hypothesis, the reaction of $ApTiCl_3$ was carried out with diethylamine in a 1:2 ratio. The exclusive formation of $Ap(Et_2N)TiCl_2$ was observed. In addition to this, the reaction goes selectively towards the formation of **II1a – II3b** (scheme 3) when one equivalent of the triethylamine was added to the amine elimination route. The earlier reported bulky aminopyridines yielded [$Ap(Et_2NH)TiCl_3$] in the similar reaction.



Scheme 3: Synthetic routes to [$ApTiCl_3$] and [$Ap(Et_2N)TiCl_2$] complexes.

$ApTiCl_3$ was obtained as the product when the corresponding aminopyridines were reacted with $TiCl_4$ in 1 : 1 in the presence of triethylamine in dichloromethane (scheme 3) or when the reaction of the lithium salt of these aminopyridines was made with one equivalent $TiCl_4$ in toluene (scheme 4). This synthetic route gave selectively bis-Ap titanium dichlorides for less bulky ligands.

All complexes were characterized by NMR spectroscopy and elemental analysis. Suitable crystals for X-ray analysis were obtained by slowly cooling the saturated *n*-



1a **I1a**

Scheme 4: Synthesis of the titanium complexes.

hexane solutions to -24 °C. Single crystal structure analysis was carried out for complexes **I2b**, **II1a**, **II2a** and **II3a**. The coordination of all four complexes is best described as distorted trigonal bipyramidal.

These titanium complexes (scheme 3, 4) are indicative of many unique structural features.

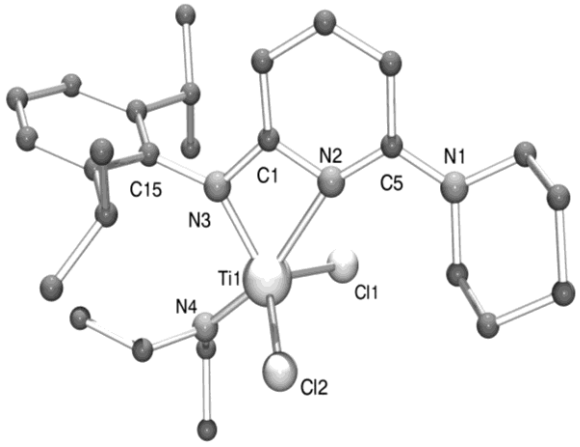


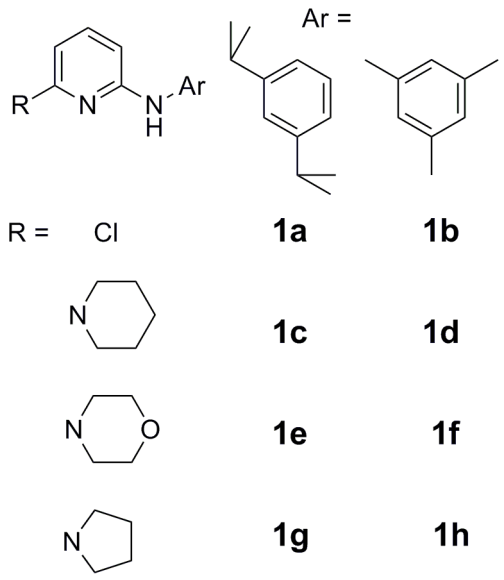
Figure 2: Molecular structure of **II1a.**

The amine function on the other side of the pyridine ring has effected the electronic situation on the pyridine ring. Taking into account the C5-N1 bond distances of all four titanium complexes (**II1a, II2a, II3a, I2b)** are between 1.35 – 1.36 Å which are longer than a C-N double bond (~1.29 Å) but shorter than a typical C-N single bond (~1.48 Å). The N1 is almost planar as the sum of all three angles around N1 is between 353.11° – 359.99°. The planarity (sp^2) hybridization of N1 together with C5-N1 distances indicates the N1 lone pair participation in the pyridine Π-system. The bond lengths N1-C5, C5-N2, N2-C1 and C1-N3 are all around 1.36 Å indicating an average bond order of 1½. The increased bond order for N1-C5 [$N_{(heterocycle)}$-$C_{(pyridine)}$] bond could also be confirmed from low temperature NMR experiments showing coal-cescent temperatures between -50 and -40 ºC for the proton resonances of the pipyridyl-, morpholyl- and pyrrolidyl-rings as a result of the increased rotation barrier.

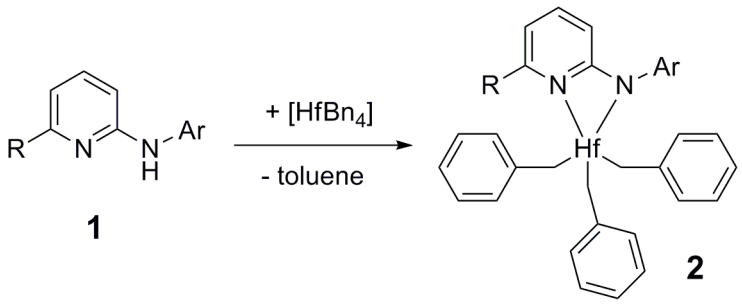
Although the aminopyridinato ligands discussed here have the higher electron donating capability yet these ligands coordinate in the amido pyridine form with a shorter Ti-N_{amido} distance (1.89 – 1.96 Å) and a longer Ti-$N_{pyridine}$ one (2.232 – 2.365 Å). Selective titanium complexes were applied for styrene as well as ethylene polymerization which showed moderate activities. The activity of these complexes increased with increasing temperature and steric bulk of the aminopyridinato ligand however ligand transfer to aluminum was observed at NMR scale reactions of trimethylauminum with these complexes. This instability of the complexes with aluminum alkyls could be a possible reason for less activity. The ^{1}H and ^{13}C NMR investigations of polymers were indicative of syndiotactic polystyrene and aluminum terminated polyethylene. Most of the complexes showed broader polydispersities indicating the presence of more than one catalytically active species during catalysis however GPC data indicates high molecular weight polymers.

3.2 Hafnium Trialkyls Stabilized by Bulky, Electron Rich Aminopyridinates

We also became interested to synthesize the hafnium complexes of the type ($ApHfBn_3$) by reacting the ligands shown in scheme (1) in 1:1 with hafnium tetrabenzyl ($HfBn_4$) at room temperature.



Scheme 1: Applied aminopyridines.



Scheme 2: Synthesis of **2**, the assignment of **1a-1h** and **2a-2h** is given in scheme 1 (Bn = benzyl).

The toluene elimination route gives high yield for these complexes (67-86 %). The hafnium complexes (**2a-2h**) were characterized by NMR, elemental analysis and selectively (**2a** and **2e**) by single crystal X- ray analysis. The overall geometry of these complexes is distorted pentagonal bipyramidal. In complex **2a**, one of the three benzyls is η^2 coordinated while in **2e** all the three bezyls are η^1 coordinated. The Hf-$N_{pyridine}$ bond length is longer than Hf-N_{amido} bond indicating the anionic function on N_{amido} atom.

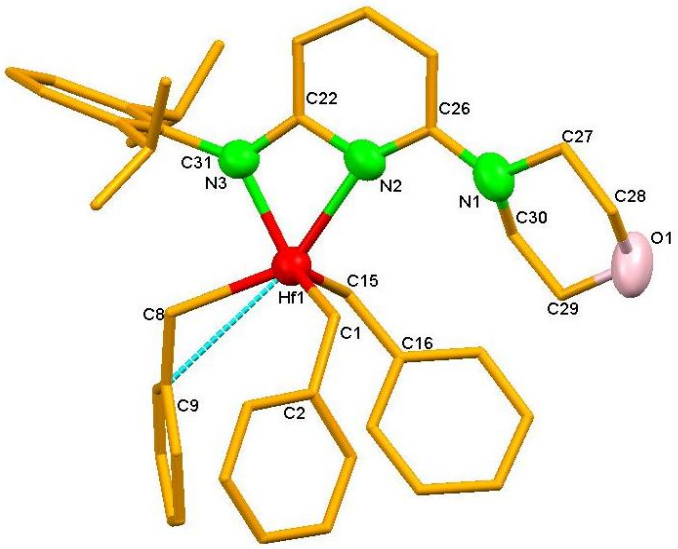


Figure 1: Molecular structure of complex **2e.**

The N1-C26 bond length is 1.379(9) Å which is in between a C-N single bond (~1.48 Å) and a C-N double bond (~1.29 Å) indicative of a bond order higher than one. The sum of all three angles around N1 is 351^{o} indicating an almost planar nitrogen atom which is more typical for a sp^{2} hybridized N-atom. The sp^{2}-hybridization of N1 together with the short N1-C26 distances shows the participation of N1 lone pair in the ligand Π-system increasing the electron donating ability of the amine functionalized Ap ligand.

NMR investigation of the compound **2** revealed one set of proton resonances for the Ap ligand and another set for all three benzyl ligands indicating a fast rotation of the Ap ligand and chemical equivalence of three benzyls in solution at room temperature. In the ^{1}H-NMR spectra, the proton resonances for the protons at the 3 and 5 position of the pyridine ring appear quite upfield (between 4.9 and 5.6 ppm). The dialkylamine substituent on the pyridine ring increases the electron donating ability but weakens the ring current of the pyridine ring. The low temperature NMR experiment conducted for hafnium compound **2c** (Figure 2) between -70 to -10 °C is indicative of a strong temperature depending shift of the piperidyl proton resonances at 1.1 and 2.8 ppm but did not split these protons. However splitting was observed for the benzyl ligand resonances at 2.4 ppm into two sets of multiplets below -50 °C with a ratio of 1:2 was observed. Probably a reversible coordination of one of the benzyl ligands to reduce the electron deficiency of the metal center makes the benzyls unequal.

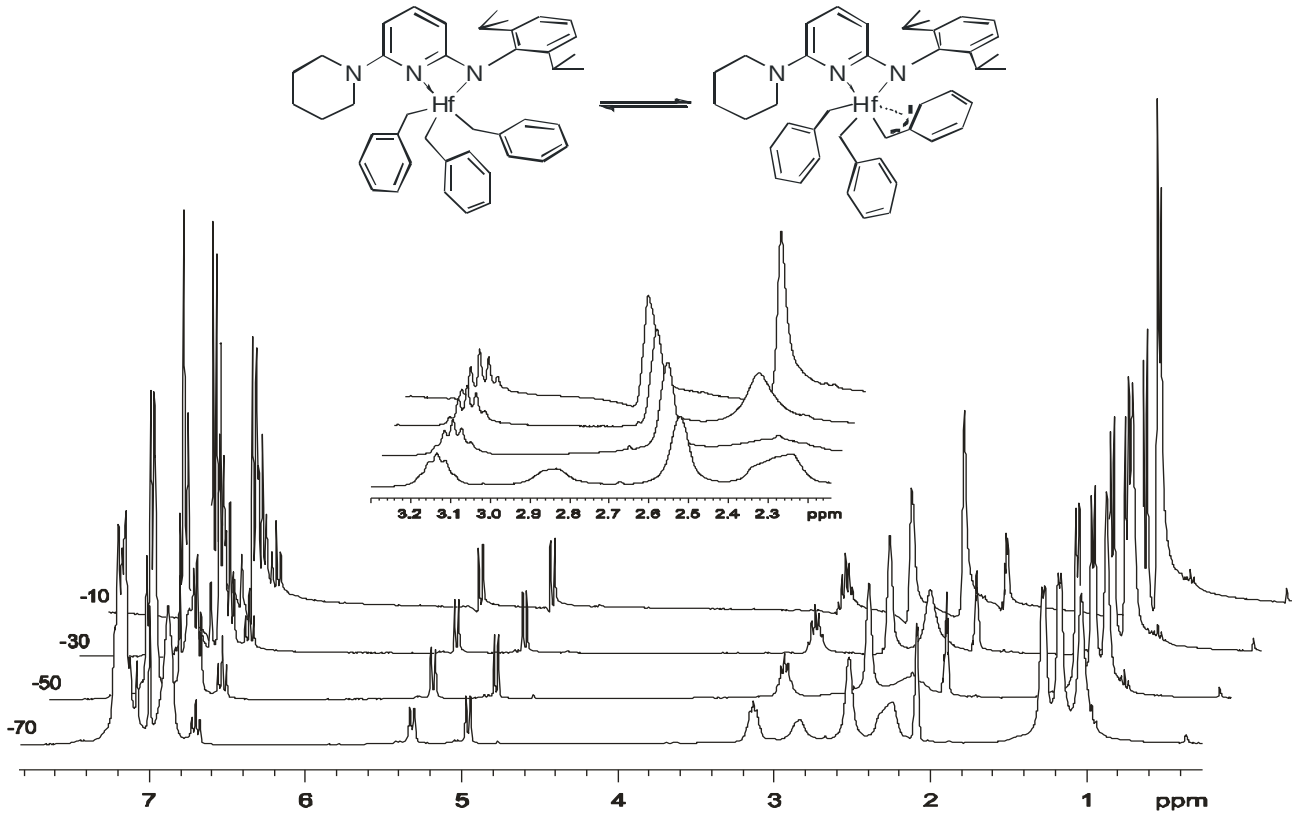
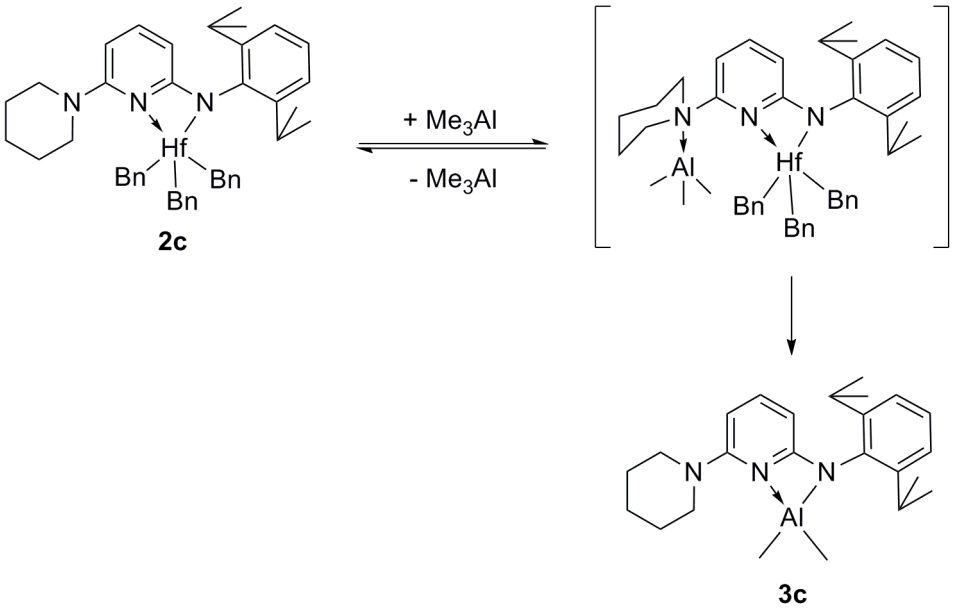


Figure 2: Variable ^{1}H low temperature NMR spectra of **2c** (toluene-d_8, -70 to -10 °C, 0 - 8 ppm).

The trialkyl hafnium complexes of the electron rich ligands were applied for the ethylene polymerization (selective examples).These complexes were not active with MAO however very low activities around 5 -10 $Kg_{PE}/mol_{cat}\cdot h\cdot bar_{ethylene,}$were observed when d-MAO was used. The inactivity is probably due to very fast ligand transfer to aluminum alkyls. Borate activation in the presence of an aluminum scavenger did not improve the activity significantly. Through proton NMR, we studied the stability of **2a** in the presence of trimethylaluminum. A very fast coordination of trimethylaluminium (scheme 3, spectrum after 5 min) followed by an immediate ligand transfer reaction was observed (spectrum after 16 h). Formation of dimethylaluminum complex **3c** when **1c** is reacted with trimethylaluminum in 1:1 ratio in toluene at room temperature gives conclusive proof for ligand transfer (Figure 3, below).



Scheme 3: Ligand transfer reaction of hafnium complex **2c**, Bn = benzyl.

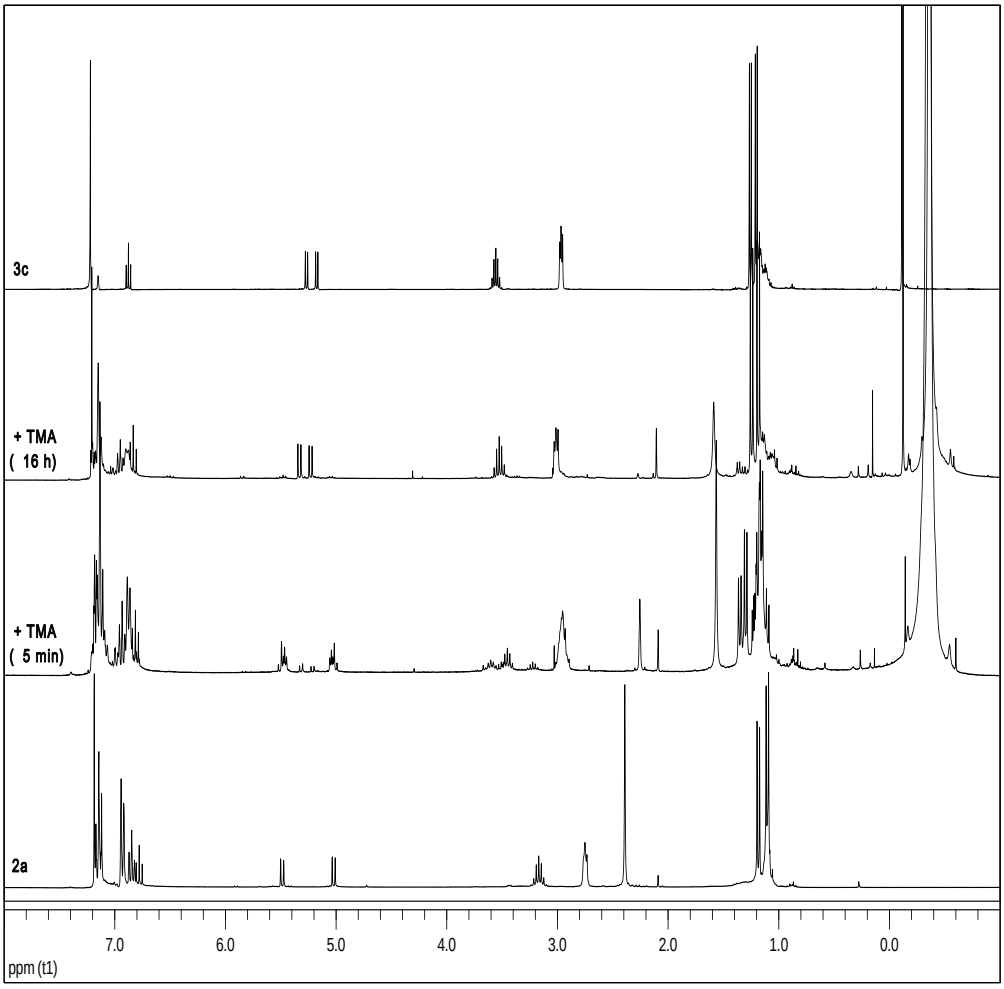
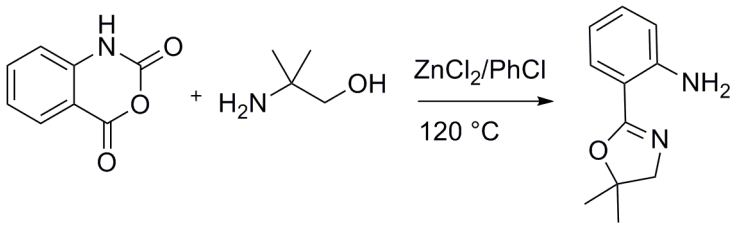


Figure 3: ^{1}H NMR spectra (C_6D_6, 26 °C, 0 - 8 ppm) of $ApAlMe_2$ (**3c**), $ApHfBn_3$ (**2c**), **2c** + 30 eq. TMA after 5 min and after 16 h.

