Early Transition Metal Complexes Stabilized by Bulky Aminopyridinato Ligands

DISSERTATION

Zur Erlangung des akademischen Grades eines
Doktors der Naturwissenschaften (Dr. rer. nat.)
im Fach Chemie der Fakultät für Biologie, Chemie und Geowissenschaften
der Universität Bayreuth

vorgelegt von
M.Phil. Awal Noor
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This thesis fulfills the requirements of the doctoral degree of the Faculty of Biology, Chemistry and Geological Sciences at the University of Bayreuth.

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Examination Committee:

Chairman: Prof. Dr. Rainer Schobert
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2. Referee: Prof. Dr. Jürgen Senker
Prof. Matthias Ballauf

The following work was undertaken during the period January 2004 to April 2008 at the Lehrstuhl für Anorganische Chemie II der Universität Bayreuth under the supervision of Prof. Dr. Rhett Kempe.

To my father, to the patience of my wife and to the innocence of my little son Aahil

Table of Contents

1. Summary

A series of early transition metal complexes stabilized by aminopyridinato ligands have been synthesized. Many of these complexes have been studied in terms of their structure and have been evaluated in terms of applications in catalysis. The overall evaluation tells about the importance of electrophilicity of the metal centre, the steric bulk of the applied ligands, and the route of syntheses.

Trialkyltantalum complexes were synthesized by salt elimination or toluene elimination by reacting the corresponding lithiated ligand with trialkyltantalum dichloride or the corresponding ligand with pentabenzyltantalum, respectively. These trialkyltantalum complexes are unusually thermally stable towards α-H elimination and form rather unstable organocations.

Bis(aminopyridinato) complexes of zirconium were prepared using salt elimination route. The steric bulk of the ligands prevented the redistribution to tris- or tetrakis(aminopyridinato) zirconium complexes. These zirconium complexes are thermally robust, highly active and selective ethylene polymerization catalysts. Ethylene is polymerized highly selectively out of a mixture of ethylene and propylene. Slight changes in the steric demand of the bulky ligand periphery can be used to tune the nature of the formed polymers by maintaining the selectivity issue. The Zr alkyl cations of the sterically more demanding version of the ligands are able to polymerize ethylene in a living fashion at 50 °C.

We also became interested in toluene elimination chemistry and observed that the bulky aminopyridinates that give selectively bis(aminopyridinato) complexes via salt metathesis chemistry lead selectively to mono(aminopyridinato) tribenzyl Zr/Hf complexes. In the solid state, one of the three benzyls is η^2-coordinated and rest are η^1-coordinated to the electron deficient metal centres. One of the three benzyls has been partially abstracted using $B(C_6F_5)_3$. The phenyl ring of B-bounded benzyl in these complexes shows an η^6-coordination and essentially blocks the vacant site of the metal centre, consequently, preventing it to polymerize ethylene at room temperature. At elevated temperature a moderate single site polymerization activity with the formation of high molecular weight polyethylene was observed for these zwitterionic complexes. The attempted abstraction of the second benzyl group failed when the zwitterionic complexes were reacted with an additional equivalent of $B(C_6F_5)_3$. However using one equivalent of $[R_2(Me)NH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$) instead of $B(C_6F_5)_3$ give catalysts which show moderate activities in ethylene polymerization. Treatment of the aminopyridinato metal tribenzyls with $[R_2(Me)NH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–

$C_{18}H_{37}$) give active ethylene polymerization catalysts, which produce low molecular weight polyethylene for the zirconium complexes and high molecular weight for the hafnium ones. Propylene polymerization under the same conditions failed, whereas during copolymerization ethylene-propylene copolymers with separated propene units and alternating sequences were observed.

The versatility of these ligands was flourished by synthesizing a titanium alkyne complex stabilized by aminopyridinato ligands which may show a very multifaceted chemistry. The reactivity of this complex was studied by the insertion of acetone into titanium carbon bond. The complex is not only quite stable at room temperature but also in solution at high temperatures under argon atmosphere despite a weakly bonded acetylene ligand.

The chemistry of low valent chromium stabilized by sterically demanding aminopyridinato ligands has been explored and first non-bridging η^2-coordinated chromium^{II} complexes were synthesized using such ligands. It was foud that reacting deprotonated ligands of the same steric bulk with the corresponding salts of the low valent chromium $^{II/III}$ can lead to mono(aminopyridinato) dimeric chromium^{II} or monomeric chromium^{III} complexes, respectively. It is worth to note that gradual decrease in the steric bulk leads to bis(aminopyridinato) mononuclear chromium complexes.

The ability of aminopyridinato ligands to stabilize transition metals in low oxidation state has been highlighted by the synthesis of a dimeric chromium^{I} complex. The X-ray crystal structure analysis revealed an exceptionally short chromium-chromium distance of 1.7488(18) Å, the shortest metal-metal bond reported so far for a stable compound. The homobimetallic chromium complex was synthesized by the reduction of aminopyridinato ligand stabilized chromium$^{II/III}$ chloride precursor with KC_8. Anaylsis of its electronic structure indicates quintuple bonding.

Zusammenfassung

Eine Reihe Übergangsmetallkomplexe, stabilisiert durch Aminopyridinatoliganden, wurde synthetisiert. Viele dieser Komplexverbindungen wurden im Hinblick auf ihre Struktur und mögliche katalytische Anwendungen untersucht. Generell wurden hierbei Erkenntnisse zur Bedeutung der Elektrophili von Metallzentren, die Rolle des sterischen Anspruches der verwendeten Liganden und die Wichtigkeit der anzuwendenden Syntheserouten erarbeitet.

Trialkyltantalkomplexe wurden mittels Salz-, und Toluoleliminierung, durch die Umsetzung des lithiierten Liganden mit Trialkyltantaldichlorid oder durch Umsetzung des Liganden mit Pentabenzyltantal dargestellt. Die so erhaltenen Trialkyltantalkomplexe sind thermisch ausgesprochen stabil im Hinblick auf die α-H-Eliminierung und bilden relativ instabile Organokationen aus.

Bis(aminopyridinato)-Komplexe des Zirkoniums wurden hergestellt mittels Salzeliminierung. Der sterische Anspruch der Liganden verhindert erstmals die Umorganisation zu Tris- oder Tetrakis(aminopyridinato)zirkoniumkomplexen. Diese Zirkoniumkomplexe sind thermisch robust, hoch aktive und selektive Ethylenpolymerisationskatalysatoren. Ethylen wird hoch selektiv aus einer Mischung von Ethylen und Propylen polymerisiert. Geringe Änderungen im sterischen Anspruch der großen Liganden erlauben es, die Natur der zu bildenden Polymere fein einzustellen unter Beibehaltung der Selektivität. Zirkoniumalkylkationen des sterisch anspruchsvollsten Liganden sind in der Lage, Ethylen lebend bei 50°C zu polymerisieren.