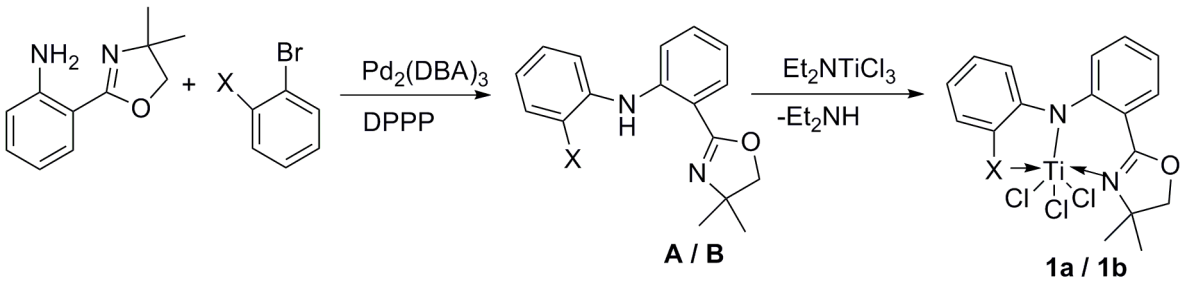
3.3 Synthesis, Structural Investigations and Ethylene Polymerization of Titanium Complexes with Tripodal Oxazoline Ligands

The activity of the Ap amido titanium dichloride and Ap titanium trichloride complexes (discussed above) was low to moderate when employed for ethylene and styrene polymerization. We assumed the low activity of these complexes due to ligand transfer to aluminum during catalysis. The hafnium complexes of the type [$ApHfBn_3$] were even less active to ethylene polymerization. We experimentally proved that there was a faster ligand transfer to aluminum in case of hafnium complexes as compared to titanium ones. To overcome the problem of ligand transfer, we decided to synthesize the tripodal ligands which could better stabilize the metal complexes in the presence of aluminum alkyls.The [2 -(4, 4-dimethyl-4, 5-dihydrooxazol-2-yl)aniline] was synthesized by $ZnCl_2$ catalysed reaction of isatoic anhydride and 2-amino-2-methylpropan-1-ol in toluene (scheme 1).



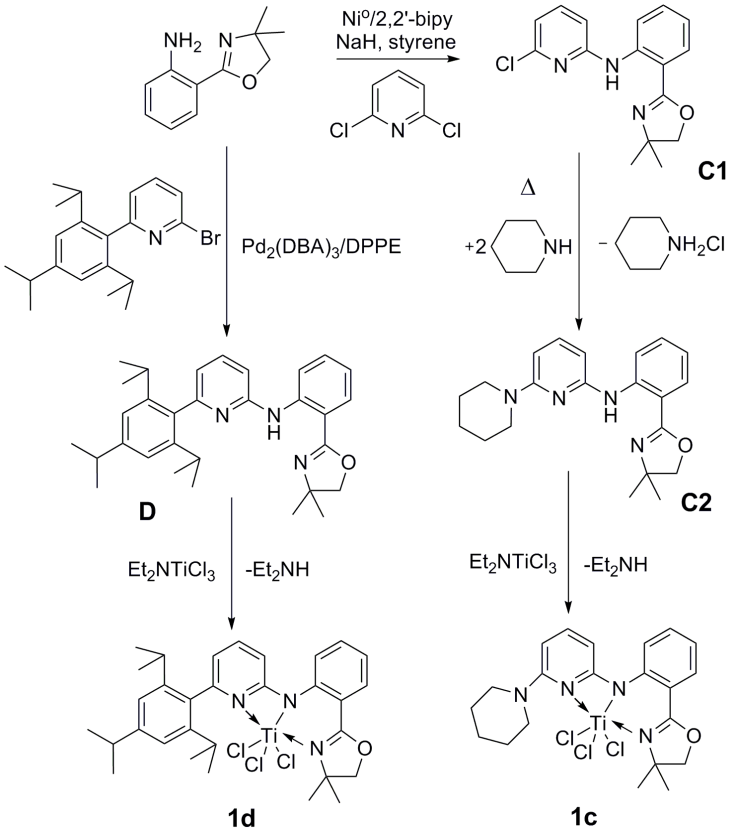
Scheme 1: Synthesis of [2-(4, 4-dimethyl-4, 5-dihydrooxazol-2-yl)aniline].

The ligand [2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2-fluorophenyl)aniline] (FOxH, **A**) and ligand [2-(4, 4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2-methoxyphenyl)aniline] (MeOOx-H, **B**) were synthesized by the $Pd_2(DBA)_3$ / DPPP catalysed cross coupling reaction of 2-[(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline] with 2-Fluoro-1-bromobenzene or 1-bromo-2-methoxybenzene in 1:1 in refluxing toluene (scheme 1). The one equiv. of each **A** and **B** was reacted with one equiv. of diethylamido titanium trichloride to afford complexes **1a** and **1b** respectively (scheme 2).



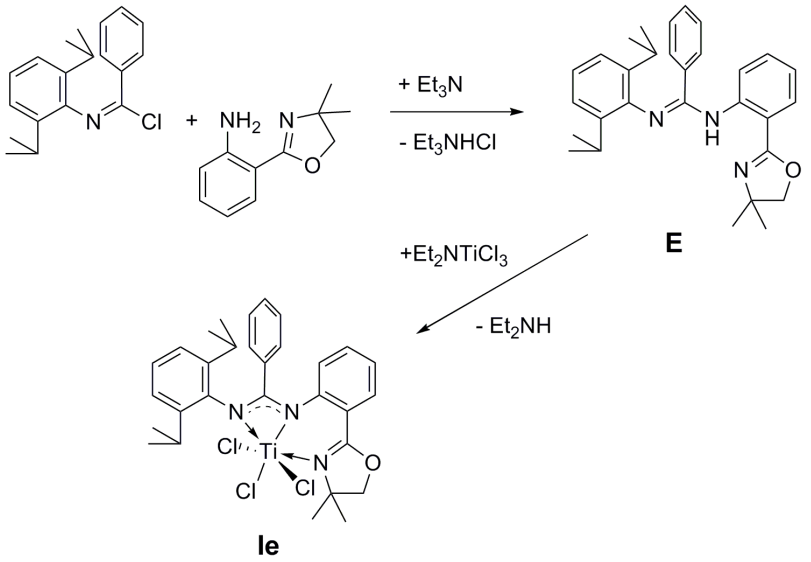
Scheme 2: Synthesis of ligands **A**, **B** and complexes **1a**, **1b** (**A**; X = F, **B**; X = OMe).

To synthesize the oxazoline substituted aminopyridines, we adopted two different synthetic routes. The recently developed $Ni^{(o)}$/2,2'-bipyridine catalyzed alkylation of 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline with 2,6-dichloropyridine followed by thermal amination of the intermediate 6-chloro-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)pyridin-2-amine (**C1**) with piperidine resulted into *N*-(2-(4,4-dimethyl-4,5-dihydro oxazol-2-yl)phenyl)-6-(piperidin-1-yl)pyridin-2-amine (**C2**, ApOxH) (scheme 3, right). $Pd_2(DBA)_3$ / DPPP catalysed hydroamination reaction was used to synthesize more bulky aminopyridine *N*-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-6-(2,4,6-triisopropylphenyl)pyridine-2-amine (**D**, Ap*OxH) (scheme 3, left). The corresponding titanium trichloride complexes (**1c**, **1d**) of the ligands **C** and **D** were synthesized by reacting the corresponding ligand with $[Et_2NTiCl_3]$ in 1:1 at room temperature (scheme 3).



Scheme 3: Synthesis of oxazoline functionalized aminopyridines **C**, **D** and complexes **1c, 1d**.

The ligand (*E*)-N'-(2,6-diisopropylphenyl)-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)benzimi-damide (**E**, AmOxH) was synthesized by refluxing the (*E*)-N-(2,6-diisopropylphenyl)benzimidoyl chloride and [2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline] in the presence of triethylamine in toluene which subsequently gives the complex **1d** under amine elimination reaction when reacted with $Et_2NT_iCl_3$ (scheme 4).



Scheme 4: Synthesis of ligand **E** and complex **1e**.

All the complexes (**1a-1e**) were characterized by NMR, elemental analysis and selectively by single crystal X-ray analysis (**1d, 1e**). The overall symmetry of both complexes can be best described as distorted octahedron with the three nitrogen and one chlorine atom in the equatorial square plane.

Some of these complexes were applied for ethylene polymerization in the presence of commercial and "dry"- methylaluminoxane (d-MAO) cocatalyst (Table 1). The complexes **1a** and **1b** showed almost no ethylene consumption however a low to moderate activity for the complexes **1c–1e** was observed.

Table 1: Ethylene polymerization*

Entry	Precat.*	T [°C]	$m_{Pol.}$ [g]	Activity [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-}$]	M_n [$kgmol^{-1}$]	M_w/M_n
1	**Ic**	70	0.22	22	-	-
2	**Id**	30	0.28	28	7840 (593000)[b]	28.0
3	**Id**	50	0.13	13	11100 (593000)[b]	73.8
4	**Id**	70	0.03	3	9400 (3530000)[b]	95.7
5[a]	**Id**	50	0.08	8	n.d.	n.d.
6	**Ie**	50	-	-	-	-
7[a]	**Ie**	50	0.33	33	5700	3.0
8[a]	**Ie**	80	-	-		

*Precatalyst: 2.0 µmol; MAO: 1.0 mmol; toluene: 150 mL; p = 2 bar; t = 15 min.[a]d-MAO. [b]M_p of higher molecular weight polymer fraction.

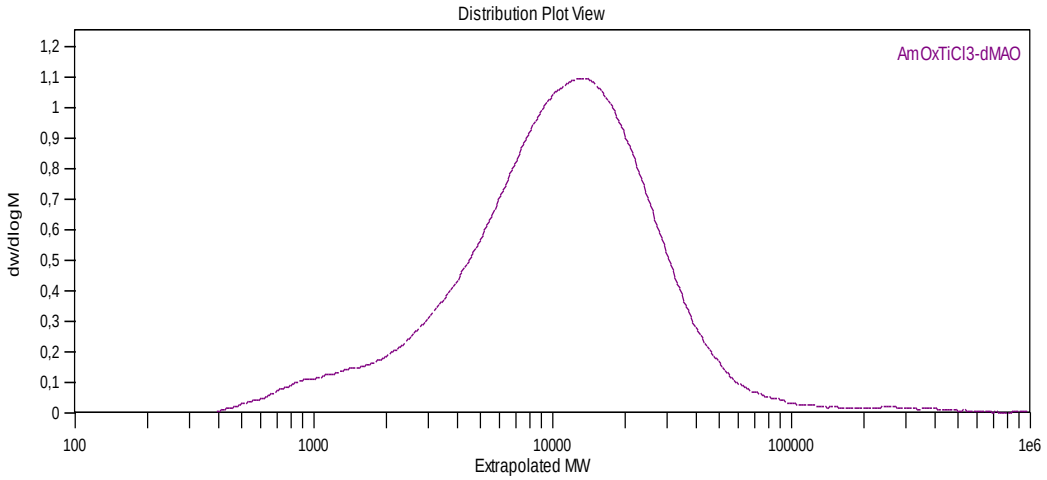


Figure 1: Molecular weight distribution observed with $AmOxTiCl_3$ precatalyst (run 7).

It was observed that the ethylene consumption was rather slow but continuous over the whole run time which indicates a less active but stable polymerization catalyst. The additional donor atom gives the stability to the catalyst towards free trimethylaluminum (TMA) but probably blocks the coordination site.

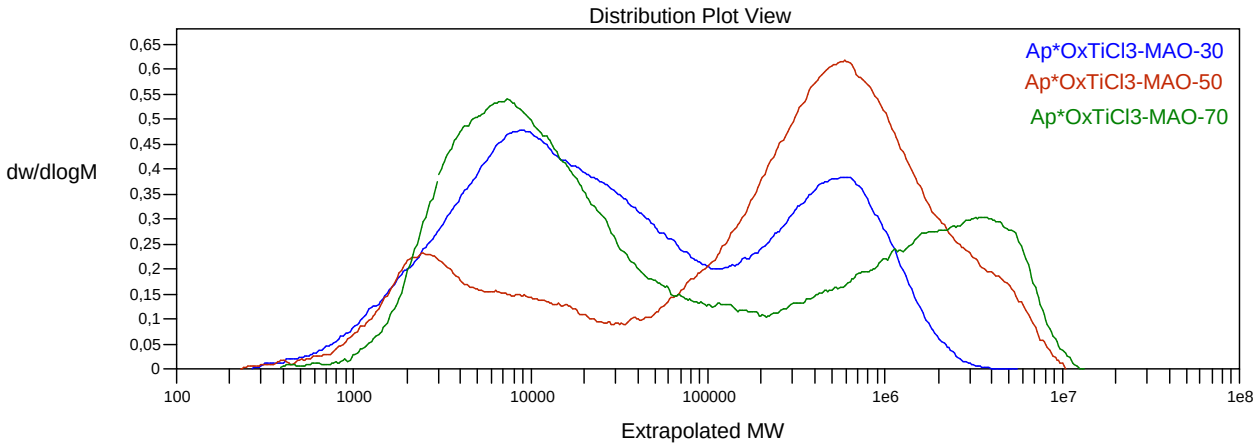


Figure 2: Molecular weight distribution of PE observed with $ApOxTiCl_3$/MAO catalyst system (run1-3).

The amidinato titanium complex **1e** gave mono-modal but low molecular weight PE (Figure 1) while the aminopyridinato titanium complexes yielded PE with a bimodal distribution including a very high molecular weight fraction indicated by the peak molecular weights of up to 3.5 million dalton (M_p Table 1, Figure 2).

3.4. Individual Contribution to Joint Publication

The results published in this thesis were obtained in collaboration with others and are published, submitted or are to be submitted as indicated below. In the following, the contributions from all the authors are specified. The asterisk indicates the corresponding author.

3.4.1 Chapter 4

This work has been published in *European Journal of Inorganic Chemistry*, entitled **'Titanium Complexes Stabilized by Bulky, Electron-Rich Aminopyridinates and their Application in Ethylene and Styrene Polymerization'**

Muhammad Hafeez, Winfried. P. Kretschmer and Rhett Kempe*[a]

I synthesized and characterised the ligands and complexes, did some polymerization experiments and wrote the publication. Dr. Winfried. P. Kretschmer made some polymerization experiments, NMR experiments and corrections in the manuscript. Rhett Kempe supervised the work and helped in scientific discussions and correcting the manuscript.

3.4.2 Chapter 5

This work has been published in *Zeitschrift für Anorganische und Allgemeine Chemie* entitled

'**Hafnium Trialkyls Stabilized by Bulky, Electron Rich Aminopyridinates'**

Muhammad Hafeez, Winfried. P. Kretschmer and Rhett Kempe*[a]

I synthesized the ligands and complexes, did the characterization and wrote the manuscript. Dr. Winfried. P. Kretschmer did the polymerization, low temperature NMR experiments, kinetic studies and was involved with making corrections in the manuscript. Rhett Kempe supervised the work and was involved in scientific discussions and correcting the manuscript.

3.4.3 Chapter 6

This work has to be submitted in *Euorpean Journal of Inorganic Chemistry* entitled

‘Synthesis, Structural Investigatigations and Ethylene Polymerization of Titanium Complexes with Tripodal Oxazoline Ligands’.

Sonja Lippert, Muhammad Hafeez, Tobias Bauer, Winfried. P. Kretschmer and Rhett Kempe*[a]

I synthesized three ligands and their corresponding titanium complexes, characterized the complexes, made the polymerization experiments and wrote the publication. Sonja Lippert synthesized some ligands and titanium complexes and made some of the polymerization studies during her B.Sc thesis work. Dr. Winfried. P. Kretschmer did GPC and was involved with making corrections in the manuscript. Rhett Kempe supervised the work and was involved in scientific discussions and correcting the manuscript.

4. Titanium Complexes Stabilized by Bulky, Electron Rich Aminopyridinates and their Application in Ethylene and Styrene Polymerization

Muhammad Hafeez, Winfried. P. Kretschmer and Rhett Kempe*[a]

[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany. Fax: +49 921 55-2157, E-mail: kempe@uni-bayreuth.de

Keywords: amido ligands / aminopyridinates / N-ligands / olefin polymerization / titanium

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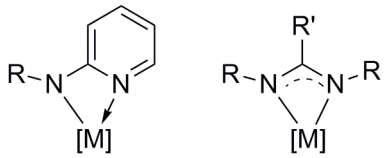
Abstract: A series of electron-rich aminopyridines with high electron density at the $N_{Pyridine}$ atom (due to an electron-donating mesomeric effect) was prepared by the Ni^{o} / 2, 2-bipyridine catalyzed arylation of anilines, followed by an uncatalyzed amination reaction. Reacting 2, 6-dichloropyridine with1 equiv. of aniline in the presence of the Ni^{o} / 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 compl-exes). 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 convent-ional 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.

4.1 Introduction

Ap complexes of the group 4 metals are promising alternatives to the widely used metallocenes of these metals in homogenous catalysis and especially in polymerization catalysis.[1-4] The aminopyridinato ligands mostly show η^2-coordination mode 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 which can be advantageous to stabilize catalytic intermediates.[1-3]

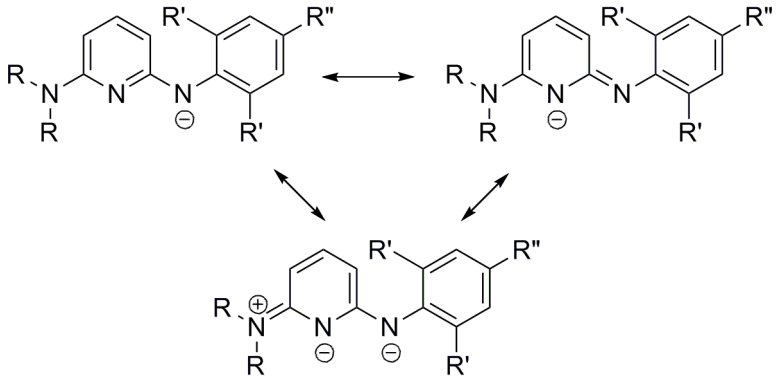


Scheme 1: Binding mode of aminopyridinato (left) and amidinato (right) ligands ([M] = group 4 metal complex moiety; R, R'= substituent).

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 either lead to more or less stable catalysts with regard to a transfer to Al.

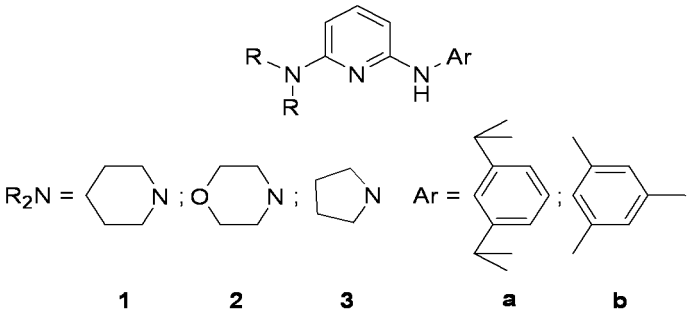
To increase the electron donation ability of aminopyridinato ligands one could introduce an amine substituent in 6 position of the pyridine ring. For details of the electron-donating mesomeric effect see (scheme 2). If the lone pair of the RR'N-substituent participates in the molecular π-system, the 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.



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

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 polymerrization of styrene before.



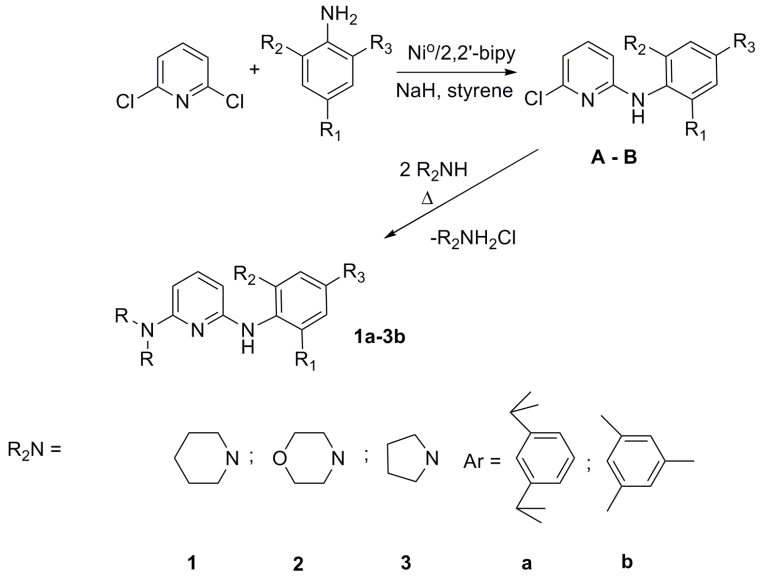
Scheme 3: Applied aminopyridines **1a**-**3b**.

4.2 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 using a Ni^0 / 2, 2'-bipyridine catalyst system - a modified version of the one developed by Fort and coworkers.[10] Subsequent transition metal free thermal amination reaction [11] of **A** and **B** were carried out successfully with piperidine, morpholine and pyrrolidine in toluene

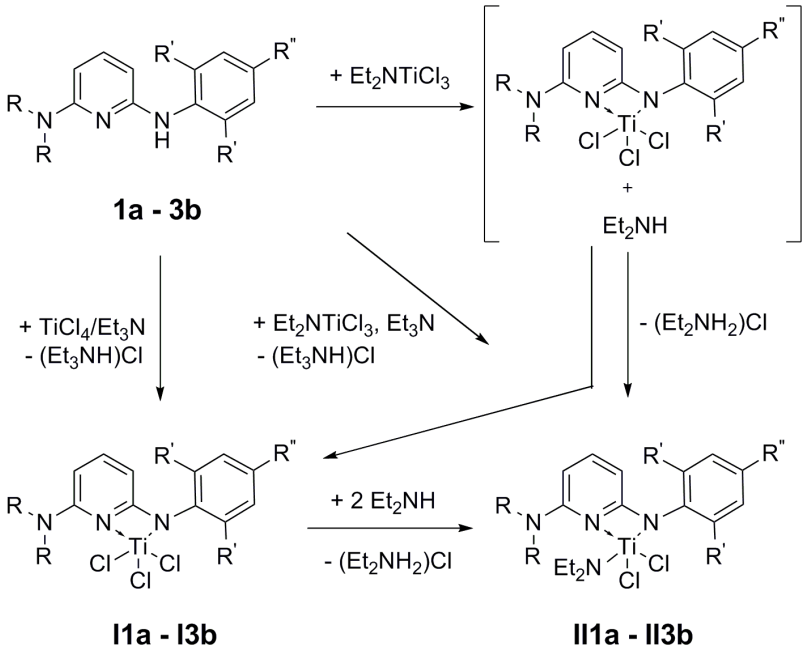
at 160 °C in pressure tubes. After separation of the ammonium chloride salt by filtration and removal of all volatiles, the residues were recrystallized in ethanol providing the corresponding N-(2, 6-diisopropylphenyl)-6-(N heterocycle)pyridin-2-amines [N-heterocycle cycle: piperidine (**1a**); morpholine (**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 lables **1a** -**3b** refer to scheme 3 (**A:** R' = isopropyl and R'' = H; **B:** R', R'' = methyl).

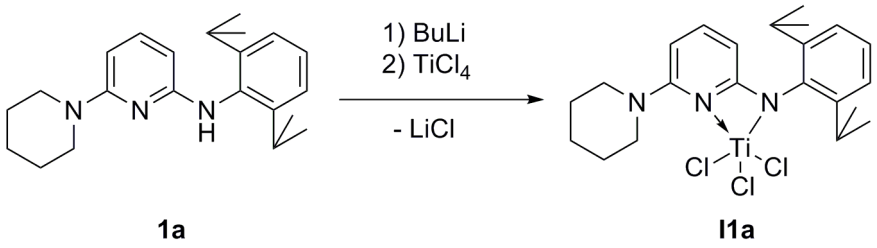
Synthesis and Structure of the Complexes

The N-[6-(dialkylamino)-pyridin-2-yl]-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 two equiv. of the prereleased diethylamine to give the [$Ap(Et_2N)TiCl_2$] complexes and diethylammonium chloride salts. In an NMR experiment, a nearly one to one ratio of both types of titanium complexes is observed. Reaction of [$ApTiCl_3$] with two equivalents of diethylamine gave the exclusive formation of [$Ap(Et_2N)TiCl_2$]. Furthermore, the addition of one equiv. triethylamine to the amine elimination route 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 [$Ap(Et_2NH)TiCl_3$] 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 one 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 **I1a**.

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 to -24 °C. The molecular structures of complexes **I2b**, **II1a**, **II2a** and **II3a** are presented in Figure 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 always in one of the apical positions.

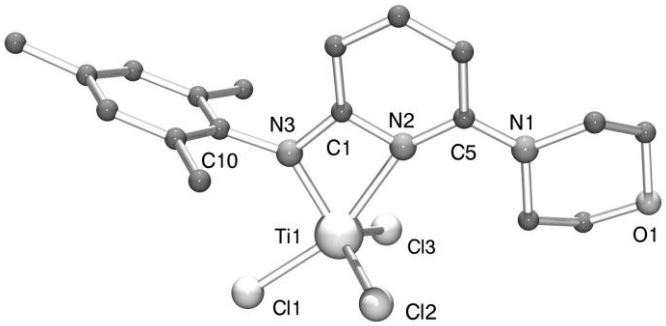


Figure 1: Molecular structure of **I2b**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5-N1 1.358(3), C5-N2 1.360(6), C1-N2 1.393(3), C1-N3 1.392(3), N2-Ti1 2.232(4), N3-Ti1 1.893(2), average. Cl-Ti1 2.239(1), N1-C5-N2 119.4(2), N2-C1-N3 107.8(2), N2-Ti1-N3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

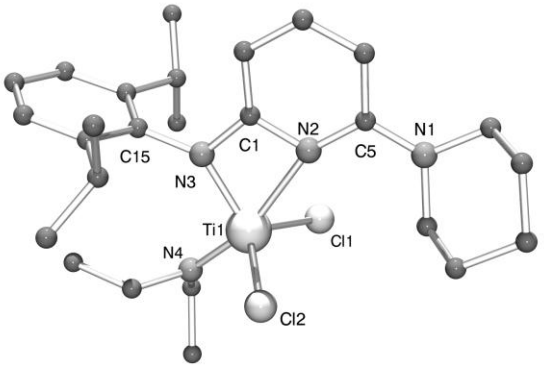


Figure 2: Molecular structure of **II1a**; Hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: C5-N1 1.369(6), C5-N2 1.349(5), C1-N2 1.380(6), C1-N3 1.401(5), N2-Ti1 2.342(4), N3-Ti1 1.931(4), N4-Ti1 1.864(4), average Cl-Ti1 2.284(2), N1-C5-N2 118.7(4), N2-C1-N3 108.2(4),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

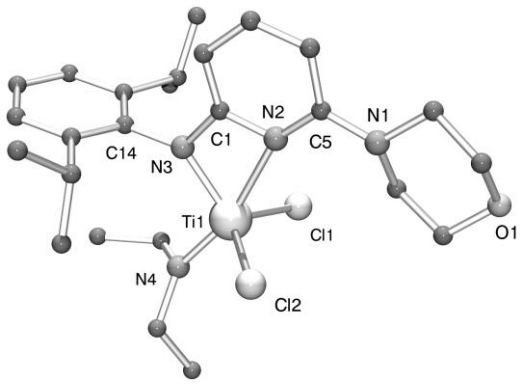


Figure 3: Molecular structure of **II2a**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5-N1 1.356(6), C5-N2 1.3576(6), C1-N2 1.357(6), C1-N3 1.396(6), N2-Ti1 2.365(4), N3-Ti1 1.928(4), N4-Ti1 1.862(4), average Cl-Ti1 2.270(2), N1-C5-N2 117.8(4), N2-C1-N3 109.2(4),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

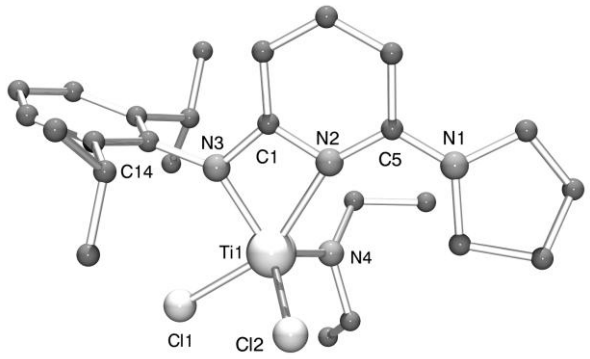


Figure 4: Molecular structure of **II3a**; Hydrogen atoms are omitted for clarity selected bond lengths [Å] and bond angles [°]: C5-N1 1.343(5), C5-N2 1.356(5), C1-N2 1.360(4), C1-N3 1.387(5), N2-Ti1 2.241(3), N3-Ti1 1.961(3), N4-Ti1 1.858(3), av. Cl-Ti1 2.294(2), N1-C5-N2 120.1(3), N2-C1-N3 107.8(3),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

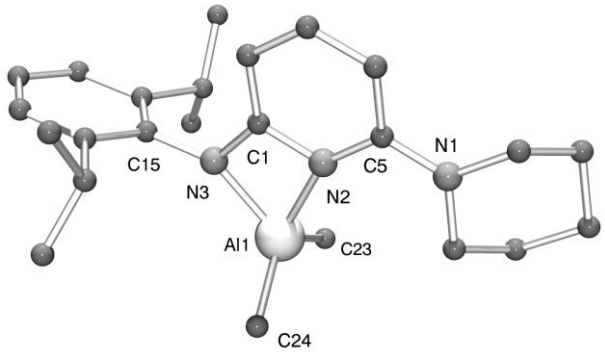


Figure 5: Molecular structure of **III1a**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5-N1 1.363(3), C5-N2 1.356(2), C1-N2 1.378(2), C1-N3 1.354(2), N2-Al1 1.985(2), N3-Al1 1.901(2), average Al1-C 1.956(2), N1-C5-N2 118.45(17), N2-C1-N3 108.09(16), N2-Al1-N3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

The C5–N1 bond lengths of all four complexes are between 1.34–1.37 Å and are clearly shorter than expected for 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 a sp^2 hybridized N atom. The sp^2 hybridization of the N1 atoms together with the short C5–N1 distances clearly indicates that the lone pair of the N1 atoms participates 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} di-

stances 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 **I1a**–**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.

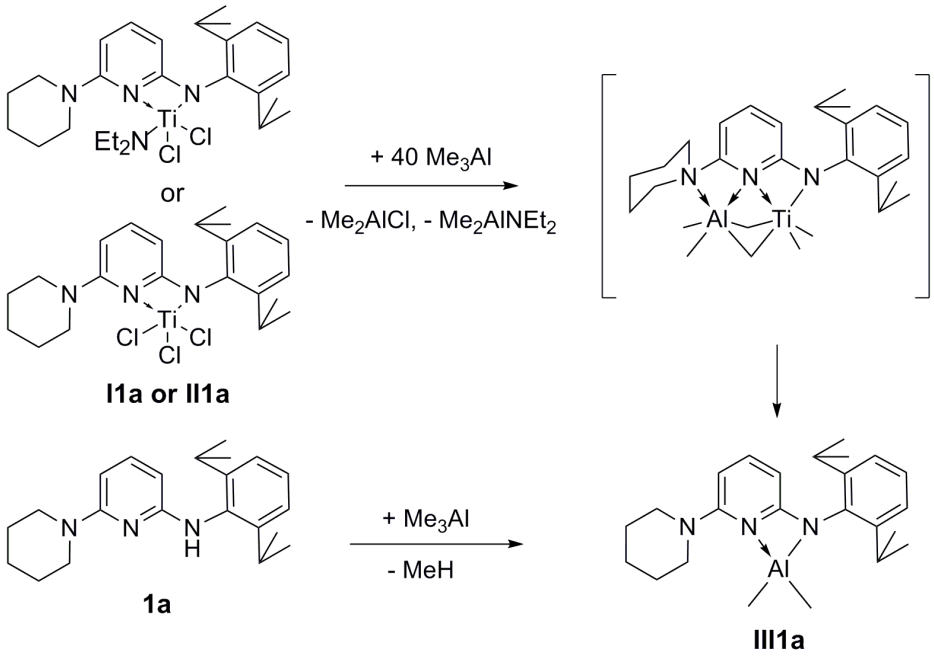
Table 1: Crystallographic data for the compounds which were investigated by single crystal X-ray structure analysis

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-1	P-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 [^{o}]	90	88.275(5)	103.060(5)	90	90
β [^{o}]	90.245(2)	83.266(5)	92.726(5)	104.578(4)	101.556(6)
γ [^{o}]	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]	0.55x0.33x0.25	0.30x0.17x0.16	0.34x0.33x0.24	0.41x0.37x0.21	0.38x0.35x0.28
Habit	Block	Prism	block	plate	Block
Colour	Red	Orange	red	Red	Colourless
Density [gcm^{-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
No of unique reflections	7828	5202	5221	5001	4378
No of observed refl. [I >2σ(I)	6203	2814	3169	2931	3020
No of parameters	475	298	304	295	255
wR2(all data)	0.109	0.123	0.203	0.131	0.107
R value [I >2σ(I)	0.039	0.070	0.074	0.053	0.048

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 comercial 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 behaviour, we studied the stability of these complexes with respect to TMA in NMR tube experiments. The NMR tubes were charged with 40 μmol of



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

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 of (**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 nitrogen function in 6 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 di-

methylaluminum 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 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 while 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 in a 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 appearence of 10 resonances in the NMR spectrum of the solution that can be assigned to the

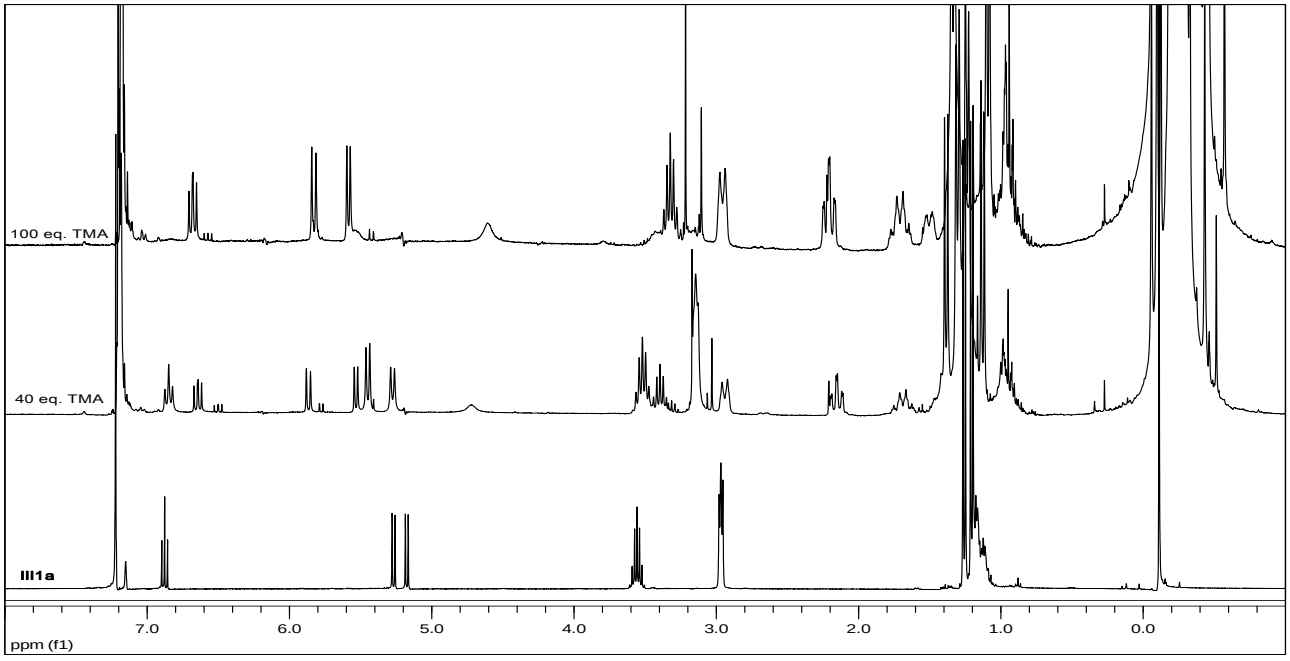
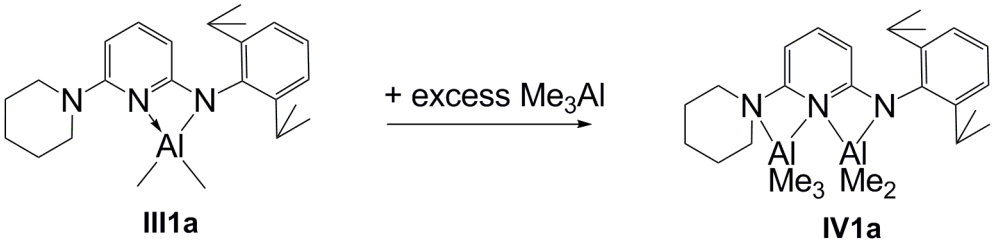


Figure 6: ^{1}H NMR spectra (C_6D_6, 26 °C) of pure **III1a**, **III1a** with 40 equiv. TMA, and **III1a** with 100 equiv. TMA.



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

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.

Due to the sensitivity of the new titanium complexes to TMA, we switched the cocatalyst to dry methylaluminoxane (d-MAO). When all the volatiles from commercially bought MAO are removed, most of the free TMA will also be removed. After activation of the 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 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 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.

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 novel titanium compounds described herein. The polymeriza-

Table 2: Details of the ethylene polymerization.[a]

Entry	Precat.[a]	T [°C]	$m_{Pol.}$ [g]	Activity [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]	M_w [$kgmol^{-1}$]	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.

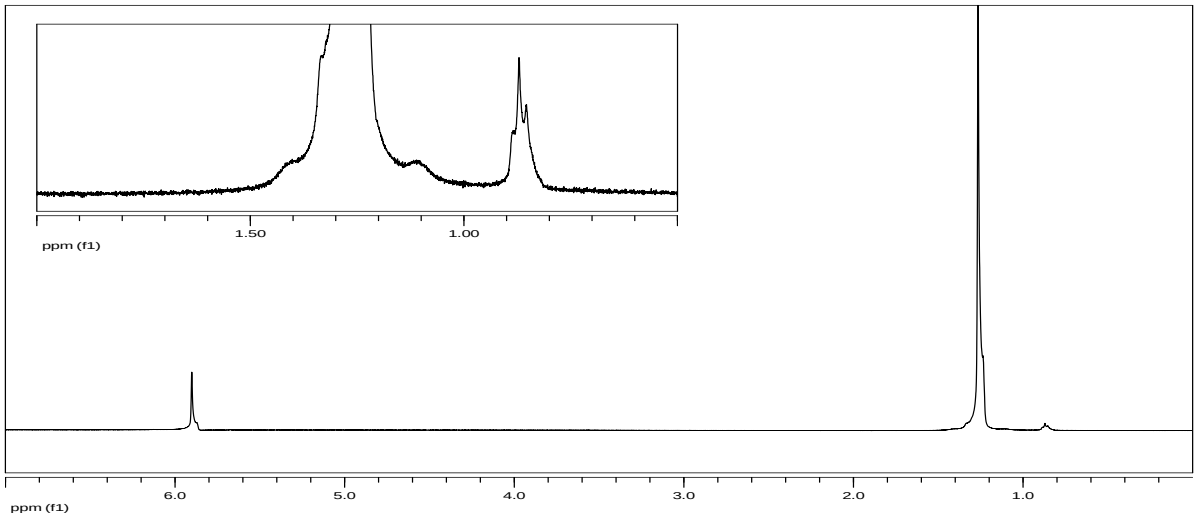


Figure 7: ^1H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of PE obtained with the II1a/d-MAO catalyst system. The spectrum was recorded after acidic workup of the reaction mixture.

tion 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 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 ^oC. The results from these experiments are presented in Table 3.

The activity of all complexes increases as a function of temperature, with maxima observed at 90 ^oC. As already observed in the ethylene polymerization runs, complexes contain-

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 [$gmol^{-1}$]	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.

ing 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 etyhelne 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 ^{1}H and ^{13}C NMR spectroscopy. The NMR spectra were collected at 80 ^{o}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.

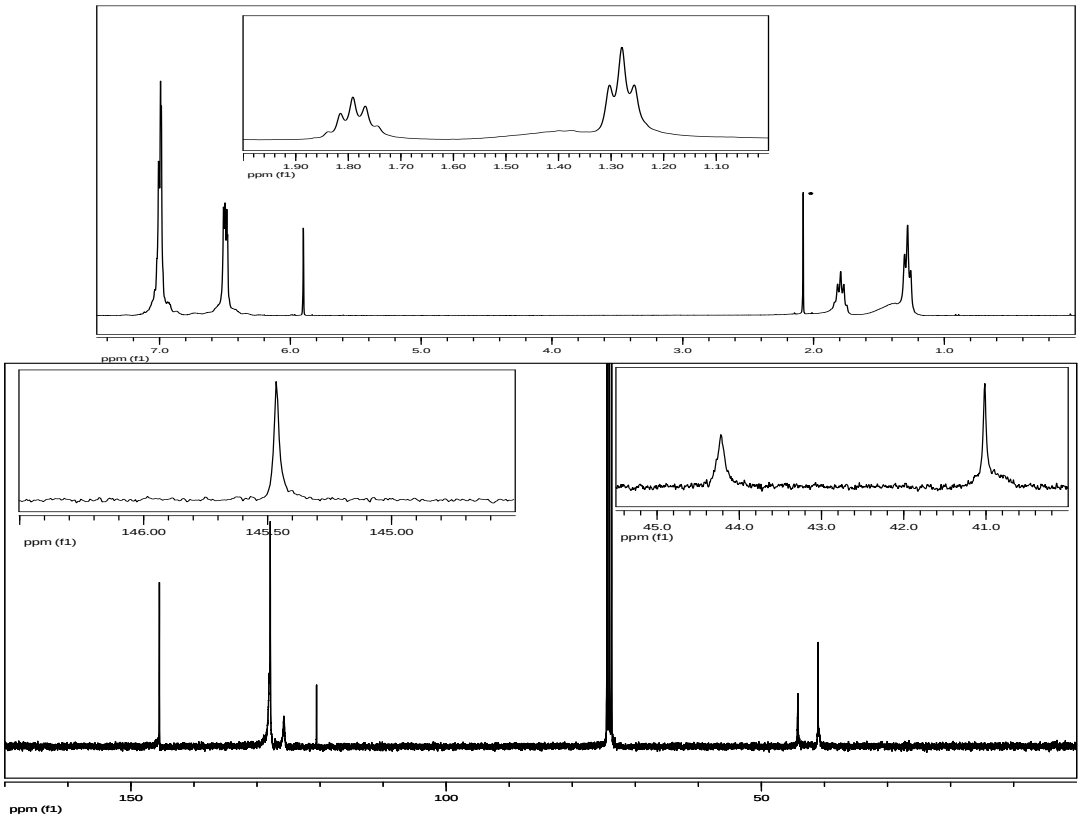


Figure 8: ^{1}H (above) and ^{13}C (below) NMR spectra ($C_2Cl_4D_2$, 80 °C) of PS obtained with the **II1a** / d-MAO catalyst system.