Wir waren weiterhin an der Toluoleliminierungschemie interessiert und beobachteten, dass sterisch anspruchsvolle Aminopyridinate, die selektiv Bis(aminopyridinate) mittels Salzmetathese ergaben, selektiv Mono(aminopyridinato)-tribenzylzirkonium-/hafniumkomplexe ergeben. Im Festkörper ist eine der drei Benzylliganden η^2 und die restlichen η^1 koordiniert, was für ein extrem elektronarmes Metallzentrum spricht. Einer der drei Benzylliganden kann selektiv mittels $B(C_6F_5)_3$ abstrahiert werden. Dabei koordiniert der Phenylring der borgebundenden Benzylgruppe η^6 am Zirkoniumzentrum und blockiert das aktive Zentrum, was zu einer äußerst geringen Ethylenpolymerisationsaktivität bei Raumtemperatur führt. Bei erhöhten Temperaturen wird für diese zwitterionischen Komplexverbindungen eine moderate Polymerisationsaktivität, die die Existenz von Einkomponentenkatalysatoren andeutet, beobachtet. Die Abstraktion einer zweiten Benzylgruppe durch Umsetzung des zwitterionischen Komplexes mit einem weiteren Äquivalent $B(C_6F_5)_3$ gelingt nicht. Nutzt man allerdings für diese Aktivierung ein Äquivalent von $[R_2(Me)NH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$) anstelle von $B(C_6F_5)_3$, entsteht ein

Katalysator, der eine moderate Ethylenpolymerisationsaktivität aufweist. Die Behandlung der Aminopyridinatometalltribenzyle mit $[R_2(Me)NH][B(C_6F_5)_4]$ ($R = C_{16}H_{33}–C_{18}H_{37}$) ergibt aktive Ethylenpolymerisationskatalysatoren, die im Falle des Zirkoniums niedermolekulares Polyethylen und im Falle von Hafnium hochmolekulares Polyethylen produzieren. Propylenpolymerisation unter analogen Bedingungen gelingt nicht. Bei einer Copolymerisation von Ethylen und Propylen werden Copolymere beobachtet mit separaten Ethyleneinheiten und alternierenden Sequenzen von Ethylen und Propylen.

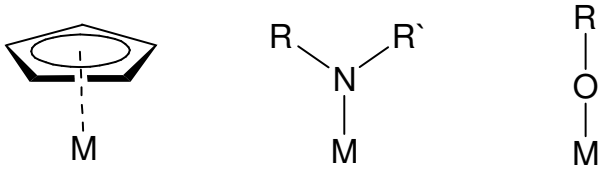
Die Vielfalt dieser Ligandenklasse wurde durch die Synthese von Titanalkinkomplexen, von denen man aufgrund der niedrigen Oxidationsstufe eine facettenreiche Chemie erwartet, bestätigt. Erste Reaktivitätsstudien wurden am Beispiel der Insertion von Aceton in die Metallkohlenstoffbindung untersucht. Der Alkinkomplex ist trotz des schwach gebundenen Alkinliganden nicht nur bei Raumtemperatur relativ stabil, sondern auch - vorausgesetzt er wird in Argonatmosphäre belassen – bei höheren Temperaturen.

Die Chemie niedervalenter Chromkomplexe, stabilisiert durch sterisch anspruchsvolle Aminopyridinatoliganden, wurde untersucht. Dabei konnte der erste η^2-gebundene $Chrom^{II}$-Komplex, der einen derartigen Liganden enthält, dargestellt werden. Die Reaktion von deprotonierten Liganden, die einen großen sterischen Anspruch besitzen, mit $Chrom^{II/III}$-Ausgangsmaterialien führt zu Mono(aminopyridinato)-$Chrom^{II}$- (dimer im Festkörper) und -$Chrom^{III}$-Komplexen (monomer im Festkörper). Das Reduzieren des sterischen Anspruchs der Liganden führt selektiv zu Bis(aminopyridinato)-Chrom-Komplexen.

Das Vermögen von Aminopyridinatoliganden Übergangsmetalle in sehr niedrigen Oxidationsstufen zu stabilisieren, wurde mit der Synthese einer dimeren $Chrom^{I}$-Verbindung untermauert. Die Kristallstrukturanalyse dieser Verbindung ergab einen außerordentlich kurzen Chrom-Chrom-Abstand von 1.7488(18) Å, der der kürzeste experimentell bestimmte Metall-Metall-Abstand für stabile Verbindungen ist. Der homobimetallische Chromkomplex wurde durch die Reduktion aminopyridinatoligandstabilisierter $Chrom^{II/III}$-Chlorid-Komplexe mittels KC_8 dargestellt. Die Analyse seiner elektronischen Struktur ergab das Vorliegen einer Fünffachbindung.

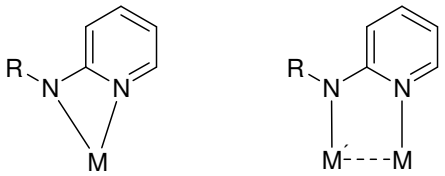
2. Introduction

In organometallic chemistry, considerable efforts have been made on modifying the reactivity of metal-carbon bonds through choice of appropriate coligands. The information thus obtained is now being extensively used in, for example, homogeneous catalysis.[1] Coligands such as the cyclopentadienyl (Cp) fragment and phosphanes have hitherto played the dominant role as anionic and neutral donor functions, respectively.[2]
The three most important Cp alternatives are alkoxy (Scheme 1, right) and amido ligands[3] (Scheme 1, centre). They have proven to be suitable for the stabilization of early, electron-poor transition metal ions in medium to 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).

Of these two alternatives, the amido ligand is especially interesting since it offers a greater variety in ligand and complex design because of the possibility for double substitution at the donor atom. Aminopyridinato ligands (Scheme 2) are an important class of amido ligands and are derived from deprotonated 2-aminopyridines.



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

They are interesting due to the flexibility of their binding modes. The first strained η^2-coordinated aminopyridinato complex (Scheme 2, left) was published by Cotton et al.,[4] and only a few compounds[5,6,7] had been investigated prior to 1996. The first early transition metal complex, a vanadium compound, was published by Gambarotta et al. in 1991.[7] Four years later, aminopyridinato ligands started to be extensively used to stabilize early transition metal ions in medium or high oxidation states. These studies can be seen in the context of the renaissance of metal-amido chemistry[8] which was initiated by the search for alternatives to

the well-known Cp ligands. An interest in these systems grew due to the unique chemistry of these ligands, which is mainly a result of the close proximity of the amido and pyridine functions.[9]

The interest of replacing Cp ligands of group 4 metals with special aminopyridinates and to study the reactivities of the resulting complexes began in 1996.[10,11] The traditional synthesis protocols such as salt metathesis failed in the case of titanium as it resulted in very low yield complex (10 %). The poor yield was thought to be due to the reduction of the titanium centre by the lithiated aminopyridinato ligands. Two solutions were found, namely ‘‘direct synthesis’’ and “amine elimination”. The direct synthesis involves the treatment of an alkyl- or aryl-substituted aminopyridine in either boiling toluene or without solvent at temperatures above 100 °C. Amine elimination has been useful for the synthesis of many group 4 metal complexes.[11,12] They have shown very high[13] activities for the polymerization of propene and 1-butene if activated with MAO, triisobutylaluminium/$B(C_6F_5)_3$ or ethylaluminium sesquichloride.[12] The use of in situ-generated mixed (amido)(chloro)zirconium complexes instead of the well-defined starting material $[(R_2N)_2Zr(thf)_2Cl_2]$ (R = CH_3, C_2H_5) leads to by-products.[14] Besides amine elimination and salt metathesis, the ‘‘direct synthesis’’ has proven to be efficient for the synthesis of zirconium complexes. Better control of the zirconium/ligand stoichiometry and structures of bis(aminopyridinato) complexes is possible by introduction of sterically demanding alkyl substituents (e.g. adamantyl) on the ligands. Scott et al. reported the synthesis and structure of bis(aminopyridinato)zirconium complexes by salt metathesis, amine and alkyl elimination reactions.[15] However, the ‘‘direct synthesis’’ with $HfCl_4$ gave the homoleptic complex.[16]