4.3 Conclusions

From the present study, a series of conclusions can be drawn; firstly, the novel 6-(N-heterocyclic)-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 [TiCl4]/Et3N 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 polystyrene was produced. In the case of ethylene polymerization, high activities were observed and aluminum terminated polyethylene for the low molecular weight products.

4.4 Experimental Section

Synthesis and Structure Analysis

All manipulations were performed with 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). Non-halogenated solvents were dried by distillation from sodium wire / benzophenone system. 2, 6-Dichloropyridine, 2, 2'-Bipyridine and 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 Isotope 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 spec-troscopic measurements were prepared by dissolving 15 mg of the polymer in 0.5 mL $C_2D_2Cl_4$ for 3 h at 100 °C before measurements were made. Gel permeation chromatogra--tography (GPC) analysis was carried out on a PL-GPC 220 (Agilent, Polymer Laboratorie--s) high temperature chromatographic unit equipped with a DP and RI detectors and two linear mixed bed columns (Olexis, 13-micron particle size). GPC analysis were performed at 150 °C 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 ext-ernal oven and were run without filtration. The molecular weights of the samples were referenced to PE (Mw = 520 - 3200000 $gmol^{-1}$) and PS (Mw = 580–2800000 $gmol^{-1}$) stan-dards. The reported values are the average of at least two independent determinations. X-ray crystal structure analyses were carried out at a STOE IPDS II diffractometer equipped with an Oxford Cryostream low temperature unit. Structure solution and refinement were accomplished using 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.

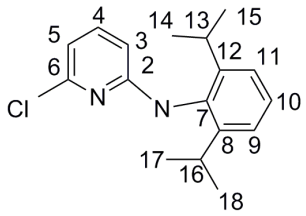
General description of ethylene polymerization experiments Performed with d-MAO

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 cocatalyst 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.

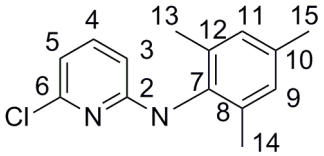
Styrene Polymerizations

Styrene polymerizations were prformed 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 µmoles of the desired catalyst. The temperature of the solution was raised to 30 ^{o}C, 60 ^{o}C or 90 ^{o}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 ^{o}C for 2 h. The insoluble syndiotactic fraction was separated from the mixture and dried first at room temperature and then in an oven at 80 ^{o}C for 12 h.

Synthesis of ligand precursors



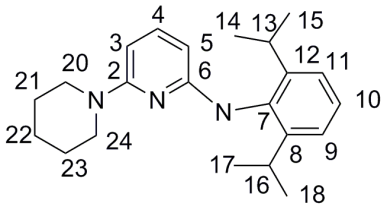
N-(2,6-Diisopropylphenyl)-(6-chloropyridin-2-yl)-amine (A): 2, 6-diisopropylaniline(5.31 g, 5.70 mL, 30. 0 mmol) and tert-amylalcohol (0.352 g, 0.45 mL, 4.0 mmol) in THF (20.0 mL) were added to a THF suspension of NaH (0.624 g, 26.0 mmol). The resulting mixture was heated at 65 ^{o}C for 2 h and then 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 sulphate and the volatiles were removed from the filtrate. The resultant yellow oil was purified by silica gel column chromatography and crystallized from *n*-hexane; yield 2.30 g (40 %). $C_{17}H_{21}ClN_2$ (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, 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-amylalcohol (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 ^{o}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 sulphate 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 ^{o}C; yield 2.0 g (41%). $C_{14}H_{15}ClN$ (246.58): 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-Chloro-pyridin-2-yl)-(2,6-diisopropyl-phenyl)-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 ^{o}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, t-he yellow oil was then crystallized from *n*-pentane at -80 ^{o}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.

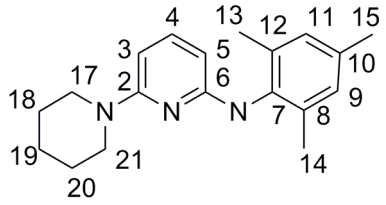
Synthesis of the Dichloride Il1a: Ligand **1a** (0.337 g, 1.0 mmol) was dissolved in *n*-hexane (15.0 mL). The ligand solution was added to a light green *n*-hexane (15 mL) solution of $(Et_2N)TiCl_3$ (0.226 g, 1.0 mmol) at room temperature. The solution's color changed from light green to dark red. 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 dropwise to a toluene (15 mL) solution of titanium tetrachloride (0.189 g, 1.0 mmol) at 0 °C. The resultant dark red solution was stirred over night. The solution was filtered and solution volume was reduced to 10.0 mL. The product was recrystallized from toluene at -24 °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 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

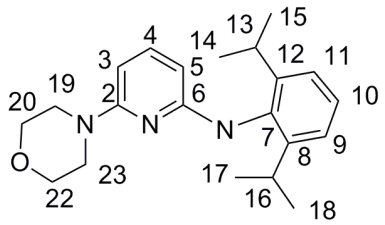
(d, 1 H, H^5), 6.88 (t, 1 H, H^4), 7.15 (t, 1 H, H^{10}), 7.22 (d, 2 H, $H^{9,\ 11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = -8.76 ($C^{CH3\text{-}Al}$), 24.22 ($C^{14,\ 15,17,18}$), 24.56 ($C^{14,15,17,18}$), 24.83 (C^{22}), 25.26 ($C^{21,23}$), 28.40 ($C^{13,16}$), 46.84 ($C^{20,24}$), 92.46 (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 N-(2,4,6-Trimethylphenyl)-(6-chloropyridin-2-yl)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 with *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 Il1b: 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 (10.0 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, $H^{CH3\text{-}CH2\text{-}N\text{-}}$), 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, $H^{CH3\text{-}CH2\text{-}N\text{-}}$), 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 ($C^{CH3\text{-}CH2\text{-}N}$), 18.48 ($C^{13,14}$), 20.90 ($C^{15}$), 25.90 ($C^{19}$), 28.20 ($C^{18,20}$), 47.39

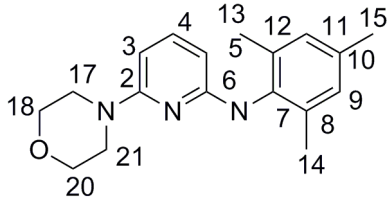
($C^{CH3\text{-}CH2\text{-}N\text{-}}$), 49.11 ($C^{17,21}$), 87.70 ($C^{3}$), 102.04 ($C^{5}$), 122.40 ($C^{9,11}$), 128.10 ($C^{10}$), 134.88 ($C^{8,12}$), 138.74 ($C^{4}$), 141.30 ($C^{7}$), 157.10 ($C^{2}$), 159.48 ($C^{6}$) ppm.



N-(2,6-Diisopropylphenyl)-6-(morpholino) pyridin-2-amine (2a): (6-Chloro-pyridin-2-yl)-(2,6-diisopropyl-phenyl)amine (1.44 g, 5.0 mmol) and morpholine (0.87 g, 10.0 mmol) in toluene (15.0 mL) were heated at 160 ^{o}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 resultant yellow oil was crystallized from *n*-hexane at -24 ^{o}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 ^{o}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, $H^{CH3\text{-}CH2\text{-}N\text{-}}$), 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, $H^{CH3\text{-}CH2\text{-}N\text{-}}$), 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 ($C^{CH3\text{-}CH2\text{-}N\text{-}}$), 25.01 ($C^{14,\ 15,\ 17,\ 18}$), 25.42 ($C^{14,\ 15,\ 17,\ 18}$), 28.41 ($C^{13,\ 16}$), 42.60 ($C^{CH3\text{-}CH2\text{-}N\text{-}}$), 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.



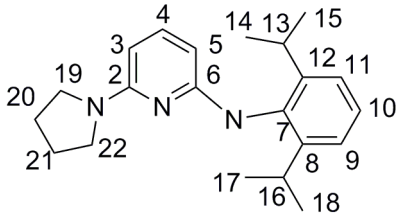
N-(2,4,6-Trimethylphenyl)-6-(morpholino)pyridin-2-amine (2b): Ligand precursor N-(2,4,6-Trimethylphenyl)-(6-chloropyridin-2-yl)-amine (1.47 g, 6.0 mmol) and morpholine (1.04 g, 12.0 mmol) in toluene (10.0 mL) were heated at 170 °C in a pressure tube. The solution was filtered and volatiles were removed 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 crystallized 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*-hexa--ne (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 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 (0.141 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. Diethyl-

amine (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, $H^{CH3\text{-}CH2\text{-}N\text{-}}$), 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, $H^{CH3\text{-}CH2\text{-}N\text{-}}$), 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 ($C^{CH3\text{-}CH2\text{-}N\text{-}}$), 18.42 ($C^{13,\ 14}$), 20.95 ($C^{15}$), 25.53 ($C^{17,\ 21}$), 46.56 ($C^{CH3\text{-}CH2\text{-}N\text{-}}$), 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.

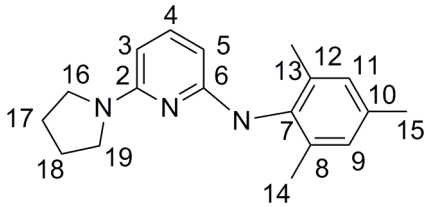
Synthesis of the Trichloride I2b: Titanium tetrachloride (0.189 g, 1.0 mmol) was added to a Schlenk tube containing dichloromethane (10.0 mL). Ligand **2b** (0.297 g, 1.0 mmol) was dissolved in dichloromethane (10.0 mL). The ligand solution was added drop wise to the titanium tetrachloride solution. 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 under vacuum. The yellow oil thus obtained was purified by silica gel column chromatography. The volatiles were removed under vacuum and resultant yellow oil was crystallized 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 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): 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 N-(2,4,6-Trimethylphenyl)-(6-chloropyridin-2-yl)-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 crystallized 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 $^{CH3\text{-}CH2\text{-}N\text{-}}$), 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, $H^{CH3\text{-}CH2\text{-}N\text{-}}$), 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 ($C^{CH3\text{-}CH2\text{-}N\text{-}}$), 18.42 ($C^{13,14}$), 20.95 ($C^{15}$), 28.20 ($C^{17,\ 18}$), 42.50 ($C^{CH3\text{-}CH2\text{-}N\text{-}}$), 46.26 ($C^{16,19}$), 92.76 (C^3), 6.30 (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 **I1a** (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), 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 recorded. (c) NMR tubes were charged with **III1a** (0.016 g, 40 µmol) and deuteriobromobenzene (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).

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5. Hafnium Trialkyls Stabilized by Bulky, Electron Rich Amino-pyridinates

Muhammad Hafeez, Winfried. P. Kretschmer, and Rhett Kempe*[a]

[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany. Fax: +49 921 55-2157, E-mail: kempe@uni-bayreuth.de

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Abstract: A series of hafnium aminopyridinates were synthesized and spectroscopically analyzed. In addition, selected examples of these hafnium complexes were characterized by X-ray single crystal structure analysis. The aminopyridinato ligands used here carry an additional dialkylamine substituent to enhance the electron donating ability of the ligands. Structural data and low temperature NMR spectroscopic investigations are indicative of the increased donating ability of the ligands. Ethylene polymerization studies revealed a rather low catalytic activity most likely due to catalyst instability. Details of the deactivation reaction were investigated by NMR spectroscopy.

5.1 Introduction

Group 4 metal alkyls stabilized by aminopyridinato (= Ap) ligands (Figure 1) have been frequently used as alternatives to metallocenes or cyclopentadienyl ligand stabilized alkyl complexes of these metals, also in terms of developing catalysts for olefin polymerization. [1–4]. Ap ligands are non-symmetric versions of bidentate mono-anionic N-ligands suited to stabilize early (and late) transition metals and can be considered as related to amidinates [5] or diketiminate [6] ligands.

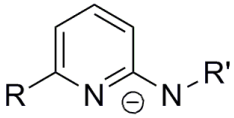


Figure 1: Aminopyridinato ligands (R, R' = alkyl, aryl or silyl substituents).

Most of the (coordination) chemistry involving Ap ligands has been dedicated to titanium [7] and zirconium.[7a,f,i,r,8]. Hafnium complexes are nearly unexplored. Pioneering work in this regard was done by *Polamo et al*. employing his direct synthesis route – the reaction of the metal chloride in the melted ligand.[9] The Ap ligands used by him have a rather low steric bulk and highly nitrogen coordinated complexes were observed. The application of bulky aminopyridinates can address ligand redistribution problems.[10] We recently reported hafnium complexes stabilized by bulky aminopyridinates [8l] and report here the synthesis and structure of hafnium tribenzyl complexes stabilized by bulky Ap ligands possessing a strong electron donation ability due to the presence of an additional dialkylamine functionality (Figure 2).

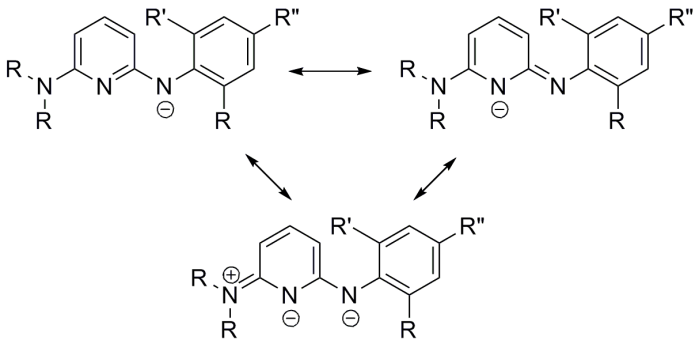


Figure 2: Schematic representation of the increased electron donor ability of Ap ligands by introducing a dialkylamine moiety (R, R', R" = alkyl substituents).

5.2 Results and Discussion

Synthesis of the complexes

The ligands used here are listed in Figure 3. They were synthesized following a published procedure.[7t]

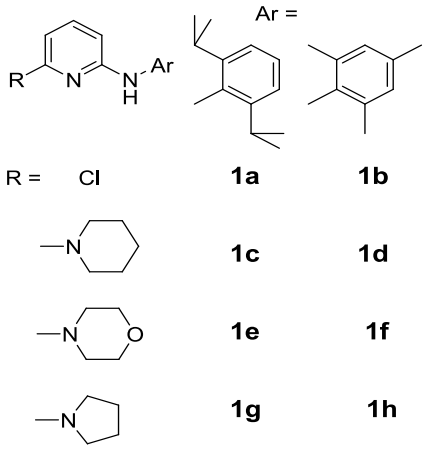
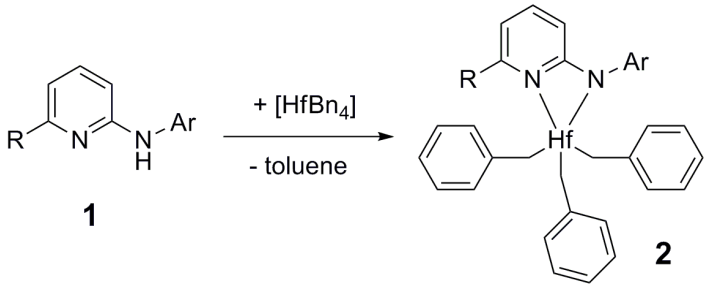


Figure 3: Applied aminopyridines.

These ligands react smoothly (1:1 ratio) with tetrabenzylhafnium ($HfBn_4$) to give mono-Ap complexes ($ApHfBn_3$) (Scheme 1). NMR scale reactions are indicative of a quantitative conversion and isolated yields of around 80 % could be obtained. Zr / Hf trialkyls stabilized by anionic N-ligands are documented for a few cases and known for amidinates, [11] Guanidinates, [12] diketiminate,[13] macrocyclic amides,[14] tropocoronands[15] and tris(pyrazolyl)borates.[16]



Scheme 1: Synthesis of **2**, for the assignment of **1a-1h** and **2a-2h**, please refer to Figure 3 (Bn = benzyl).

NMR investigation of the compounds **2** revealed (as expected) one set of proton resonances for the Ap ligand and another set for all three benzyl ligands indicating a dynamic coordination. In the ^1H NMR spectra of **2c–h**, the proton resonances for the 3 and 5 position of the pyridine ring appear between 4.9 and 5.6 ppm. These signals are quite up field for pyridine or aromatic protons and more typical for olefinic protons. The dialkylamine substituent increases the electron donating ability but weakens the ring current of the pyridine ring. In the case of the earlier reported $ApTiCl_3$ complexes, [7t] we could confirm the increased bond order for the $C_{pyridine}$–$N_{dialkylamine}$ bond by observing a high rotation barrier in low temperature NMR experiments. A similar experiment for hafnium compound **2c** (Figure 4) between –70 to –10 °C showed a very strong temperature depending shift of the piperidyl proton resonances at δ = 2.8 and 1.1 ppm but did not result in a chemical inequivalence of the same protons. However, for the benzyl ligand resonances at 2.4 ppm, a split into two sets of multiplet signals below –50 °C with a ratio of 1:2 was observed. This is most likely due to a reversible η^3 coordination of one of the benzyl ligands to reduce the electron deficit of the metal atom.

Structural studies

Crystals of **2a** suitable for X-ray analysis were grown from a concentrated *n*-hexane solution at room temperature. For the molecular structure of **2a** please see Figure 5 below.

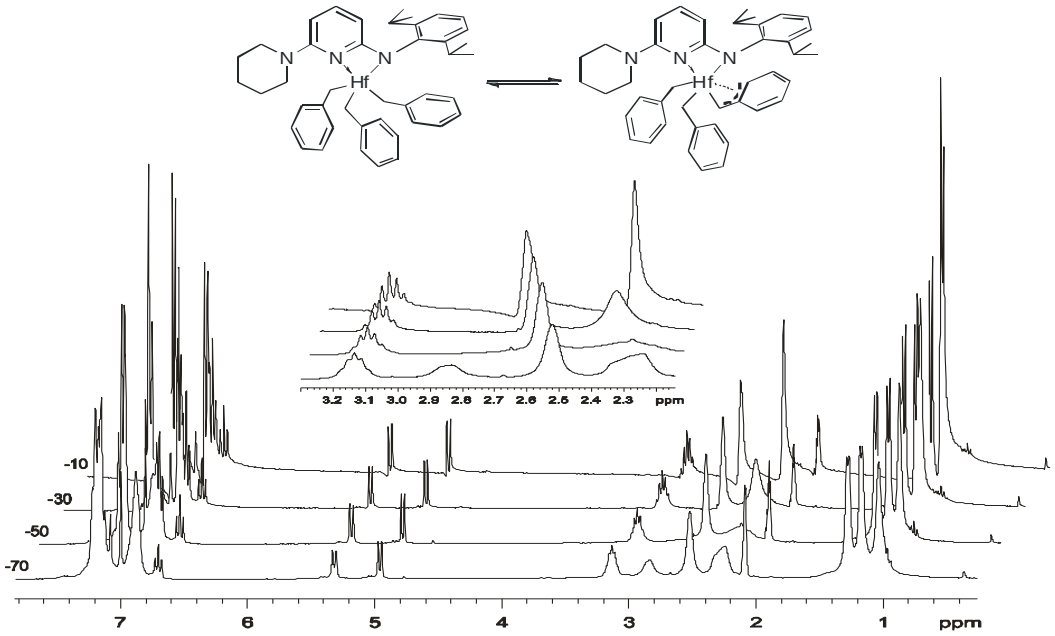


Figure 4: Variable ^{1}H low temperature NMR spectra of **2c** ([D_8 toluene]), -70 to -10 °C, 0 - 8 ppm).

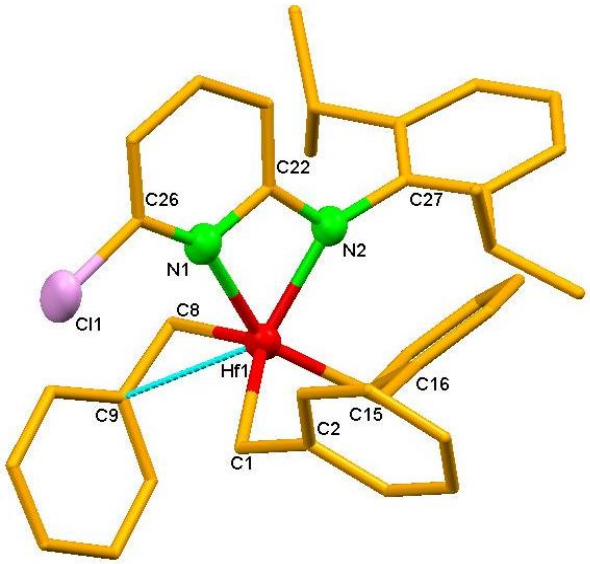


Figure 5: Molecular structure of complex 2a: Selected bond lengths /Å and bond angles /°: Hf1–C1 2.259(7), Hf1–C8 2.213(8), Hf1–C9 2.645(9), Hf1–C15 2.230(8), Hf1–N1 2.389(7), Hf1–N2 2.146(6), C1–C2 1.477(11), C8–C9 1.466(11), C15–C16 1.494(10), C26–Cl1 1.736(8), N1–C22 1.370(9), N1–C26 1.329(10), N2–C22 1.348(9), N2–C27 1.447(9), C2–C1–Hf1 109.5(1), C9–C8–Hf1 89.5(5), C16–C15–Hf1 122.2 (5), N2–Hf1–N1 58.3(2).

Crystallographic data are given in Table 1. Two of the three benzyl ligands are η^1-coordinated [C2–C1–Hf1 109.6 (4)°, C16–C15–Hf1 122.3(5)°] whereas the third one is η^2-coordinated [C9–C8–Hf1 90.5 (5)°]. The Hf–CH2 bond lengths of the η^2 coordinated benz-

yl ligand is slightly shorter than that of the two other Hf–CH2 distances. The Hf–N_{py} bond length [2.385(6) Å] is significantly longer than the Hf–N_{amido} bond length [2.14(6) Å], indicating that the anionic function of the ligand is localized on the amido nitrogen atom (N2).

Table 1: Selected experimental details of the X-ray crystal structure analyses.

Compound	**2a**	**2e**
Formula	$C_{38}H_{41}ClHfN_2$	$C_{42}H_{49}HfN_3O$
Formula weight	739.67	790.33
Crystal system	triclinic	Monoclinic
Space group	$P1^-$	P2(1)/n
a /Å	10.836 (1)	9.878 (1)
b / Å	11.069 (1)	34.175 (2)
c / Å	14.320 (1)	11.904 (1)
α / ^{o}	74.569 (6)	
β / ^{o}	87.029 (7)	112.831 (3)
γ / ^{o}	78.008 (7)	
Cell volume	1619.5 (2)	3704(3)
Z	2	4
Crystal size [mm]	0.41× 0.37×0.31	0.34 × 0.23 × 0.11
Habit	prism	Plate
Colour	yellow	Yellow
Density	1.52	1.42
T (K)	133	133
Theta range	1.48-25.72	1.2- 25.64
Unique reflections	6090	6982
Observed reflections	4973	3339
No of parameters	379	424
wR2(all data)	0.117	0.038
R value	0.049	0.079

Compound **2e** was crystallized from *n*-hexane solution at –24 °C. The molecular structure of **2e** is given in Figure 6 and crystallographic details are listed in Table 1. In contrast to **2a**, all the three benzyl ligands are η^1-coordinated. Hf–CH_2–C_{ipso} angles between 117.2(6) and 109.7(6)° were observed. The averaged Hf–CH_2 bond is 2.222 Å, which is slightly sh-

orter than the average value of such a bond (2.2696 Å). [17] The N1–C26 bond length is 1.379 (9) Å, which is in between a Csp^2–N double (approx. 1.29 Å) and a Csp^2–N single bond (approx.1.48 Å) indicating a bond order higher than one.[18] The calculated sum of all angles around N1 is 351° indicating an almost planar nitrogen atom, which is more typical for a sp^2 hybridized nitrogen atom. The sp^2 hybridization of N1 together with the short N1–C26 distances is indicative that the lone pair of N1 participats in the ligands π-system increasing the electron donating ability of the amine functionalized Ap ligand.

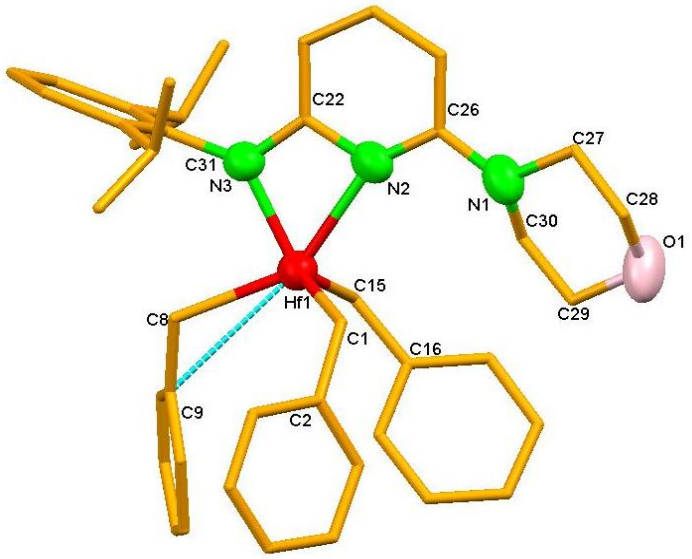


Figure 6: Molecular structure of complex **2e**: Selected bond lengths /Å and bond angles /°: Hf1–C1 2.218(7), Hf1–C8 2.238(7), Hf1–C15 2.210(8), Hf1–N2 2.364(6), Hf1–N3 2.092(5), N2–C22 1.378(8), N2–C26 1.362(8), N1–C26 1.379(9), N3–C22 1.345(8), C2–C1–Hf1 122.0(5), C9–C8–Hf1 113.8(5), C16–C15–Hf1 117.2(6), N3–C22–N2 109.7(6), N2–C26–N1 116.4(7), N3–Hf1–N2 59.43(19).

Reactions of the Hafnium Complexes with Trialkyl Aluminum Compounds

Ethylene polymerization studies with selected examples of the tribenzyl complexes revealed no activity for the activation with MAO and very low activities of around 5–10 $kg_{PE}/mol_{cat}\cdot h\cdot bar_{ethylene}$ in the presence of d MAO (trimethylaluminum component was removed). Borate activation in the presence of a aluminum scavenger did not improve the activity significantly. We ascribe this observation to transfer of Ap ligand from hafnium to aluminum. The Ap ligand might become transferred from hafnium to aluminum and the Ap ligand free hafnium compound is inactive.[8i] To support this hypothesis, we studied the stability of **2c** against trimethylaluminum (TMA, Figure 7). A very fast coordination of TMA

(Scheme 2, spectrum after 5 min) with a subsequent ligand transfer reaction was observed (spectrum after 16 h). To confirm the ligand transfer we independently synthesized the corresponding Ap containing dimethylaluminum complex **3c** by the reaction of the aminopyridine **1c** with one equivalent of TMA in toluene according to a published procedure (Figure 7, above).[7i]

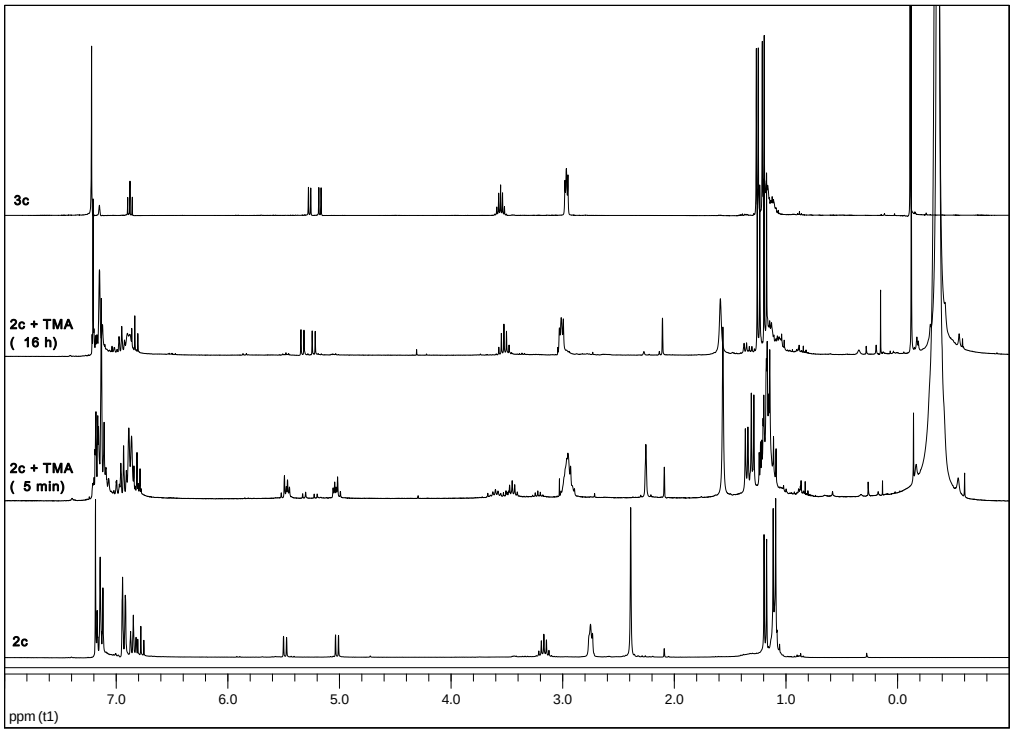
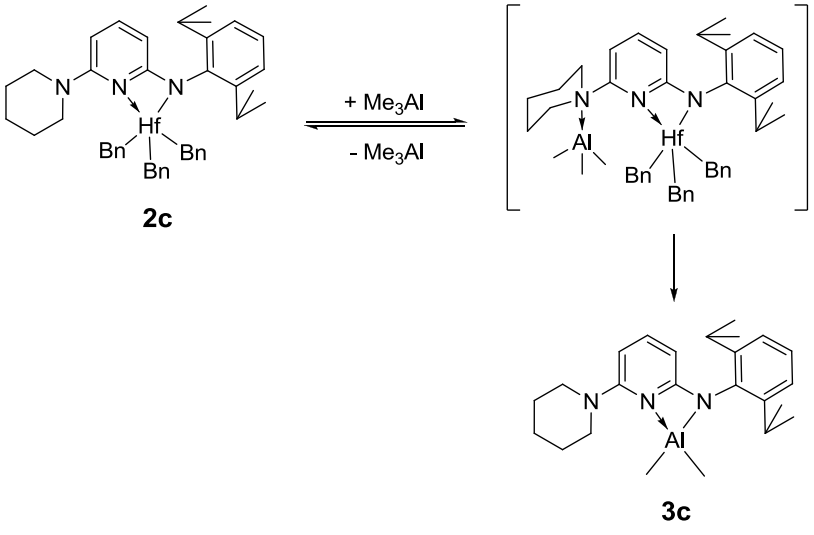


Figure 7: ^{1}H NMR spectra (C_6D_6, 26 °C, 0 - 8 ppm) of $ApAlMe_2$ (**3c**) top, $ApHfBn_3$ (**2c**) bottom, **2c** + 30 eq. TMA after 5 min and after 16 h (middle).



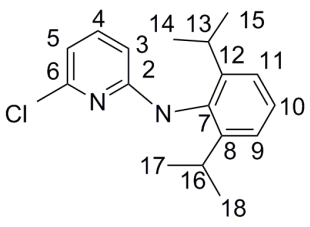
Scheme 2: Ligand transfer reaction.

5.3 Conclusions

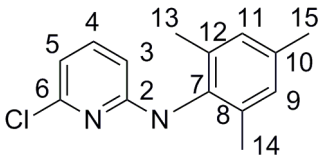
Several conclusions can be drawn from this study. First, mono-Ap hafnium complexes are selectively formed by reacting tetrabenzylhafnium with the corresponding bulky amino-pyridines. Second, the additional dialkylamine substituent increases the electron donor ability of the Ap ligand. Third, a low ethylene polymerization activity was observed due to fast aluminum coordination at the Ap ligand and a subsequent but slower transfer of the Ap ligand towards aluminum during the polymerization reaction.

5.4 Experimental Section

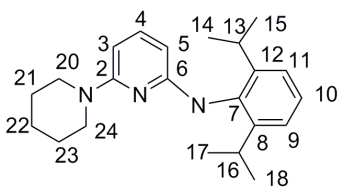
All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk type glassware on a dual manifold Schlenk line or in an nitrogen filled glove box (mBraun 120-G) with a high capacity recirculator (< 0.1 ppm O_2). Deuterated solvents were obtained from Eurisotop. Benzene-d_6 was dried with sodium/potassium alloy and bromobenzene-d_5 over molecular sieves, degassed and distilled prior to use. Commercial $HfCl_4$ (Across Organics) was used as received. Tetrabenzylhafnium was prepared according to the literature procedures. [19] NMR spectra were recorded on a Varian Inova (400 MHz) or Varian Inova (300 MHz) spectrometer. The chemical shifts are reported in ppm referenced to internal TMS for ^{1}H and ^{13}C. Elemental analyses (CHN) were determined using Vario ELIII instrument. X-ray crystal structure analyses were performed by using STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[20] SHELXL97,[21] and WinGX.[22] Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-849066 (compound **2a**) and CCDC-849067 (compound **2e**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk; web: www.ccdc.cam.ac.uk/conts/retrieving.html.



Synthesis of 2a: Aminopyridine **1a** (0.288 g, 1.0 mmol in 15.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The color changed from yellow to red. The resultant solution was stirred for 12 h at room temperature. The toluene was removed under vacuum and the yellow product was extracted with *n*- hexane. The volume of the *n*-hexane extract was reduced and the product was crystallized at –24 °C. Yield 0.50 g (67 %). $C_{38}H_{41}ClHfN_2$ (739.27): calcd. C 61.68, H 5.59, N 3.79; found C 61.45, H 5.50, N 3.38 %.^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.96 (d, 6 H, $H^{14, 15, 17, 18}$), 1.16 (d, 6 H, $H^{14,15,17,18}$), 2.40 (s, 6 H, $H^{CH2benzyl}$), 3.05 (sept, 2 H, $H^{13,16}$), 5.20 (d, 1 H, H^3), 5.91 (d, 1 H, H^5), 6.35 (t, 1 H, H^4), 6.86 (d, 6 H, $H^{CHbenzyl}$), 6.87-7.20 (m, 12 H, $H^{9,10,11,CHbenzyl}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.98 ($C^{14,15,17,18}$), 24.13 ($C^{14,15,17,18}$), 25.20 ($C^{13,16}$), 80.02 ($C^{CH2\ benzyl}$), 96.25 (C^3), 97.90 (C^5), 122.90 (C^{benzyl}), 128.20 ($C^{9,11}$), 129.20 (C^{benzyl}), 129.62 (C^{10}), 133.50 ($C^{8,12}$), 137.80 (C^4), 142.87 (C^{benzyl}), 143.09 (C^7), 144.14 (C^{benzyl}), 144.67 (C^2), 159.38 (C^6) ppm.

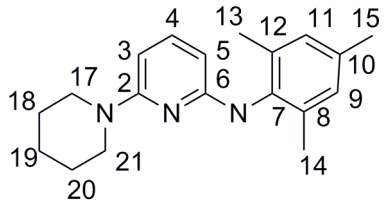


Synthesis of 2b: Aminopyridine **1b** (0.246 g, 1.0 mmol in 20.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 25.0 mL toluene). The color changed from yellow to red. The resultant solution was stirred for 12 h at room temperature. The toluene was removed under vacuum and the yellow product was extracted and crystallized with *n*-hexane at –24 °C. Yield 0.485 g (69 %). $C_{35}H_{35}ClHfN_2$ (697.22): calcd. C 60.24, H 5.06, N 4.02; found C 59.78, H 5.50, N 4.22 %. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.18 (s, 6 H, $H^{13, 14}$), 2.24 (s, 3 H, H^{15}), 2.38 (s. 6 H, $H^{CH2\ benzyl}$), 5.18 (d, 1 H, H^3), 6.42 (d, 1 H, H^5), 6.65 (t, 1 H, H^4), 6.84 (d, 6 H, $H^{CH2benzyl}$), 6.90-7.20 (m, 11 H, $H^{9, 11,CH\ benzyl}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 18.60 ($C^{13, 14}$), 20.68 (C^{15}), 95.51 (C^3), 97.12 (C^5), 122.80 ($C^{9, 11}$), 127.60 (C^{benzyl}), 128.76 (C^{10}), 129.20 (C^{benzyl}), 129.40 (C^{benzyl}), 134.69 ($C^{8, 12}$), 143.78 (C^4), 143.94 (C^{benzyl}), 156.30 (C^7), 158.78 (C^2), 164.70 (C^6) ppm.

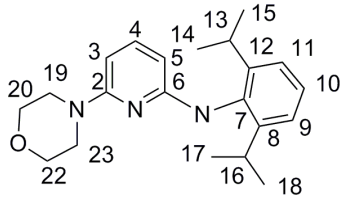


Synthesis of 2c: Aminopyridine **1c** (0.337 g, 1.0 mmol in 15.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 25.0 mL toluene). The color changed from yellow

to red. The resultant solution was stirred for twelve hours at room temperature. The toluene was removed and the yellow product was extracted and crystallized with *n*-hexane at –24 °C. Yield 0.630 g (80 %). $C_{43}H_{51}HfN_3$ (787.90): calcd. C 65.49, H 6.52, N 5.33; found C 64.99, H 6.15, N 5.59 %. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.11 (m, 12 H, $H^{14,15,17,18,21,22,23}$), 1.21 (d, 6 H, $H^{14,15,17,18}$), 2.41 (s, 6 H, $H^{CH2\ benzyl}$), 2.77 (t, 4 H, $H^{20,24}$), 3.19 (sept, 2 H, $H^{13,16}$), 5.03 (d, 1 H, H^3), 5.49 (d, 1 H, H^5), 6.77 (t, 1 H, H^4), 6.94 (d, 6 H, $H^{CHbenzyl}$), 6.98-7.22 (m, 12 H, $H^{9,10,11,\ CHbenzyl}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.98 ($C^{14,15,17,18}$), 24.13 ($C^{14,\ 15,17,18}$), 25.18 ($C^{13,16}$), 25.66 (C^{22}), 28.78 ($C^{21,23}$), 45.20 ($C^{20,24}$), 79.23 ($C^{CH2\ benzyl}$), 96.25 (C^3), 97.90 (C^5), 122.90 (C^{benzyl}), 128.20 ($C^{9,11}$), 129.20 (C^{benzyl}), 129.62 (C^{10}), 133.50 ($C^{8,12}$), 137.80 (C^4), 142.87 (C^{benzyl}), 143.09 (C^7), 144.14 (C^{benzyl}), 144.67 (C^6), 159.38 (C^2) ppm.

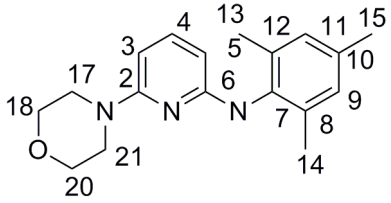


Synthesis of 2d: Aminopyridine **1d** (0.295 g, 1.0 mmol in 20.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 25.0 mL toluene). The color changed from yellow to red. The solution was stirred for 12 h at room temperature. The toluene was removed under vacuum and the yellow product was extracted and crystallized with *n*-hexane at –24 °C. Yield 0.60 g (80 %). $C_{40}H_{45}HfN_3$ (745.85): calcd. C 64.36, H 6.08, N 5.63; found C 64.75, H 5.65, N 5.43 %. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ= 1.40 (m, 6 H, $H^{18,19,20}$), 2.14 (s, 9 H, $H^{13,14,15}$), 2.43 (s. 6 H, $H^{CH2\ benzyl}$), 3.44 (t, 4 H, $H^{17,21}$), 5.47 (d, 1 H, H^3), 5.93 (d, 1 H, H^5), 6.79 (s, 2 H, $H^{9,11}$), 6.84 (t, 1 H, H^4), 6.95-7.20 (m, 10 H, $H^{10,\ CHbenzyl}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 18.39 ($C^{13,14}$), 20.85 (C^{15}), 25.62 (C^{19}), 28.60 ($C^{18,20}$), 49.50 ($C^{17,21}$), 89.40 (C^{benzyl}), 129.40 (C^{benzyl}),134.20 ($C^{8,12}$),141.86 (C^{10}),143.78 (C^4),143.96 (C^{benzyl}), 156.30 ($C^{CH2benzyl}$), 95.40 (C^3), 96.58 (C^5), 122.79 ($C^{9,11}$), 127.60 (C^{benzyl}), 128.90 (C^{10}), 129.22 (C^7), 158.78 (C^2) 164.70 (C^6) ppm.