In order to tune the reactive sites of the corresponding transition metal complexes in much better way ligands having two aminopyridine moieties were also used. For example the reaction of the siloxane-bridged bis(aminopyridine) with $[(Me_2N)_3TiCl]$ yielded mixed (amido)(chloro) complexes.[17] Activation of the complexes with MAO gave rise to low[18] activities in ethylene polymerization and no activity was observed for higher olefins. Structural studies of the precatalysts showed planar coordination of the bis(aminopyridinato) ligands and the ligands thus ‘‘cut’’ the complexes into two parts. This results in a separation of the coordination site of the growing alkyl chain and the coordination site for olefins during the polymerization process. Such a separation leads to a high insertion barrier and a correspondingly slow polymerization process.

A more detailed investigation of the group-5 metal coordination chemistry was started by Polamo et al.. He applied the ‘‘direct synthesis’’ method to prepare a variety of niobium and

tantalum complexes in high oxidation states.[19,20] Very high[18] ethylene polymerization activities were observed for the tantalum complexes if the complexes were activated with MAO.[21] Treatment of $[(dme)NbCl_3(PhC{\equiv}CSiMe_3)]$[22] with 3 equiv. of in situ lithiated (4-methyl-pyridin-2-yl)trimethylsilanyl-amine gave the orange-red tris(aminopyridinato) alkylniobium complex. The niobacyclopropene ring in this complex is extremely stable and does not react with ketones, styrene oxide, alkynes and olefins. However, complexes containing two amido ligands are accessible by using the sterically more demanding deprotonated (6-methyl-pyridin-2-yl)trimethylsilanyl-amine which can then be alkylated using CH_3Li where the methyl group could be partially abstracted by $B(C_6F_5)_3$ a zwitterionic compound and a single component ethylene polymerization catalyst.[23]

Aminopyridinato ligands can coordinate a variety of early transition metal complexes in the strained η^2-fashion. This binding mode may initiate a special reactivity. The motivation for this work was not only to overcome the problems associated with the different synthetic routes but also to study the effect of steric bulk in terms of achieving the desired products. It describes the effect of the steric bulk to avoid ligand redistribution to tris- or tetrakis(aminopyridinato) zirconium complexes independent of the remaining ligands and that how slight changes in the steric demand of the applied ligands can change the nature of the formed polymer. The ability of these ligands to stabilize low valent transition metals was studied. It also highlights a homobimetallic Cr^I complex which carries the shortest metal-metal bond distance of 1.7488 Å, measured to date. Overall this thesis introduces a lot of new aminopyridinate chemistry not only in terms of synthetic and structural chemistry of many of the synthesized complexes but also in terms of catalytic reactivity.

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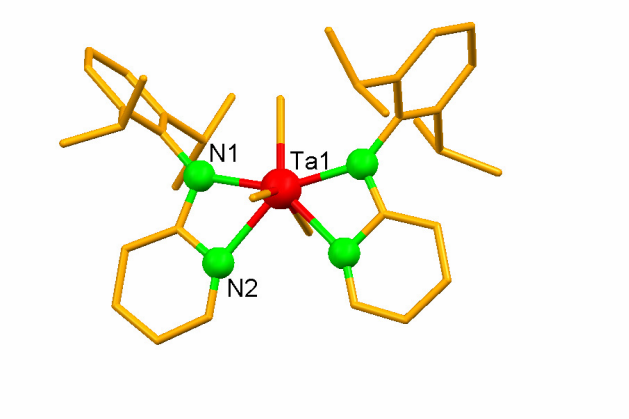
3. Overview of Thesis –Results

This thesis comprises of six publications which are presented in chapter 4 to 9.

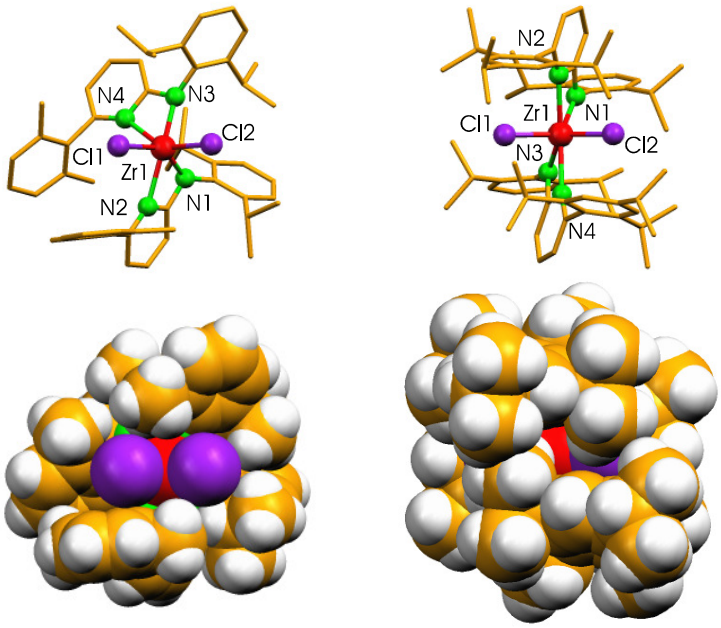
3.1. Trialkyltantalum Complexes Stabilized by Aminopyridinato Ligands



Trialkyltantalum complexes stabilized by aminopyridinato ligands can be synthesized by salt metathesis or toluene elimination. The reaction of 2 equiv. of (4-methylpyridin-2-yl)(trimethylsilyl)amine or (6-methylpyridin-2-yl)(trimethylsilyl)amine with pentabenzyltantalum afforded tribenzyltantalum(V) complexes by toluene elimination. Analogous reaction using (2,6-diisopropylphenyl)(pyridin-2-yl)amine failed. Lithiation of (2,6-diisopropylphenyl)(pyridin-2-yl)amine followed by the reaction with tribenzyltantalum dichloride gave rise to the corresponding tribenzyl complex. Other alkyltantalum complexes stabilized by this ligand environment can be prepared in good yields by treating tantalum pentachloride with 2 equiv. of lithiated (2,6-diisopropylphenyl)(pyridin-2-yl)amine to form a bis(aminopyridinato)tantalum trichloride. The success of salt metathesis using lithiated ligand and $TaCl_5$ is in contrast to the "direct synthesis" route which was developed due to problems with the salt metathesis approach in similar reactions. The reaction of this trichloride with 3 equiv. of alkyllithium compounds like methyllithium affords the corresponding trialkyltantalum complexes. They adopt the coordination of either a capped octahedron or a pentagonal bipyramid depending on the steric demand of the aminopyridinato ligand. These trialkyls are unusually thermally stable towards α-H-elimination e.g., heating of the trimethyl complex in toluene at 80 °C for 40 minutes did not affect the structure of the compound. However harsher conditions i.e., heating to 120 °C for 30 minutes leads to slow decomposition without any signs of methylidene complex formation. Ethylene polymerization activity of trichloro complex after activation with PMAO is low. Thus, it was expected to see a significant better catalyst performance by starting from the methyl complex and activating

with trialkylammonium tetrakis(pentafluorophenyl)borate. No significant improvement in terms of activity was found by changing the activation procedure. The generation of cationic complexes was studied in NMR tube scale reaction. The resulting organocation is not stable in solution and decomposes rapidly into unidentified species. This instability of these cations might be the reason for the low activity in ethylene polymerization.