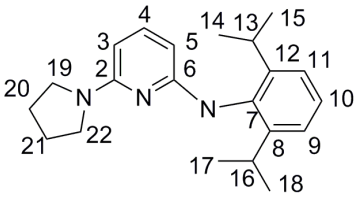


Synthesis of 2e: Aminopyridine **1e** (0.339 g, 1.0 mmol in 15.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The color changed from yellow

to red. The resultant solution was stirred for 12 h at room temperature. The toluene was removed under vacuum and the yellow product was extracted and crystallized with *n*-hexane at –24 °C. Yield 0.68 g (86 %). $C_{42}H_{49}HfN_3O$ (790.35): calcd. C 63.81, H 6.25, N 5.32; found, C 64.35, H 5.80, N 5.36 % .^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.11 (d, 6 H, $H^{14,\ 15,17,18}$), 1.21 (d, 6 H, $H^{14,15,17,18}$), 2.41 (s, 6 H, $H^{CH2benzyl}$), 2.64 (t, 4 H, $H^{19,23}$), 2.71 (t, 4 H, $H^{20,22}$), 3.19 (sept, 2 H, $H^{13,16}$), 5.10 (d, 1 H, H^3), 5.49 (d, 1 H, H^5), 6.77 (t, 1 H, H^4), 6.88 (d, 6 H, H^{benzyl}), 6.94-7.20 (m, 12 H, $H^{9,10,11,CH\ benzyl}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 23.98 ($C^{14,15,17,18}$), 24.13 ($C^{14,15,17,18}$), 25.18 ($C^{13,16}$), 48.25 ($C^{19,23}$), 66.20 ($C^{20,22}$), 79.23 ($C^{CH2benzyl}$), 96.25 (C^3), 97.90 (C^5), 122.90 (C^{benzyl}), 128.20 ($C^{9,11}$), 129.20 (C^{benzyl}), 129.62 (C^{10}), 133.50 ($C^{8,12}$), 137.80 (C^4), 142.87 (C^{benzyl}), 143.09 (C^7), 144.14 (C^{benzyl}), 144.67 (C^6), 159.38 (C^2) ppm.

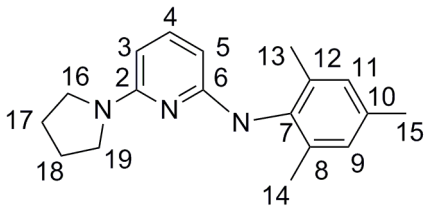


Synthesis of 2f: Aminopyridine **1f** (0.296 g, 1.0 mmol in 20.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The resultant solution was stirred for 12 h at room temperature. The toluene was removed and the yellow product was extracted and crystallized with *n*-hexane at –24 °C. Yield 0.63 g (84 %). $C_{39}H_{43}HfN_3O$ (747.83): calcd. C 62.58, H 5.79, N 5.62; found C 63.15, H 5.24, N 5.33 %.^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 2.04 (s, 6 H, $H^{CH2\ benzyl}$), 2.19 (s, 6 H, $H^{13,14}$), 2.26 (s, 3 H, H^{15}), 2.64 (t, 4 H, $H^{17,21}$), 3.28 (t, 4 H, $H^{18,20}$), 5.16 (d, 1 H, H^3), 5.40 (d, 1 H, H^5),6.80 (t, 6 H, H^{benzyl}), 6.84 (t, 1 H, H^4), 6.95-7.20 (m, 11 H, $H^{9,11,CH\ benzyl}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 18.39 ($C^{13,14}$), 20.85 (C^{15}), 48.02 ($C^{17,21}$), 65.86 ($C^{18,20}$), 89.52 ($C^{CH2\ benzyl}$), 95.51 (C^3), 96.66 (C^5), 122.79 ($C^{9,11}$), 127.60 (C^{benzyl}), 128.90 (C^{10}), 129.22 (C^{benzyl}), 129.40 (C^{benzyl}), 134.20 ($C^{8,12}$), 141.86 (C^{10}), 143.78 (C^4), 143.96 (C^{benzyl}), 156.30 (C^7), 158.78 (C^2), 164.70 (C^6) ppm.



Synthesis of 2g: Aminopyridine **1g** (0.323 g, 1.0 mmol in 20.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The resultant solution was stir-

ed for 12 h at room temperature. The toluene was removed and the yellow product was extracted and crystallized with *n*-hexane at –24 °C. Yield 0.60 g (77 %). $C_{42}H_{49}HfN_3$ (773.88): calcd. C 65.13, H 6.38, N 5.43; found C 64.78, H 6.12, N 5.90 %. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.17 (m, 10 H, $H^{14,15,17,18,20,21}$), 1.30 (d, 6 H, $H^{14,15,17,18}$), 2.45 (t, 4 H, $H^{19,22}$), 2.67 (s, 6 H, $H^{CH2\ benzyl}$), 3.41 (sept, 2 H, $H^{13,16}$), 4.96 (d, 1 H, H^3), 5.27 (d, 1 H, H^5), 6.75 (t, 1 H, H^4), 6.86 (d, 6 H, H^{benzyl}), 6.94-7.20 (m, 12 H, $H^{9,10,11,\ CH\ benzyl}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 24.13 ($C^{14,15,17,18}$), 24.42 ($C^{14,15,17,18}$), 25.57 ($C^{13,16}$), 28.95 ($C^{20,21}$), 47.81 ($C^{19,22}$), 89.65 ($C^{CH2\ benzyl}$), 91.39 (C^3), 96.19 (C^5), 122.08 (C^{benzyl}), 124.02 ($C^{9,11}$), 126.47 (C^{benzyl}), 128.38 (C^{10}), 133.50 ($C^{8,12}$), 142.20 (C^4), 142.87 (C^{benzyl}), 143.09 (C^7), 144.14 (C^{benzyl}), 154.49 (C^6), 165.32 (C^2) ppm.



Synthesis of 2h: Aminopyridine **1h** (0.281 g, 1.0 mmol in 15.0 mL toluene) was added to tetrabenzylhafnium (0.543 g, 1.0 mmol in 20.0 mL toluene). The resultant solution was stirred for 12 h at room temperature. The toluene was removed and the yellow product was extracted and crystallized with *n*-hexane at –24 °C. Yield 0.560 g (76 %). $C_{39}H_{43}HfN_3$ (732.27): calcd. C 63.97, H 5.92, N 5.74; found C 63.85, H 5.72, N 5.62 %. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.20 (t, 4 H, $H^{17,18}$), 2.25 (s, 6 H, $H^{13,14}$), 2.26 (s, 3 H, H^{15}), 2.41 (s, 6 H, $H^{CH2benzyl}$), 2.70 (t, 4 H, $H^{17,18}$), 5.06 (d, 1 H, H^3), 5.28 (d, 1 H, H^5), 6.80 (d, 6 H, H^{benzyl}), 6.84 (t, 1 H, H^4), 6.95-7.20 (m, 11 H, $H^{9,11,\ CHbenzyl}$) ppm. ^{13}C NMR (400 MHz, C_6D_6, 298K): δ = 18.54 ($C^{13,14}$), 20.82 (C^{15}), 24.79 ($C^{17,18}$), 47.87 ($C^{16,19}$), 89.39 ($C^{CH2\ benzyl}$), 90.41 (C^3), 96.25 (C^5), 122.20 ($C^{9,11}$), 127.03 (C^{benzyl}), 128.90 (C^{10}), 129.46 (C^{benzyl}), 133.91 ($C^{8,12}$), 134.60 (C^7), 142.60 (C^{10}), 142.71 (C^{benzyl}), 143.78 (C^4), 154.84 (C^2), 163.38 (C^6) ppm.

NMR Tube Reactions with TMA

A NMR tube was charged with **2c** (20 mg, 0.025 mmol), deuterobenzene (0.5 mL) together with TMA (54 mg, 0.750 mmol). Afterwards, the tube was sealed, shaken for 5 min.and measured.

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Synthesis, Structural Investigations and Ethylene Polymerization of Titanium Complexes with Tripodal Oxazoline Ligands

Sonja Lippert, Muhammad Hafeez, Tobias Bauer, Winfried P. Kretschmer and Rhett Kempe*[a]

[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany. Fax:+4992155-2157, E-mail: kempe@uni-bayreuth.de

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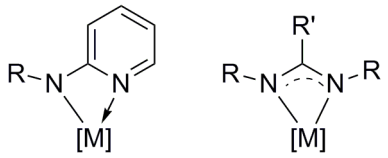
Abstract: A series of tripodal nitrogen containing ligands including amidine and aminopyridines with extra oxazoline functionality were prepared. The corresponding titanium complexes bearing such ligands were synthesized by diethylamine elimination route. Diethylamidotitanium trichloride [Et_2NTiCl_3] reacts with the functionalized anilines, 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2-fluorophenyl)-aniline (FOxH) and 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2-methoxyphenyl)aniline (MeOOxH), the amidine (*E*)-*N'*-(2,6-diisopropylphenyl)-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl) benzimidamide (AmOxH), and the aminopyridines *N*-(2-(4,4-dimethyl-4,5-dihydro oxazol-2-yl)phenyl)-6-(piperidin-1-yl)pyridin-2-amine (ApOxH) and *N*-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-6-(2,4,6-triisopropyl phenyl)pyridin-2-amine (Ap*OxH), under diethylamine elimination to form the corresponding titanium trichlorides [$FOxTiCl_3$], [$MeOOxTiCl_3$], [$AmOxTiCl_3$], [$ApOxTiCl_3$] and [$Ap^*OxTiCl_3$] in excellent yields. These compounds were characterized by spectroscopic methods, and X-ray crystal structure analysis (selected complexes). Furthermore, their behavior in ethylene polymerization was explored. The complexes show moderate activity towards ethylene if activated with MAO. The observed PE's were analyzed by HT-GPC and were found to be of low molecular weight for the amidinate $AmOxTiCl_3$ but of very high one (Mp up to 3.5 million g/mol) for the aminopyridinate ($Ap^*OxTiCl_3$) titanium complex.

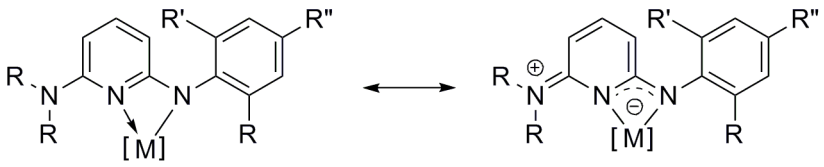
6.1 Introduction

Amidinates (= Am) and Aminopyridinates (= Ap) of the group 4 metals are promising alternatives to the widely used metallocenes of these metals, for instance, in polymerization catalysis.[1,2,3] Both ligands are related to each other and show (mostly) a η^2-coordination mode if coordinating to early transition metals (Scheme 1).[4] We have recently used bulky aminopyridinates to stabilize titanium based polymerization catalysts.[5]



Scheme 1. Binding mode of aminopyridinato (left) and amidinato (right) ligands ([M] = group 4 metal complex moiety; R = R'= alkyl or aryl substituents).

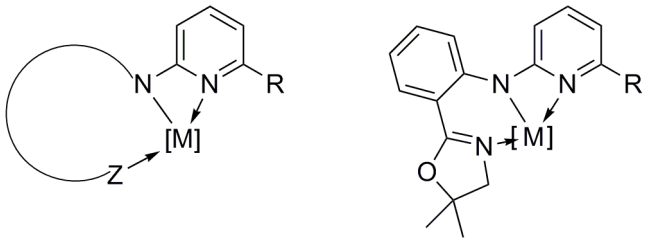
These complexes were found to be highly active in ethylene homo- and α-olefin copolymerization together with a good response towards cyclic olefins when activated with "dry"-methylaluminoxane (d-MAO), but were almost inactive when free trimethyl aluminum (TMA) containing MAO was used. We suspected that ligand transfer to aluminum as observed earlier for aminopyridinates might be responsible for the inactivity.[6] To address the ligand transfer issue, the electron donating ability of the Ap ligands (Scheme 2) was significantly increased to alter the rate of ligand transfer. However, this approach lead to less stable catalysts with regard to a ligand transfer to Al.[7]



Scheme 2. Mesomeric structures of 2,6-diaminopyridinato metal complexes (R, R', R" = alkyl substituents).

We therefore thought that the introduction of an additional linker (Scheme 3, left) in a ring closure position may solve the ligand transfer problem and may lead to more stable polymerization catalyst. A strong binding can be expected from the oxazoline moiety (Scheme 3,

right),[8] which was used before in group 4 metal chemistry. [9]



Scheme 3. Ap ligands with a beneficial electron donating Atom in chelating position (R = aryl substituents).

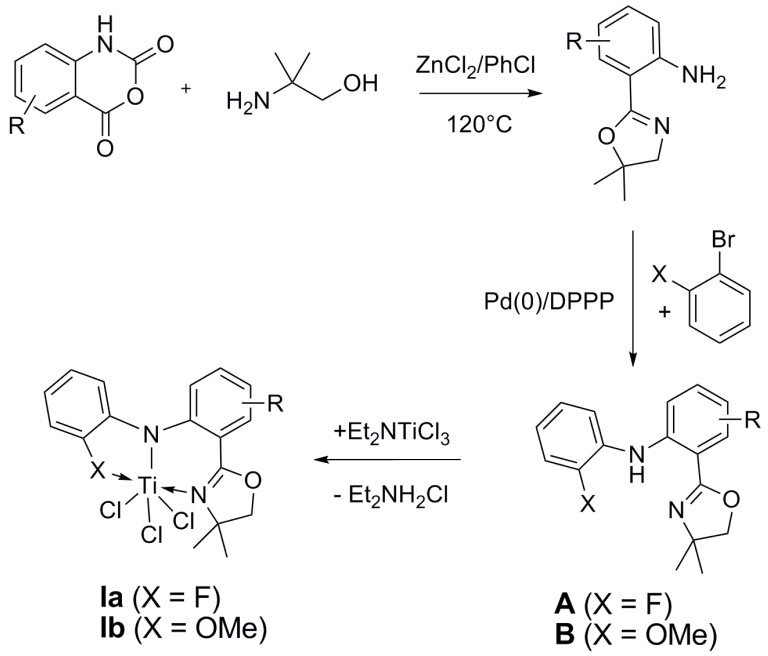
Amidine [10] and aminopyridine [11] bearing an oxazoline moiety have been used earlier to stabilize palladium and zinc complexes. Herein, we report the synthesis of novel aminopyridines, related anilines, and amidines functionalized by an oxazoline side arm. Furthermore, the synthesis of titanium complexes stabilized by such ligands is reported as well as ethylene polymerization studies with the selected of these complexes.

6.2 Results and Discussion

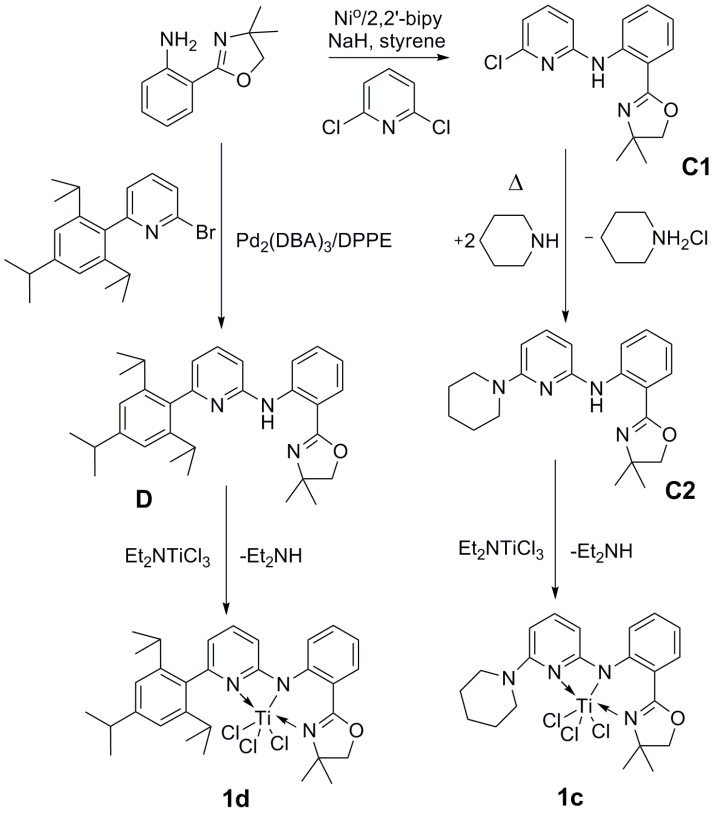
Synthesis and structural investigation

2-Oxazoline substituted anilines can be easily synthesized in high yields by a zinc chloride catalyzed reaction of isatoic anhydride with 2-aminoalcohols.[12] Subsequent reaction with 1-bromo-2-fluoro- or 1-bromo-2-methoxybenzene in the presence of tris(dibenzilidineacetone)-dipalladium(0)/1,3 bis(diphenylphosphino)propane (= DPPP) gives the fluorine and methoxy functionalized tripodal anilines 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2-fluorophenyl)-aniline (FOxH, **A**) and 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2-methoxyphenyl) aniline (MeOOxH, **B**) in about 50 – 61 % isolated yield, respectively.[13] Further reactions of the ligands **A** and **B** in toluene with 1 equivalent diethylamido titanium trichloride give under diethylamine elimination the corresponding titanium complexes **1a** and **1b** as dark red crystals in good yields (Scheme 4).

For the oxazoline substituted aminopyridines, two different synthetic routes have been chosen. The recently developed $Ni^{(0)}$/2,2'-bipyridine catalyzed amination [9] of 2,6-dichloropyridine with 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline followed by a thermal aminatio-



Scheme 4. Synthesis of oxazoline substituted anilines, the bifunctional tripodal ligands **A** (X = F) and **B** (X = OMe) and their corresponding titanium complexes.

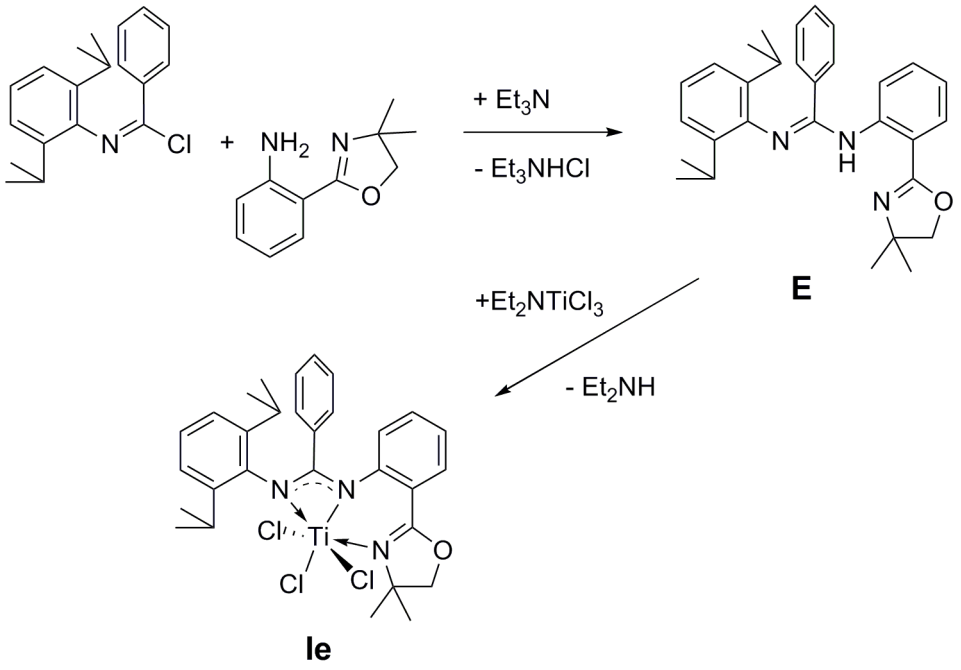


Scheme 5. Synthesis of oxazoline functionalized aminopyridines **C** and **D**.

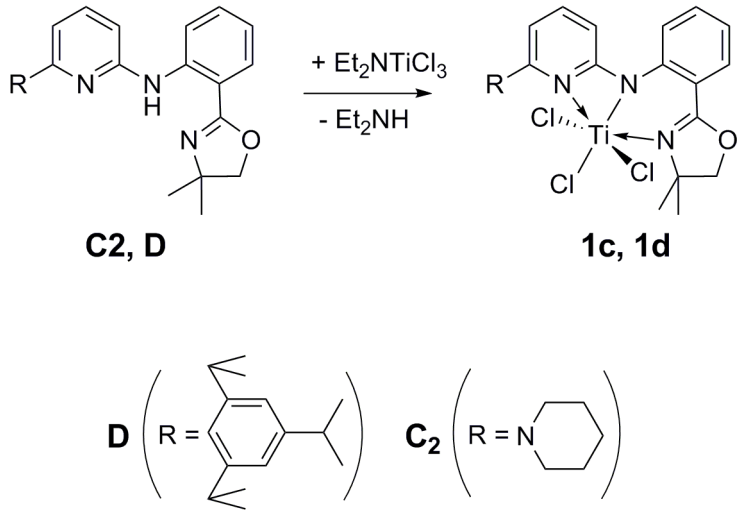
n of the intermediate 6-chloro-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl) phenyl) pyridin-2-amine (**C1**) with piperidine gave *N*-(2-(4,4-dimethyl-4,5-dihydro oxazol-2-yl)phenyl)-6-(piperidin-1-yl)pyridin-2-amine (**C2**, ApOxH) in an overall yield of 30 % (scheme 5, right). For the more bulky aminopyridine *N*-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-6-(2,4,6-triisopropyl phenyl)pyridin-2-amine (**D**, Ap*OxH), a well established palladium(0) catalyzed arylation of anilines, starting from 2-bromo-6-(2,4,6-triisopropylphenyl)pyridine in 60 % yield was used (scheme 5, right).[14]

In contrast to the aminopyridines, the oxazoline functionalized amidine (*E*)-*N'*-(2,6-diisopropylphenyl)-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl) benzimidamide (**E**, AmOxH) is easily available by a catalyst free reaction of (*E*)-*N*-(2,6-diisopropyl-phenyl)benzimidoyl chloride with 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline in the presence of triethylamine (scheme 6). The corresponding titanium complexes bearing such amipyridinato or amidinato ligands were easily synthesized by the above described reaction of free ligand with 1 equivalent of dietylamido titanium trichloride in toluene under diethylamine elimination (scheme 6 and 7). For the titanium complexes ApOxTiCl$_3$ (**1c**) and Ap*OxTiCl$_3$ (**1d**) blue green crystals were observed while the relative AmOxTiCl$_3$ (**1f**) gave red cubes. All titanium complexes were characterized by ^{1}H and ^{13}C-NMR spectroscopy and elemental analysis. For the selected compounds **1d** and **1e**, single crystal structure analysis was carried out. Suitable crystals were obtained by slow cooling of saturated toluene solutions to room temperature. The molecular structures of **1d** and **1e** are presented in Figure 1 and 2, respectively. X-ray crystal structure analysis details are given in Table 1. The overall symmetry of both complexes can best be described as distorted octahedron with the three nitrogen and one chlorine atom in the equatorial square plane.

In both complexes, all the three N-Ti distances are fairly identical between 2.02 and 2.13 Å with a slight elongation for N1-Ti in **1d** and N3-Ti in **1e**. This is in contrast to the often observed amido pyridine form with a short Ti-N$_{amido}$ distance and a long Ti-N$_{pyridine}$ one. [4] For both the complexes, the Cl1-Ti–Cl3 angle is almost linear, with stronger deformation of 171.8^o in **1e**. The relatively short Csp^2-Nsp^2 single bond (**1d**, N2-C23 = 1.37 Å; **1e**, N2-C8 = 1.39 Å) together with the long Csp^2-Csp^2 aromatic bond (**1d**, C22-C23 = 1.41 Å; **1e**, C8-C13 = 1.41 Å) indicates a delocalization of the negative charge over the whole π-system including the aryl and the lone pair of N3 in the oxazoline moiety. Therefore a high complex stability might be expected.



Scheme 6. Synthesis of oxazoline functionalized amidine **E** and amidinato titanium trichloride **1e**.



Scheme 7. Synthesis of aminopyridinato titanium complexes **1c** and **1d**.

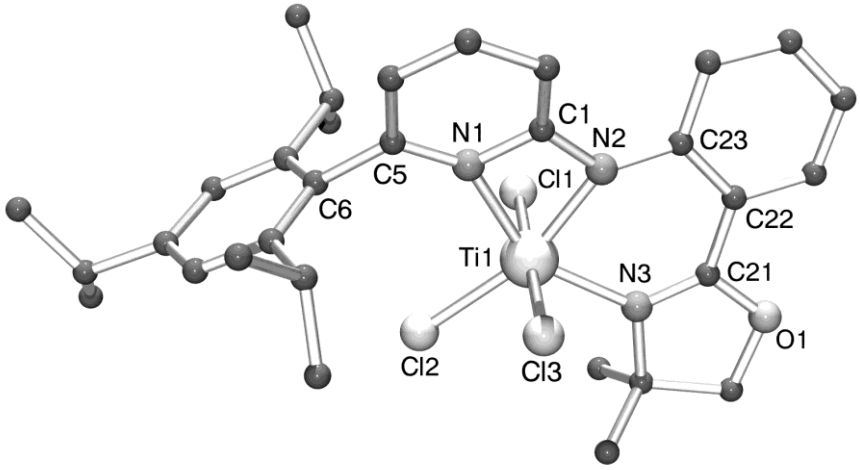


Figure 1: Molecular structure of **Id**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C5-N1 1.366(6), C1-N1 1.355(6), C1-N2 1.386(6), C23-N2 1.377(6), C22-C23 1.412(7), C21-C22 1.441(7), C21-N3 1.296(6), C21-O1 1.354(6), N1-Ti1 2.135(4), N2-Ti1 2.016(4), N3-Ti1 2.079(4), av. Cl-Ti1 2.31, Cl1-Ti1-Cl3 178.85(7), C6-C5-N1 119.3(5), C1-N2-C23 127.4(4), N1-Ti1-N2 63.31(17), N2-Ti1-N3 84.37(16).

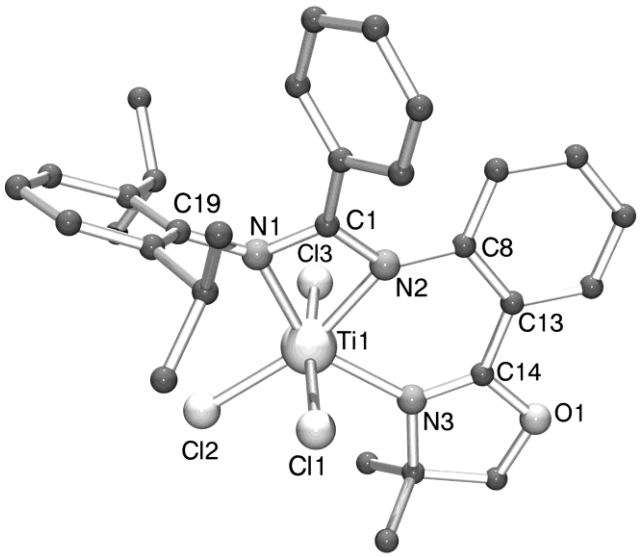


Figure 2: Molecular structure of **Ie**, hydrogen atoms are omitted for clarity, selected bond lengths [Å] and bond angles [°]: C19-N1 1.447(4), C1-N1 1.327(4), C1-N2 1.355(4), C8-N2 1.388(4), C8-C13 1.410(4), C13-C14 1.444(4), C14-N3 1.305(4), C14-O1 1.354(4), N1-Ti1 2.077(3), N2-Ti1 2.052(2), N3-Ti1 2.110(3), av. Cl-Ti1 2.30, Cl1-Ti1-Cl3 171.77(4), N1-C1-N2 108.0(3), C1-N2-C8 128.9(2), N1-Ti1-N2 63.40(9), N2-Ti1-N3 82.89(1).

Table 1: Crystallographic data for the compounds **Id** and **Ie** which were investigated by single crystal X-ray structure analysis.

Compound	**Id**	**Ie**
Formula	$C_{37}H_{44}Cl_3N_3OTi$	$C_{30}H_{34}Cl_3N_3OTi$
Formula weight	701.00	606.85
Crystal system	monoclinic	orthorhombic
Space group	P2(1)/n	$P2_12_12_1$
a [Å]	15.6400(11)	10.3520(4)
b [Å]	10.12.60(7)	16.5750(7)
c [Å]	22.9120(14)	17.1530(7)
α [°]	90.0	90.0
β [°]	101.280(5)	90.0
γ [°]	90.0	90.0
Cell volume [$Å^3$]	3558.5(4)	2943.2(2)
Z	4	4
Crystal size [mm^3]	0.17x0.15x0.14	0.30x0.24x0.14
Colour	blue	red
Density [gcm^{-3})	1.308	1.370
T (K)	133(2)	133(2)
Theta range	1.45-23.64	1.71-24.60
Unique reflections	5320	4943
Observed refl. [$I>2\sigma I$]	2684	3885
No. of parameters	414	349
wR2(all data)	0.120	0.072
R value [$I>2\sigma I$]	0.054	0.035

Olefin Polymerization

To gain more insight into the stabilization of the electron deficient titanium metal center by the additional donor functionality, the complexes were tested in ethylene polymerization in the presence of commercial and “dry”- methylaluminoxane (MAO) co-catalysts (Table 2).

Complexes **1a** and **1b** showed almost no ethylene consumption while for precatalysts **1c** – **1e**, a low to moderate activity was observed.

Table 2. Ethylene polymerization.*

Entry	Precat.*	T [°C]	$m_{Pol.}$ [g]	Activity [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-}$]	M_n [$kgmol^{-1}$]	M_w/M_n
1	**Ic**	70	0.22	22		
2	**Id**	30	0.28	28	7840 (593000)[b]	28.0
3	**Id**	50	0.13	13	11100 (593000)[b]	73.8
4	**Id**	70	0.03	3	9400 (3530000)[b]	95.7
5[a]	**Id**	50	0.08	8	n.d.	n.d.
6	**Ie**	50	-	-	n.d	n.d
7[a]	**Ie**	50	0.33	33	5700	3.0
8[a]	**Ie**	80	-	-	-	-

*Precatalyst: 2.0 µmol; MAO: 1.0 mmol; toluene: 150 mL; p = 2 bar; t = 15 min.

[a]d-MAO. [b]Mp of higher molecular weight polymer fraction.

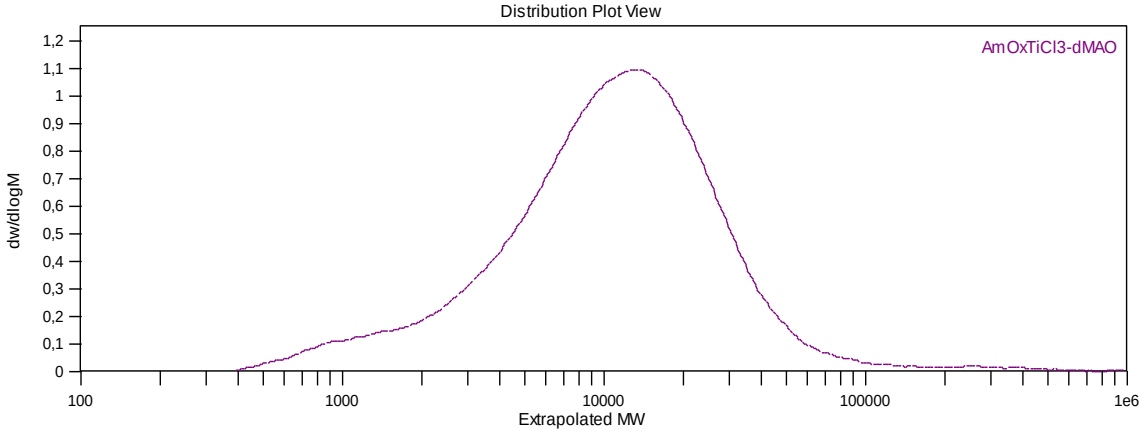


Figure 3: Molecular weight distribution observed with $AmOxTiCl_3$ precatalyst (run 7).

It is notable that the ethylene consumption was slow but continuous over the whole run time. This indicates a slow but stable polymerization catalyst. The enhancement of the catalyst stability towards free trimethylaluminum (TMA) comes together with probably blocking a coordination site by the additional donating atom. Such low to moderate activity was observed earlier for titanium complexes with planar tridentate ligands.[15] It is also notable that for the amidinato titanium compound **1e,** monomodal but low molecular weight PE was observed (Figure 3), while the aminopyridinato titanium congeners yielded PE with

a bimodal distribution including a very high molecular weight fraction indicated by the peak molecular weight of up to 3.5 million dalton (M_p Table 2, Figure 4).

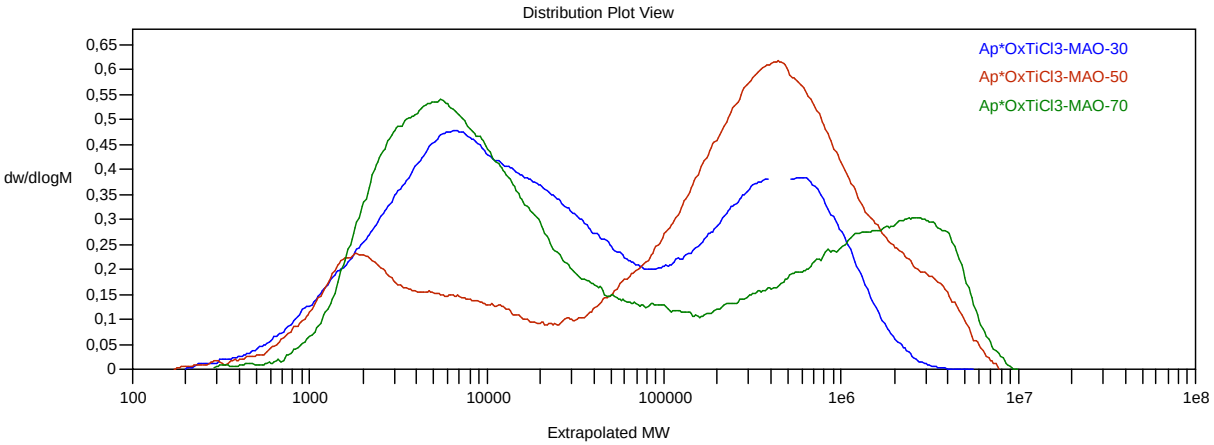


Figure 4: Molecular weight distribution of PE observed with $ApOxTiCl_3$ / MAO catalyst system (run 1 – 3).

6.3 Conclusions

From the present studies, a series of conclusions can be drawn. **Firstly**, titanium complexes with novel tripodal oxazoline functionalized aminopyridines and amidines can be synthesized by applying diethylamine elimination route. **Secondly**, the higher stability towards ligand transfer can be confirmed by observing an ethylene polymerization activity in the presence of free trimethylaluminum. **Thirdly**, the aminopyridinate Ap*OxTiCl3 produced very high molecular weight polyethylene.

6.4 Experimental Section

Synthesis and Structure Analysis

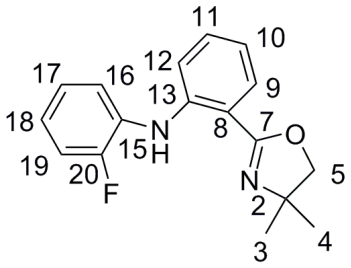
All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk type glassware on a dual manifold Schlenk line or in an argon filled glove box (Braun 120-G) with a high-capacity recirculator (<0.1 ppm O_2). Non halogenated solvents were dried by distillation from sodium wire/benzophenone. 2,6-Dichloropyridine, 2,2'-Bipyridine and Piperidine were purchased from AlfaAesar. Nickel acetate and t-amyl alcohol were purchased from Acros.-6-(2, 4, 6-triisopropylphenyl)pyridinine [6a] and titanium precursor (Et_2NTiCl_3) [16] were prepared as described in the literature. Deuterated solvents

were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled prior to use. NMR spectra were recorded with a Varian ARX 400 MHz or Varian ARX 300 MHz and chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses (CHN) were carried out using a Vario EL III instrument. D-MAO was prepared by removal of all 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 $C_2D_2Cl_4$ at 100 °C for 3 h before measuring. Gel permeation chromatography (GPC) analysis was carried out on a PL-GPC 220 (Agilent, Polymer Laboratories) high temperature chromatographic unit equipped with a DP and RI detectors and two linear mixed bed columns (Olexis, 13-micron particle size) at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.05 wt.-%, conc. = 1 mg/mL) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (Mw = 520 - 3200000 $gmol^{-1}$) and polystyrene (Mw = 580–2800000 $gmol^{-1}$) standards. The reported values are the average of at least two independent determinations. X-ray crystal structure analysis was carried out at a STOE IPDS II diffractometer equipped with an Oxford Cryostream low temperature unit. Structure solution and refinement were accomplished using SIR97 [17] SHELXL-97 [18] and WinGX.[19] Selected details of the X-ray crystal structure analyses are listed in Table 1. CCDC-XXX (compound **I**) and CCDC-XXX (compound **II**) 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 with MAO

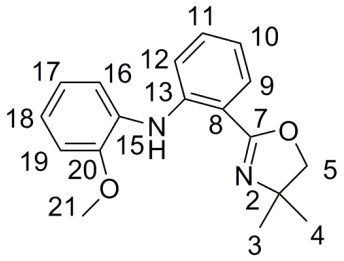
The catalytic ethylene polymerization reactions were performed in a 250 mL glass autoclave (Buechi) in semi-batch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature and pressure controlled and equipped with separated toluene, catalyst and cocatalyst 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 MAO, as not mentioned differently in the text. After pressurizing with ethylene to reach 2 bar total pressure, the autoclave was equilibrated for 5 min. Subsequently, 1 mL of a 0.002 M catalyst stock solution in toluene was injected to start the reaction. During the run, the ethylene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing flow. After 15 min. reaction time, the reactor was vented and the residual aluminum alkyls were destroyed by addition of 50 mL of ethanol. 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 subsequently in vacuum at 80 °C.



Synthesis of 2- (4,4 – dimethyl -4,5-dihydrooxazol-2-yl)-N-(2-fluorophenyl)aniline (A): [2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline] (4.0 g, 21.0 mmol), Tris[dibenzilideneacetondipalladium(0)] (0.381 g, 0.417 mmol), 1, 3-Bis(diphenylphosphino)propane (0.344 g, 0.837 mmol), sodium tertiary butoxide (2.49 g, 25.93 mmol) were taken in a Schlenk tube in a glove box. This mixture was dissolved in 60 mL toluene. 2-Fluoro-1-bromobenzene (3.63 g, 2.3 mL, 21.0 mmol) was added to this solution. The resulting solution was refluxed for five days. On cooling distilled water (50.0 mL) and diethyl ether (50.0 mL) were added and the organic layer was separated by solvent extraction. The inorganic layer was washed three times with diethylether (3 × 20.0 mL). The combined organic layers were washed with a saturated sodium chloride solution and were dried over sodium sulphate. The volatiles were removed under vacuum and the product was crystallized at -24 ^{o}C. Yield 3.0 g (50 %). $C_{17}H_{17}FN_2O$: calcd. C 71.80, H 6.03, N 9.86; found C 71.82, H 6.20, N 10.03. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.35 (s, 6 H, $H^{3,4}$), 4.02 (s, 2 H, H^{5}), 6.79-7.27 (m, 3 H, $H^{12,16,18}$), 7.27 (t, 1 H, H^{11}), 7.81 (d, 1 H, H^{9}), 6.89 (t, 1 H, H^{10}), 7.03 (d, 1 H, H^{19}) ,10.54 (br. s. 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 28.82 ($C^{3,4}$), 68.13 (C^{2}), 77.66 (C^{5}), 111.35 (C^{19}), 113.27 (C^{16}), 116.11 (C^{10}), 116.37 (C^{18}), 117.63 (C^{17}), 122.86 (C^{8}), 124.36 (C^{12}), 129.91 (C^{11}), 132.02 (C^{9}), 132.40 (C^{15}), 145.18 (C^{13}), 154.14 (C^{20}), 162.17 (C^{7}) ppm.

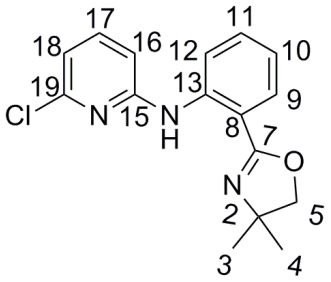
Synthesis of [2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2 fluorophenyl)anilido]titanium trichloride (Ia): Ligand **A** (0.284 g, 1.0 mmol) was dissolved in 15.0 mL toluene. Diethylamido titanium trichloride (0.226 g, 1.0 mmol) was dissolved in 15.0 mL toluene. The ligand solution was added dropwise to the Diethylamido titanium trichloride solution. The resultant solution was stirred overnight at room temperature. The toluene was removed under vacuum and the product was extracted with 150.0 mL *n*-hexane. The solution volume was reduced to 50.0 mL and the product was crystallized at -24 ^{o}C. Yield 0.290 g (66 %) $C_{17}H_{16}Cl_3FN_2OTi$ (437.55): calcd. C 46.95, H 3.69, N 6.50; found C 46.95, H 3.51, N 7.09. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.21 (s, 6 H, $H^{3,4}$), 4.24 (s, 2 H, H^{5}), 6.54-6.69 (m, 3 H, $H^{12,16,18}$), 6.78 (t, 1 H, H^{10}), 6.80-6.94 (m, 2 H, $H^{17,9}$), 7.95 (d, 1H, H^{19}), 8.46 (t, 1H, H^{11}) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 27.76 ($C^{3,4}$), 58.97 (C^{21}), 80.95 (C^{5}), 67.16 (C^{2}), 114.01 (C^{19}), 118.60 (C^{12}), 122.58 (C^{18}), 124.44 (C^{15}), 127.52 (C^{17}), 129.79 (C^{9}), 130.33 (C^{16}), 134.40 (C^{11}), 143.22 (C^{10}), 152.13 (C^{8}), 153.80 (C^{13}), 157.05 (C^{20}), 166.04 (C^{7}) ppm.