3.2. Highly Active/Selective and Adjustable Zirconium Polymerization Catalysts Stabilized by Aminopyridinato Ligands

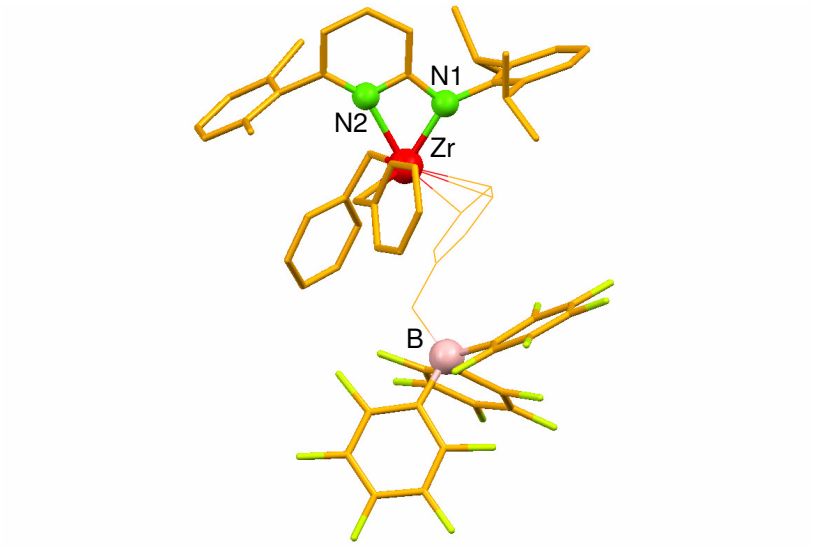


Here a substantial enhancement of the aminopyridinato ligand stabilized early transition metal chemistry by introducing the sterically very demanding 2,6-dialkylphenyl substituted aminopyridinato ligands derived from (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridin-2-yl]-amine (ApH) and (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridin-2-yl]-amine (Ap*H) is described. The corresponding bis(aminopyridinato) zirconium dichloride complexes, [Ap_2ZrCl_2] and [$Ap^*_2ZrCl_2$] and the dimethyl analogues, [Ap_2ZrMe_2] and [$Ap^*_2ZrMe_2$] (Me = methyl) were synthesized, using standard salt metathesis routes. The enough steric bulk of the ligands avoided the redistribution to tris- or tetrakis(aminopyridinato) zirconium complexes which limited the organozirconium chemistry of aminopyridinato ligand in the past. Single-crystal X-ray diffraction was carried out for the dichloro derivatives. Both zirconium metal centers have a distorted octahedral environment with a *cis*-orientation of the chloride ligands in [Ap_2ZrCl_2] and a closer to *trans*-arrangement in [$Ap^*_2ZrCl_2$]. The dimethyl derivatives are proven to be highly active ethylene polymerization catalysts after activation with [$R_2N(Me)H][B(C_6F_5)_4$] (R = $C_{16}H_{33}$–$C_{18}H_{37}$).

During attempted co-polymerizations of α-olefins (propylene) and ethylene high activity and selectivity for ethylene and nearly no co-monomer incorporation was observed. Such monomer selectivity especially in combination with high temperature stability could be of relevance for instance in chain shuttling polymerizations.

Increasing the steric bulk of the ligand going from (2,6-dimethylphenyl) to (2,4,6-triisopropylphenyl) substituted pyridines, switches the catalyst system from producing long chain α-olefins to polymerization of ethylene in a living fashion. In contrast to the dimethyl complexes only [Ap_2*$ZrCl_2$] in the presence of MAO at elevated temperature gave decent polymerization activity. NMR investigations of the reaction of dichloro complexes with 25 equiv. of MAO or $AlMe_3$ at room temperature revealed, that [Ap_2ZrCl_2] decomposes under ligand transfer to aluminium and forms [$ApAlMe_2$], while [Ap_2*$ZrCl_2$] remains almost unreacted under the same conditions. The aminopyridinato dimethyl aluminum complexes, [$ApAlMe_2$] and [Ap*$AlMe_2$] were synthesized independently and structurally characterized. These aluminum complexes show no catalytic activity towards ethylene, when ‘‘activated’’ with [$R_2N(Me)H$][$B(C_6F_5)_4$].

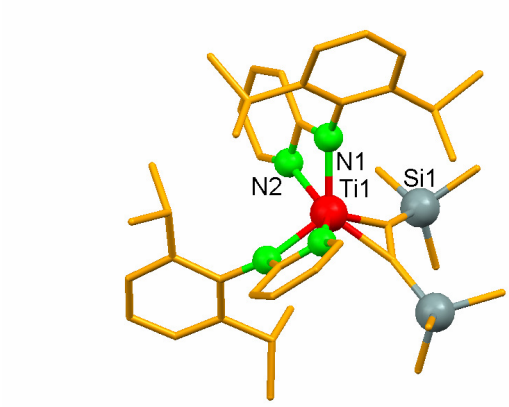
3.3. Zirconium and Hafnium Complexes Stabilized by very Bulky Aminopyridinato Ligands



We also became interested in toluene elimination chemistry and observed that the bulky aminopyridinates that give selectively bis(aminopyridinato) complexes via salt metathesis lead selectively to mono(aminopyridinato)tribenzyl Zr/Hf complexes. Mono(aminopyridinato) complexes of the type [$ApM(CH_2C_6H_5)_3$] [M = Zr, Hf and Ap = Aminopyridinato] were prepared by reacting three different sterically demanding aminopyridines with one equivalent of tetrabenzyl zirconium or tetrabenzyl hafnium in quantitative yields.

Mono(aminopyridinates) of these metals are rare and the corresponding trialkyls are unknown. First structurally characterized heteroleptic examples of hafnium aminopyridinate are reported. X-ray analysis show distorted tetrahedral geometry for these complexes where one of the three benzyls is η^2-coordinated in the solid state. However all of the three benzyls are equivalent in solution as evidenced ba ^{1}H NMR spectra. Treatment of these neutral complexes with $B(C_6F_5)_3$ afforded the corresponding zwitterionic dibenzyl complexes. η^6-Coordination of the phenyl ring of the B-bounded benzyl group to the metal centre was supported by ^{1}H NMR and confirmed by single crystal analysis. At room temperature these zwitterionic complexes show very low activity for ethylene polymerization as the coordination site is blocked by η^6-coordinated phenyl ring. At elevated temperature a moderate single site polymerization activity with the formation of high molecular weight polyethylene (PE) was observed. The attempted abstraction of the second benzyl group failed when the zwitterionic complexes were reacted with an additional equivalent of $B(C_6F_5)_3$. However, using one equivalent of $[R_2(Me)NH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$) instead of $B(C_6F_5)_3$, the resulting catalysts show moderate activities towards ethylene in polymerization. Treatment of the aminopyridinato metal tribenzyls with $[R_2(Me)NH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$) give active ethylene polymerization catalysts, which produce low molecular weight PE for the zirconium complexes and high molecular weight PE for hafnium ones. Propylene polymerization under the same conditions failed while ethylene-propylene copolymers with separated propene units and alternating sequences were observed.

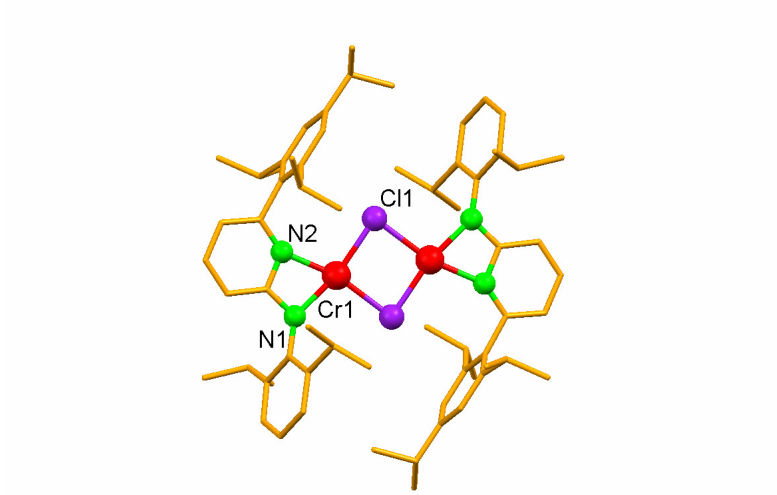
3.4. Acetylenetitanium Complex Stabilized by Aminopyridinato Ligands



Alkyne complexes of group-IV metallocenes can be used synthetically for many purposes. However, ligands other then Cp have been investigated rarely. In order to investigate such alternatives, aminopyridinato ligands were employed. The reduction of bis(aminopyridinato) titanium dichloride complex using magnesium in the presence of bis(trimethylsilyl)acetylene

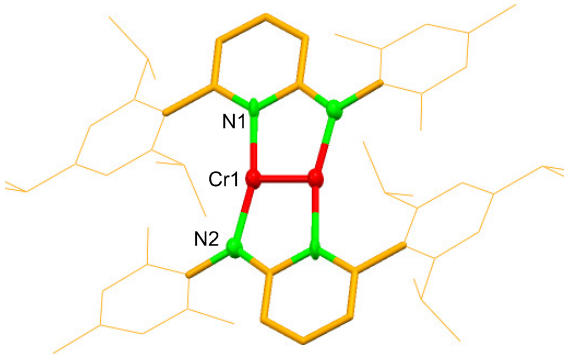
led to the first example of such complexes stabilized by aminopyridinato ligands. The complex was isolated from the reaction mixture and characterized by NMR and X-ray analysis. The coordination environment around titanium is formed by four nitrogen atoms of the two aminopyridinato ligands and a substituted acetylene ligand. The spectroscopic data of the complex justifies it as a weakly coordinated titanium alkyne complex. The reactivity of this complex was studied by insertion of acetone into titanium carbon bond by reacting with one equivalent of acetone in hexane. The complex is not only quite stable at room temperature but also in solution at high temperature despite a weakly bonded alkyne ligand. Reduction of bis(aminopyridinato) titanium dichloride with KC_8 in the absence of any supporting group leads to tris(aminopyridinato) titanium complex, most probably a ligand rearrangement product.

3.5. Synthesis and Structure of Low Valent Chromium Complexes Stabilized by η^2-Coordinated Aminopyridinato Ligands



The chemistry of low valent chromium stabilized by sterically demanding aminopyridinato ligands was explored in terms of the importance of the steric bulk of the applied ligands. In the past, the attempts to prepare such ligands resulted in the formation of homoleptic Cr^{III} or bridging Cr^{II} complexes due to the lack of enough steric bulk. The first ever η^2-coordinated Cr^{II} aminopyridinate complex was synthesized and structurally characterized. X-ray analysis show distorted octahedral geometry for the monomeric mono(aminopyridinato) Cr^{III} complexes and distorted square plannar coordination for the dimeric Cr^{II} complexes. The less bulky version of such ligands selectively gave rise to monomeric bis(aminopyridinato) chromium complexes.

3.6. Metal-Metal Distances at the Limit: A Coordination Compound with an Ultra Short Cr-Cr Bond



It highlights the synthesis and the structure of the homobimetallic chromium complex which shows the shortest metal-metal bond distance of 1.7488 Å, of a stable compound measured to date. The reduction of the aminopyridinato ligand stabilized chromium$^{II/III}$ chloride complexes leads to a homobimetallic chromium complex. The short Cr-Cr bond distance shows higher than 4-fold bonding for this complex. The ^{1}H NMR spectrum of the product revealed it to be a diamagnetic compound. Further insight on the bonding situation was obtained from computational studies. The electronic structure of the complex was studied in position space by means of the topological analysis of the calculated DFT-electron density and the electron localizability indicator (ELI-D), as well as by calculation of the delocalization index which show $(\sigma_g)^2(\pi_u)^4(\delta_g)^4$-configuration for the chromium majority MOs. The two δ_g-MOs always occupy HOMO and HOMO-1, the two π_u-MOs HOMO-5 and HOMO-6, respectively. Energetically in-between these two groups the σ_g-MO and two ligand-centered MOs with a strong N_{amido} contribution can be found. It was calculated that σ_g-MO, the two π_u-MO and one of the two δ_g-MO show pELI-D maxima in the region between the two Cr atoms. The residual δ_g-MO shows four pELI-D maxima at each Cr atom (according to the shape of δ_d-orbital) but not in the interatomic region. A delocalization index $\delta(\Omega_{Cr1}, \Omega_{Cr2}) = 4.2$ was calculated, which significantly differs from the formal bond order of 5.0. However, this finding is consistent with the fact that δd-MOs are weakly bonding.

3.7. Individual Contribution to Joint Publications

The results presented in this thesis were obtained in collaboration with others and published or to be submitted as indicated below. In the following the contributions of all the co-authors to the different publications are specified. The asterisk denotes the corresponding author.

Chapter 4

This work is published in *Eur. J. Inorg. Chem.*, **2006**, 2683-2689, under the title, **"Synthesis and Structure of Trialkyltantalum Complexes Stabilized by Aminopyridinato Ligands"** Awal Noor, Winfried Kretschmer and Rhett Kempe*.

I have synthesized and characterized all the compounds presented in this work and the publication was written by me.

Winfried Kretschmer did the polymerization experiments.