Synthesis of 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2-methoxyphenyl)aniline (B): [2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl) aniline] (4.0 g, 21.0 mmol), Tris[dibenzilideneacetondipalladium(0)] (0.381 g, 0.417 mmol), 1,3-Bis(diphenylphosphino)propane (0. 344 g, 0.837 mmol), sodium tertiary butoxide (2.59 g, 27.0 mmol) were taken in a Schlenk tube in a glove box. This mixture was dissolved in 60.0 mL toluene. 1-bromo-2-methoxybenzene (3.92 g, 2.6 mL, 21.0 mmol) was added to this solution. The resulting solution was refluxed for five days. On cooling distilled water (50.0 mL) and diethyl ether (50.0 mL) were added and the organic layer was separated by solvent extraction. The inorganic layer was washed three times with diethyl ether (3 × 20.0 mL). The combined organic layers were washed with a saturated sodium chloride solution and were dried over sodium sulphate. The volatiles were removed under vacuum and the product was crystallized at -24 ^{o}C. Yield 3.50 g (61 %). $C_{18}H_{20}N_2O_2$ (296.36): calcd. C 72.95, H 6.80, N 9.55; found C 72.78, H 6.95, N 10.07.^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.18 (s, 6 H, $H^{3,4}$), 3.41 (s, 3 H, H^{21}

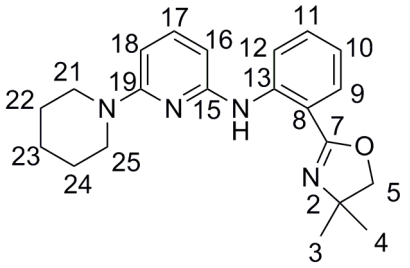
), 3.62 (s, 2 H, (d, 1 H, H^{12}), 7.56 (t, 1 H, H^{17}), 8.18 (d, 1 H, H^{19}), 10.97 (br. s. 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 28.41 ($C^{3,4}$), 55.27 (C^{21}), 67.80 (C^2), 77.07 (C^5), 111.34 (C^{19}), 111.92 (C^{16}), 113.43 (C^{10}), 116.88 (C^{12}), 120.90 (C^{18}), 121.63 (C^{17}), 123.16 (C^8), 130.24 (C^9), 131.35 (C^{15}), 132.05 (C^{11}), 146.25 (C^{13}), 152.36 (C^{20}), 162.35 (C^7) ppm.

Synthesis of [2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-N-(2-methoxyphenyl)anilido] titanium trichloride (Ib): Ligand **B** (0.296 g, 1.0 mmol) was dissolved in 15.0 mL toluene. Diethylamido titanium trichloride (0.226 g, 1.0 mmol) was dissolved in 15.0 mL toluene. The ligand solution was added dropwise to the Diethylamido titanium trichloride solution. The resultant solution was stirred overnight at room temperature. The toluene was removed under vacuum and the product was extracted with 140.0 mL *n*-hexane. The solution volume was reduced to 50.0 mL and the product was crystallized at -24 ^oC. Yield 0.285 g (63 %). $C_{18}H_{19}Cl_3N_2O_2Ti$ (449.37): calcd. C 48.07, H 4.26, N 6.23; found C 48.23, H 4.73, N 6.70. ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 1.21 (s, 6 H, $H^{3,4}$), 2.81 (s, 3 H, H^{21}), 4.24 (s, 2 H, H^5), 6.39 – 7.10 (m, 5 H, $H^{9,16,17,18,19}$), 7.49 (t, 1 H, H^{10}), 7.95 (t, 1 H, H^{11}), 8.46 (d, 1 H, H^{12}) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 28.41 ($C^{3,4}$), 55.39 (C^5), 58.75 (C^{21}), 72.01 (C^2), 111.29 (C^{10}), 114.01 (C^{18}), 117.36 (C^{11}), 120.70 (C^{17}), 122.92 (C^{12}), 124.24 (C^{16}), 125.10 (C^9), 128.55 (C^{19}), 131.43 (C^{13}), 136.12 (C^8), 143.22 (C^{15}), 151.25 (C^{20}), 156.28 (C^7) ppm.



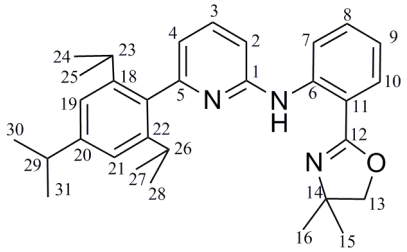
Synthesis of 6-chloro-N-[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)pyridin-2 amine] (C1): [2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline] (3.80 g, 20. 0 mmol) and t-amylalcohol (0.352 g, 0.45 mL, 4.0 mmol) in 20.0 mL THF were added to a THF suspension of NaH (0.720 g, 30.0 mmol). The resulting mixture was heated at 65 ^oC for two hours and 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 further heated for two hours.To the cool mixture 2, 6-dichloropyridine (2.96 g, 20.0 mmol) and styrene (0.11 mL, 0.099 g, 0.95 mmol) was added and the reaction mixture was refluxed for two hours. After cooling water (2.0

mL) and dichloromethane (100.0 mL) were added. The reaction mixture was filtered over sodium sulphate and the volatiles were removed from filtrate. The yellow oil thus obtained was purified by silica gel column chromatography and was crystallized in *n*-hexane.Yield 2.50 g (40 %). $C_{16}H_{16}ClN_3O$ (301.77): calcd. C 63.66, H 5.35, N 13.93; found C 64.12, H 5.25, N 14.43. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.37 (s, 6 H, $H^{3,4}$), 4.01 (s, 2 H, H^5), 6.63 (d, 1 H, H^{16}), 6.92 (d, 1 H, H^{18}), 7.21 (t, 1 H, H^{17}), 7.39-7.41 (m, 2 H, $H^{9, 10}$), 7.43 (d, 1 H, H^{12}), 8.69 (d, 1 H, H^9), 11.81 (br. s. 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 28.82 ($C^{3,4}$), 44.99 (C^5), 68.11 (C^2), 110.61 (C^{16}), 112.21 (C^{18}), 114.60 (C^{12}), 117.84 (C^{10}), 119.76 (C^9), 129.38 (C^{11}), 132.47 (C^8), 139.30 (C^{13}), 142.11 (C^{17}), 149.24 (C^{15}), 155.31 (C^{19}), 162.43 (C^7) ppm.



Synthesis of N-[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-6-(piperidin-1-yl)pyridin-2-amine] (C2): 6-chloro-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)pyridin-2-amine (**C1**), (1.0 g, 3.32 mmol) and piperidine (0.868 g, 10.2 mmol, 1.0 mL) were taken in a pressure tube containing 15.0 mL toluene. The resultant solution was heated at 170 ^{o}C for six days. After cooling, the reaction mixture was filtered. The solvent was removed from filtrate under vacuum. The yellow oil thus obtained was purified by the silica gel column chromatography. The volatiles were removed under vacuum and the yellow oil was dissolved in 10.0 mL *n*-hexane and crystallized at -24 ^{o}C. Yield 0.80 g (68 %). $C_{21}H_{26}N_4O$ (350.46): calcd. C 71.97, H 7.48, N 15.99; found C 72.40, H 7.37, N 15.70. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.32 (s, 6 H, $H^{3,4}$), 1.36 (m, 6 H , $H^{22,23,24}$), 3.45 (t, 4 H, $H^{21,25}$), 3.59 (s, 2 H, H^5), 6.05 (d, 1 H, H^{18}), 6.76 (t, 1 H, H^{17}), 7.27-7.31 (m, 2 H, $H^{9,11}$), 7.71 (d, 1 H, H^{12}), 8.62 (d, 1 H ,H^{18}), 11.32 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 25.10 ($C^{3,4}$), 25.63 (C^{23}), 28.34 ($C^{22,24}$), 46.72 ($C^{21,25}$), 69.11 (C^2), 75.30 (C^5), 98.32 (C^{16}), 100.71 (C^{18}), 111.89 (C^8), 118.37 (C^{12}), 128.32 (C^9), 129.70 (C^{11}), 132.10 (C^8), 138.79 (C^{17}), 144.19 (C^{13}), 154.70 (C^{15}), 159.18 (C^{19}), 162.77 (C^7) ppm.

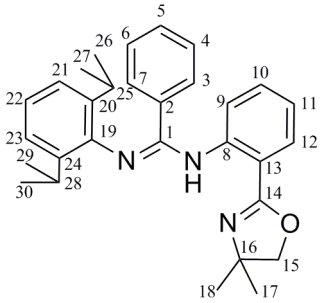
Synthesis of N-[2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-6-(piperidin-1-yl)pyridin-2-amido] titanium trichloride (Ic): Ligand **C2** (0.350 g, 1.0 mmol) was dissolved in 15.0 mL toluene. Diethylamido titanium trichloride (0.226 g, 1.0 mmol) was dissolved in 15.0 mL toluene. The ligand solution was added dropwise to the Diethylamido titanium trichloride solution. The resultant solution was stirred overnight at room temperature. The toluene was removed under vacuum and the product was extracted with 130.0 mL *n*-hexane. The solution volume was reduced to 50.0 mL and the product was crystallized at -24 ^{o}C. Yield 0.310 g (61 %). $C_{21}H_{25}Cl_3N_4OTi$ (503.43): calcd. C 50.16, H 5.00, N 11.13; found C 50.64, H 5.59, N 11.43. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.07 (s, 6 H, $H^{3,4}$), 1.20-1.42 (m, 6 H , $H^{22,23,24}$), 3.43 (t, 4 H, $H^{21,25}$), 3.51 (s, 2 H, H^{5}), 6.17 (d, 1 H, H^{16}), 6.36 (d, 1 H, H^{18}), 6.80 (t, 1 H, H^{17}), 6.90 (t, 1 H, H^{10}), 7.36 (t, 1 H, H^{11}), 8.12 (d, 1 H, H^{12}) , 9.17 (d, 1 H, H^{9}) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 25.75 (C^{23}), 26.45 ($C^{3,4}$), 28.30 ($C^{22,24}$), 45.48 ($C^{21,25}$), 55.36 (C^{5}), 67.90 (C^{2}), 112.01 (C^{10}), 113.52 (C^{18}), 116.97 (C^{11}), 120.9l (C^{17}), 121.68 (C^{12}), 123.25 (C^{16}), 130.30 (C^{19}), 131.43 (C^{13}), 132.40 (C^{9}), 146.25 (C^{15}), 152.36 (C^{7}) ppm.



Synthesis of N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-6-(2,4,6-triisopropylphenyl) pyridin-2-amine (D): 2-Bromo-6-(2,4,6-triisopropylphenyl)pyridine (3.60 g, 10.00 mmol), aniline (1.90 g, 10.00 mmol), sodium tert-butoxide (1.09 g, 11.30 mmol), tris(benzylidenaceton) dipalladium(0) (0.17 g, 0.18 mmol) and 1,3-bis(diphenylphosphino) propane (0.16 g, 0.36 mmol) were transferred in a Schlenk vessel and suspended in 100 mL of toluene. The resulting mixture was heated for 24 h at 95 °C. After cooling down to room temperature, 50 mL of diethylether together with 50 mL of water were added to quench the reaction. The organic layer was separated and washed two times with 25 mL of water. The water layer was once extracted with 25 mL of diethylether and the combined organic layers were dried over sodium sulphate. After removal of all volatiles, the residue was extracted with 100 mL of hot *n*-hexane. The hexane solution was filtered and stored at -30 °C to give colourless crystals. Yield 1.90 g (41 %). $C_{31}H_{39}N_3O$: calcd. C 79.28, H 8.37, .N 8.95; found C 78.90, H 8.30, N 8.60. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.04 (s, 6H,

$H^{15,16}$), 1.24 (d, 18 H, $H^{24,25,27,28,30,31}$), 2.60 (sept, 1 H, $H^{23,26,29}$), 2.80 (sept, 1 H, $H^{23,26,29}$), 3.00 (sept, 1 H, $H^{23,26,29}$), 3.48 (s, 2 H, H^{13}), 6.62 (m, 3 H, $H^{2,4,7}$), 6.91 (t, 1 H, H^{10}),7.09 (t, 1 H, H^{3}), 7.13 (s, 2 H, $H^{19,21}$), 7.21 (d,1 H, H^{8}), 8.02 (d, 1 H, H^{10}), 9.33 (d, 1H, H^{NH}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 24.30 ($C^{24,25,27,28,30,31}$), 28.30 ($C^{15,16}$), 30.90 ($C^{23,29}$), 34.80 (C^{26}), 67.70 (C^{13}), 77.00 (C^{14}), 105.00 (C^{2}), 110.20 (C^{4}), 116.50 (C^{7}), 118.40 (C^{9}), 120.80 ($C^{19,21}$), 129.40 (C^{10}), 132.80 (C^{8}), 136.80 (C^{3}), 143.60 (C^{6}), 146.80 ($C^{18,20,22}$), 155.70 (C^{5}), 158.70 (C^{1}), 162.80 (C^{12}) ppm.

Synthesis of [N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-6-(2,4,6-triisopropyl-phenyl) pyridin-2-amido]titanium trichloride (Id): N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-6-(2,4,6-triisopropylphenyl) pyridin-2-amine (0.99 g, 2.11 mmol) and Et_2NTiCl_3 (0.48 g, 2.11 mmol) were transferred in a Schlenk vessel and were dissolved in 20 mL of toluene. The resulting mixture was heated up to 50 °C for 12 h. After cooling to room temperature, dark blue crystals were observed. The supernatant solution was decanted off and the crystals were dried under reduced pressure. Yield 0.58 g (43 %). $C_{31}H_{38}Cl_3N_3OTi$: calcd. C 59.78, H 6.15, N 6.75; found C 59.10, H 6.10, N 6.50. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.18 (d, 6 H, $H^{24,25,27,28,30,31}$), 1.28 (d, 6 H, $H^{24,25,27,28,30,31}$), 1.45 (s, 6 H, $H^{15,16}$), 2.60 (sept, 1 H, $H^{23,26,29}$), 1.78 (d, 6 H, $H^{24,25,27,28,30,31}$), 2.88 (sept, 1H, H^{29}), 3.18 (sept, 2 H, $H^{23,26}$), 3.22 (s, 2 H, H^{13}), 6.62 (d, 1 H, H^{2}), 6.64 (t, 1 H, H^{9}), 6.72 (d, 1 H, H^{4}), 6.84 (d, 1 H, H^{10}), 7.00 (t, 1 H, H^{3}), 7.05 (t, 1 H, H^{8}), 7.13 (s, 2 H, $H^{19,21}$), 7.34 (s, 2 H, H^{8}), 7.94 (d, 1 H, H^{10}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 24.30 ($C^{24,25,27,28,30,31}$), 28.30 ($C^{15,16}$), 30.90 ($C^{23,29}$), 34.80 (C^{26}), 67.70 (C^{13}), 77.00 (C^{14}), 105.00 (C^{2}), 110.20 (C^{4}), 116.50 (C^{7}), 118.40 (C^{9}), 120.80 ($C^{19,21}$), 129.40 (C^{10}), 132.80 (C^{8}),136.80 (C^{3}), 143.60 (C^{6}), 146.80 ($C^{18,20,22}$), 155.70 (C^{5}), 158.70 (C^{1}), 162.80 (C^{12}) ppm.



Synthesis of (E)-N'-(2,6-diisopropylphenyl)-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)benzimidamide (E): (*E*)-N- (2,6-diisopropylphenyl) benzimidoyl chloride (2.15 g,

7.19 mmol) was dissolved in 25 mL of toluene before successive 2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)aniline (1.37 g, 7.19 mmol) and triethylamine (1.30 mL, 0.94 mmol) were added. After refluxing for two hours, the reaction mixture was poured into 50 mL of water. The organic layer was separated and washed two times with 25.00 mL water. The combined water phase was extracted with 25.00 mL of diethylether. The combined organic layer was dried with Na_2SO_4 and filtered before all volatiles were removed. The residue was recrystallized from ethanol (50.00 mL). Yield 2.92 g (89.50 %). $C_{30}H_{35}N_3O$: calcd. C 79.43, H 7.78, N 9.26; found C 79.30, H 7.65, N 9.70. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.89 (s, 6 H, $H^{17,18}$), 1.23 (d, 12 H, $H^{26,27,29,30}$), 3.34 (sept, 2 H, $H^{25,28}$), 3.45 (s, 2 H, H^{15}), 6.80 (br. s, 1 H, H^9), 6.93 (br. s, 1 H, H^{11}), 7.00-7.15 (m, 8 H, $H^{3,4,5,6,7,10,21,23}$), 7.58 (br. s, 1 H, H^{22}), 8.04 (d, 1 H, H^{12}), 9.80 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 22.20 ($C^{26,27,29,30}$), 24.10 ($C^{26,27,29,30}$), 28.00 ($C^{17,18}$), 28.70 ($C^{25,28}$), 67.60 (C^{15}), 77.40 (C^{16}), 113.30 (C^9), 119.20 (C^{11}), 120.00 (C^{13}), 123.10 ($C^{21,22,24}$), 127.70 ($C^{3,4,6,7}$), 129.30 (C^6), 132.20 (C^{10}), 135.00 (C^2), 136.30 (C^{14}), 138.10 ($C^{20,24}$), 143.40 (C^{19}), 145.80 (C^8), 152.20 (C^1), 162.20 (C^{14}) ppm.

Synthesis of [(*E*)-N'-(2,6-diisopropylphenyl)-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)benzimidamido]titanium trichloride (Ie): (*E*)-N'-(2,6-diisopropylphenyl)-N-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)benzimidamide (0.99 g, 2.18 mmol) and Et_2NTiCl_3 (0.49 g, 2.18 mmol) were transferred in a Schlenk vessel and dissolved in 20 mL of toluene. The resulting mixture was heated upto 50 °C for 12 h. Slow cooling to room temperature afforded dark red crystals. The supernatant solution was decanted off and the crystals were dried under reduced pressure. Yield 0.84 g (64 %). $C_{30}H_{34}Cl_3N_3OTi$: calcd. C 59.38, H 5.65, N 6.92; found C 58.76, H 5.43, N 6.80. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.85 (s, 6 H, $H^{17,18}$), 1.62 (d, 6 H, $H^{26,27,29,30}$), 1.64 (d, 6 H, $H^{26,27,29,30}$), 3.59 (s, 2 H, H^{15}), 4.05 (sept, 2 H, $H^{25,28}$), 6.31 (d, 1 H, H^9), 6.65 (dd, 1 H, H^{11}), 6.78 (t, 2 H, $H^{21,23}$), 6.82 (d, 1 H, H^{10}), 7.04-7.08 (m, 5 H, $H^{3,4,5,6,7}$), 7.11 (br. s, 1 H, H^{22}), 8.04 (d, 1 H, H^{12}) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 22.30 ($C^{26,27,29,30}$), 26.00 ($C^{26,27,29,30}$), 28.10 ($C^{17,18}$), 28.40 ($C^{25,28}$), 71.60 (C^{15}), 80.00 (C^{16}), 115.40 (C^9), 117.20 (C^{11}), 122.70 (C^{13}), 124.30 ($C^{21,22,24}$), 129.20 ($C^{3,4,6,7}$), 130.10 (C^6), 131.10 (C^{10}), 131.60 (C^2), 134.00 (C^{14}), 136.10 ($C^{20,24}$), 142.00 (C^{19}), 143.20 (C^8), 144.20 (C^1), 163.30 (C^{14}) ppm.

Acknowledgments

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7. List of Publications

The following publications have been published or submitted or are to be submitted during the work on this thesis:

1) M. Hafeez, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem*. **2011**, *36*, 5512-5522.

'Titanium Complexes Stabilized by Bulky, Electron-Rich Aminopyridinates and their Application in Ethylene and Styrene Polymerization'

2) M. Hafeez, W. P. Kretschmer, R. Kempe, *ZAAC*, **2012**, *638*, 324-330.
'Hafnium Trialkyls Stablilized by Bulky Electron Rich Aminopyridinates'

3) S. Lippert, M. Hafeez, T. Bauer, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem*. (to be submitted).

'Synthesis, Structural Investigatigations and Ethylene Polymerization of Titanium Complexes with Tripodal Oxazoline Ligands'

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9. Declaration / Erklärung

I hereby declare that I have written this work by myself and that no other sources than those mentioned in this work have been used.

This work has so far neither been submitted to the Faculty of Biology, Chemistry and Earth Sciences at the University of Bayreuth nor to any other scientific institution for the purpose of a doctoral thesis.

Hiermit versichere ich an Eides statt, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel und Quellen angefertigt habe.

Diese Arbeit wurde bisher weder an der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht.

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Muhammad Hafeez