Rhett Kempe supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

Chapter 5

This work is published in *J. Organomet. Chem.*, **2007**, *692,* 4569-4579, under the title, **"Highly Active/Selective and Adjustable Zirconium Polymerization Catalysts Stabilized by Aminopyridinato Ligands"** Winfried P. Kretschmer*, Bart Hessen, Awal Noor, Natalie M. Scott, Rhett Kempe*.

Winfried P. Kretschmer did most of the polymerization experiments and the polymer analysis. He synthesized the aluminium complexes, did the NMR studies of the ligand transfer and helped me to understand the system. The publication was written jointly with Winfried P. Kretschmer.

Bart Hessen provided the polymerization and GPC facility.

I have synthesized and characterized the zirconium compounds of this work and did some of the polymerization studies.

Natalie M. Scott did some of the initial synthetic work.

Rhett Kempe supervised this work and was involved in scientific discussions and suggestions.

Chapter 6

This work is to be submitted to *Eur. J. Inorg. Chem.*, under the title, **"Synthesis and Structure of Zirconium and Hafnium Complexes Stabilized by very Bulky Aminopyridinato Ligands"** Awal Noor, Winfried P. Kretschmer, Germund Glatz, Auke Meetsma, Rhett Kempe*.

I have synthesized and characterized all the compounds presented in this work and the publication was written by me.

Polymerization experiments were done jointly with Winfried P. Kretschmer.

Germund Glatz and Auke Meetsma did X-ray analyses of the compounds published in this work.

Rhett Kempe supervised this work and was involved in scientific discussions, suggestions and correction of the manuscript.

Chapter 7

This work has been accepted in *Eur. J. Inorg. Chem.*, under the title, **"Acetylenetitanium Complex Stabilized by Aminopyridinato Ligands"** Awal Noor, Rhett Kempe*.

I have synthesized and characterized all the compounds presented in this work and the publication was written by me.

Rhett Kempe supervised this work and was involved in scientific discussions, suggestions and correction of the manuscript.

Chapter 8

This work is to be submitted under the title, **"Synthesis and Structure of Low Valent Chromium Complexes Stabilized by η^2-Coordinated Aminopyridinato Ligands"** Awal Noor, Germund Glatz, Rhett Kempe*.

I have synthesized and characterized all the compounds presented in this work and the manuscript was written by me.

Germund Glatz did X-ray analyses of the compounds described in this work.

Rhett Kempe supervised this work and was involved in scientific discussions, suggestions and correction of the manuscript.

Chapter 9

This work is submitted to *Angew. Chem.* under the title, **"Metal-Metal Distances at the Limit: A Coordination Compound with an Ultra Short Cr-Cr Bond"** Awal Noor, Frank R. Wagner, Rhett Kempe*.

I have synthesized and characterized all the compounds presented in this work.

Frank R. Wagner did the computational studies reported in this paper.

Rhett Kempe supervised this work and was involved in scientific discussions and suggestions.

The manuscript was written by Rhett Kempe, Frank R. Wagner and me.

4. Synthesis and Structure of Trialkyltantalum Complexes Stabilized by Aminopyridinato Ligands

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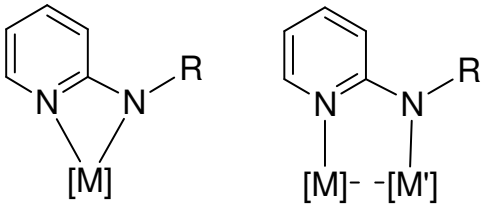
Keywords: Amido ligands / Aminopyridinato ligands / N ligands / Olefin polymerization / Tantalum
Published in *European Journal of Inorganic Chemistry,* 2006, 2683-2689.

Abstract: (4-Methylpyridin-2-yl)(trimethylsilyl)amine (**1**), (6-methylpyridin-2-yl)(trimethylsilyl)amine (**2**), and (2,6-diisopropylphenyl)(pyridin-2-yl)amine (**3**) were deprotonated and used as ligands to synthesize trialkyltantalum complexes. The reaction of 2 equiv. of **1** or **2** with pentabenzyltantalum afforded tribenzyltantalum(V) complexes by toluene elimination. Analogous reaction using **3** failed. Lithiation of **3** followed by the reaction with tribenzyltantalum dichloride gave rise to the corresponding tribenzyl complex. Other alkyltantalum complexes stabilized by this ligand environment can be prepared by treating tantalum pentachloride with 2 equiv. of lithiated **3** to form a bis(aminopyridinato)tantalum trichloride. The reaction of this trichloride with 3 equiv. of alkyllithium compounds like methyllithium affords the corresponding trialkyltantalum complexes. X-ray diffraction studies of four of the synthesized complexes were carried out. They adopt two different coordination environments, either slightly distorted capped octahedrons (sterically less demanding aminopyridinato ligands) or pentagonal bipyramids (bulkier aminopyridinato ligands). The alkyl species were surprisingly stable at elevated temperatures and no formation of mixed alkyl/alkylidene complexes was observed. Alkyl cation formation and the behaviour of a selection of these compounds in olefin polymerization were explored.

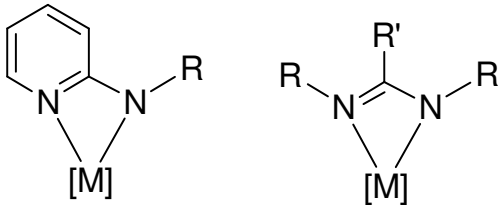
4.1. Introduction

Aminopyridinato ligands[1] are interesting amido ligands due to the flexibility of their binding mode and the ligand "asymmetry". The dominating binding mode in early transition metal and lanthanide chemistry[2] is the strained η^2-coordination (Scheme 1, left). The bridging binding mode (Scheme 1, right) is characteristic for late metal complexes. Of course, there are exceptions like homoleptic strained η^2 bound aminopyridinato palladium complexes.[3] The ligand "asymmetry" caused by the two different donor functionalities–the pyridine and the amido function might be considered as an additional interesting feature especially in comparison to the closest "relatives" the amidinates.[4]



Scheme 1. Important binding modes of deprotonated 2-aminopyridines ([M] and [M'] = transition metal moiety; R = aryl, silyl or alkyl substituent).

Group 5 metal complexes stabilized by aminopyridinato ligands (Scheme 2, left) have been investigated to a lesser extent than related amidinate[5] complexes (Scheme 2, right).



Scheme 2: Aminopyridinato (left) and amidinate (right) ligands ([M] = group 5 metal complex moiety; R, R' = substituent).

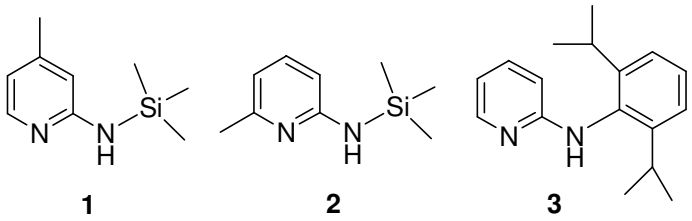
The first Ap (Ap = aminopyridinato) group-5 metal complex was published by Gambarotta 15 years ago.[6] A more detailed investigation of some aspects of the coordination chemistry of these ligands was started by Polamo. He applied the "direct synthesis" method to prepare a variety of niobium and tantalum complexes stabilized by aminopyridinato ligands.[7,8,9,10] Interesting examples of low oxidation state group 5 metal aminopyridinato complexes have been described by Gambarotta and Cotton.[11] Reactivity studies employing organometallic species are still very rare.[12,13] Because of this lack we became interested in alkyltantalum complexes. We also expect an easy access into this chemistry because of the recently

published Kol synthesis of $[Ta(CH_2C_6H_5)_5]$.[14,15] We report here on the synthesis and structure of organotantalum complexes stabilized by aminopyridinato ligands. The formation of organocations and the relevance to olefin polymerization of a selection of these species is also discussed.

4.2. Results and Discussion

Synthesis of Ligands

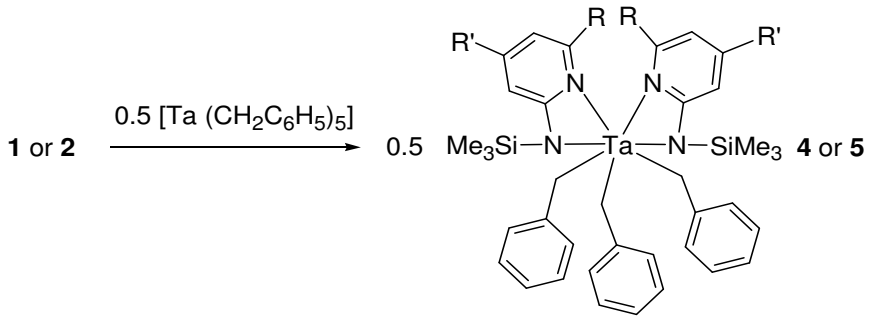
Compounds **1** and **2** were prepared as reported.[16,17] The aminopyridine **3** can be synthesized by palladium-catalyzed arylamination.[18] The reaction of 2-bromopyridine with 2,6-diisopropylaniline and sodium *tert*-butoxide in the presence of a Pd catalyst in toluene (90 °C, 48 h) leads after workup and purification by crystallization to compound **3** (Scheme 3) in good yield (70 %).



Scheme 3: Applied aminopyridines.

Synthesis and Structure of Tantalum Complexes

Reaction of 2 equiv. of **1** with $[Ta(CH_2C_6H_5)_5]$ in hexane at 60 °C results in the formation of **4** by toluene elimination (Scheme 4). No formation of benzylidene functionalities is observed by NMR spectroscopy in the course of this reaction. Complex **4** was isolated after workup in hexane in moderate yield as a yellow crystalline material.



Scheme 4: Synthesis of **4** and **5** (**4**: R =H, R' = CH_3; **5**: R = H, R' = CH_3).

The three benzyl groups show a broad doublet at 2.96 ppm at room temperature indicative of a fast ligand exchange. Crystals suitable for X-ray analysis were grown from a hexane solution. Details of the X-ray crystal structure analysis are summarized in Table 3. The molecular structure of **4** is shown in Figure 1. The coordination of **4** is best described as a distorted capped octahedron. The methylene carbon of one of the benzyl ligands (C15) as well as the two pyridine-N-atoms occupy the first triangle and C8 as well as the two amido-N-atoms the second triangle.

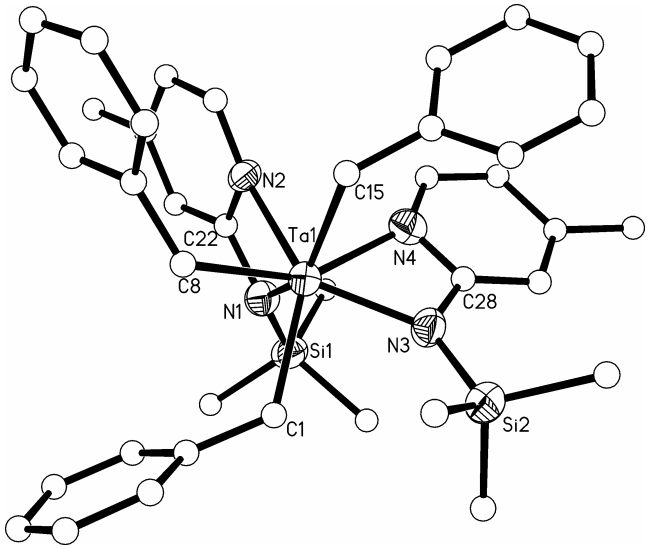


Figure 1. Molecular structure of **4**; selected bond lengths [Å] and angles [°]: Ta–C1 2.248(9), Ta–N4 2.230(8), Ta–N2 2.266(8), Ta–N1 2.123(10), Ta–N3 2.132(8), Ta–C8 2.264(1), Ta–C15 2.257(10), N2–C22 1.332(13), N1–C22 1.400(13), N3–C28 1.376(13); N1–Ta–N2 61.00(3), N1–C22–N2 109.49(8), Ta–N2–C22 92.05(6), Ta–N1–C22 96.31(6), N4–Ta–N3 59.10(3), N3–C28–N4 109.06(8), Ta–N3–C28 96.53(6), Ta–N4–C28 93.21(6), C1–Ta–C8 78.28(4), C15–Ta–C8 78.60(4), C1–Ta–C15 126.83(4).

In order to apply a slightly increased steric bulk at the close proximity of the metal centre two equiv. of **2** were reacted with $[Ta(CH_2C_6H_5)_5]$ under same conditions as applied for **4**. The resulting benzyl complex **5** was obtained in moderate yield (Scheme 4). The three benzyl groups give two doublets at 2.98 and 3.18 ppm. The product was characterized by X-ray analysis (molecular structure is shown in Figure 2) in addition to NMR spectroscopy. Details of the X-ray crystal structure analysis are summarized in Table 3. The coordination of **5** is best described as a capped octahedron (first triangle N1, N2 and N4; second triangle N3, C15 and C22). In both cases, the rigid aminopyridinato ligands induce distortion from the ideal symmetry. The Ta-C bond lenghts lay in the ranges of 2.247-2.318 Å and 2.248-2.264 Å

respectively for **4** and **5**, which clearly indicate η^1 binding of all benzyl groups in the solid state.

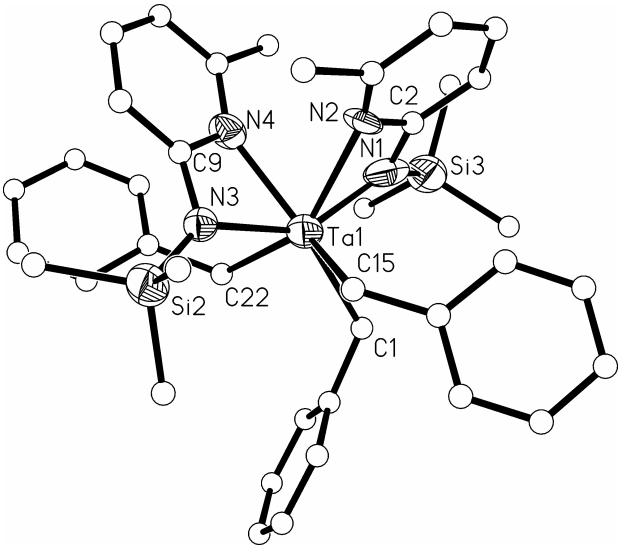
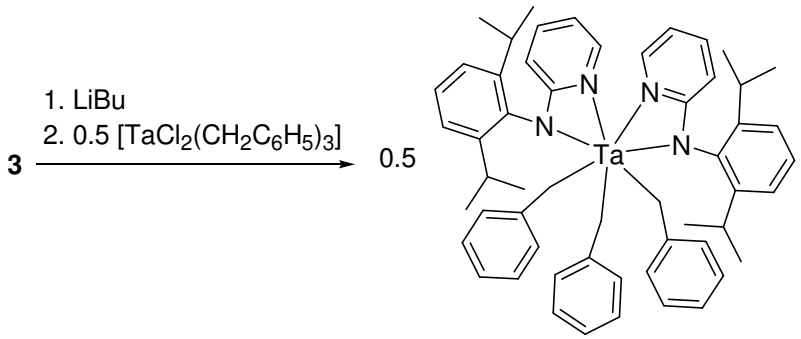


Figure 2. Molecular structure of **5**; selected bond lengths [Å] and angles [°]: Ta–C1 2.250(11), Ta–N2 2.382(10), Ta–N4 2.248(10), Ta–N1 2.069(11), Ta–N3 2.212(9), Ta–C15 2.247(11), Ta–C22 2.318(10), N2–C2 1.379(16), N4–C9 1.355(14), N1–C2 1.375(15), N3–C9 1.391(13); C1–Ta–C15 81.09(5), C1–Ta–C22 76.15(4), C15–Ta–C22 130.18(5), N1–Ta–N2 60.31(4), N1–C2–N2 109.77(12), Ta–N1–C2 101.02(8), Ta–N2–C2 87.22(9), N4–Ta–N3 61.44(3), Ta–N3–C9 93.36(7), Ta–N4–C9 92.80(7), N4–C9–N3 112.12(11).

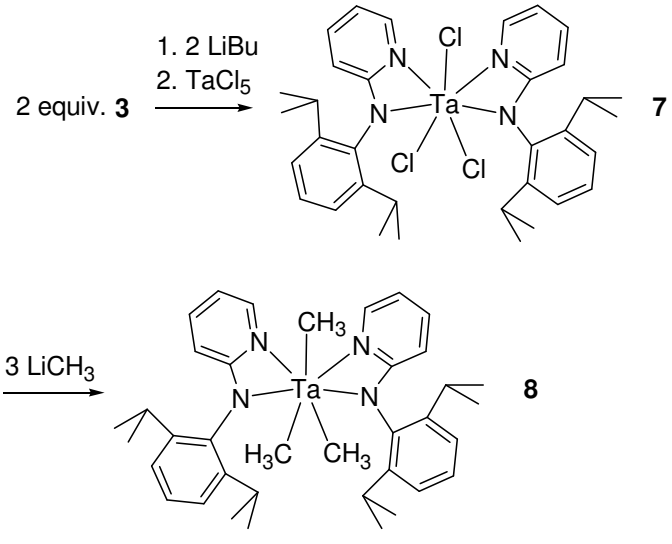
In order to increase the steric bulk of the used aminopyridinato ligands drastically we introduced the 2,6-diisopropylphenyl substituent at the amido nitrogen atom instead of the $SiMe_3$ group. Application of the toluene elimination route starting from $[Ta(CH_2C_6H_5)_5]$ was not successful and salt metathesis was adopted. The reaction of 2 equiv. of the lithium salt of **3** with $[TaCl_2(CH_2C_6H_5)_3]$[14] at room temperature (Scheme 5) resulted in the formation of the tribenzyl complex **6**. The ^1H NMR spectra of this compound shows two different sets of signals for benzyl protons. One signal corresponds to four methylene protons of the benzyl substituents and the other to the remaining two. We propose a pentagonal-bipyramidal arrangement in solution with the two amino and one of the benzyl moieties in the equatorial plane. Because of the steric bulk of the deprotonated **3** no exchange on the NMR time scale at room temperature is observed. Two benzyl resonances were found, one at δ = 3.60 ppm and the second at δ = 2.79 ppm.



6

Scheme 5: Synthesis of **6**.

The first Schrock-type alkylidene complex, [Ta($CH_2{}^tBu)_3$-(CH^tBu)], was prepared in 1974.[19] Various mono- and polydentate ligand systems that support this functionality have been introduced in recent years and several synthetic methodologies are known that lead to the alkylidene complexes like, for instance, an α-elimination reaction sequence from dialkyl precursors.[20] However, the complexes **4**, **5**, and **6** do not form mixed benzyl/benzylidene complexes neither during the synthesis nor by treatment of the trialkyltantalum complexes at elevated temperatures (80 °C). In order to prepare other trialkyltantalum complexes supported by deprotonated **3**- the sterically most demanding of the three ligands described in this publication we synthesized the corresponding tantalum trichloride species **7** (Scheme 6).



Scheme 6: Synthesis of **7** and **8**.

Compound **7** can be synthesized by the reaction of **3** with $TaCl_5$ (Polamo method "direct synthesis"[7]). Because of a relatively low yield using this "direct synthesis" salt metathesis (Scheme 6) was applied and gave rise to **7** in better yield. The success of salt metathesis using lithiated **3** and $TaCl_5$ is in contrast to Polamo's observations. He developed his method due to problems with the salt metathesis approach in similar reactions. The trimethyl tantalum complex **8** results when 3 equiv. of LiMe were treated with **7**. The X-ray crystal structures of **7** (Figure 3) and **8** (Figure 4) revealed a distorted pentagonal bipyramidal coordination. In **7** the two chloro ligands occupy the axial positions of the polyhedra and the two pairs of nitrogen and the third chloride ion form the pentagonal (equatorial) plane.

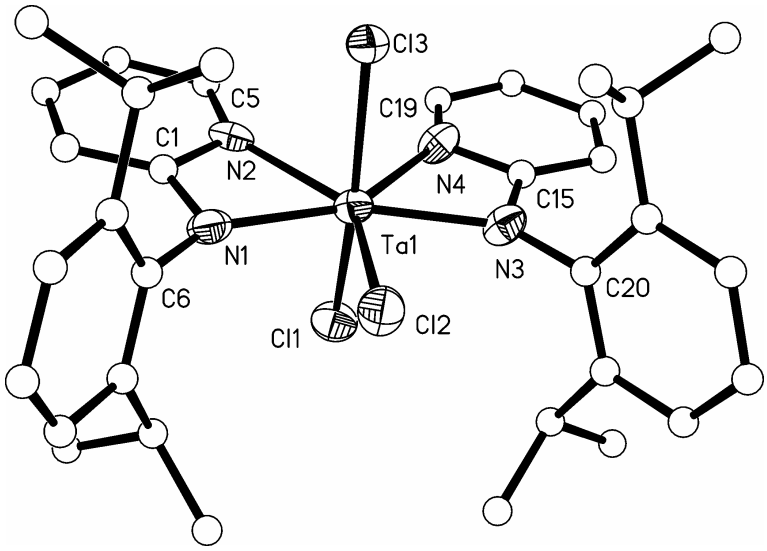


Figure 3. Molecular structure of **7**; selected bond lengths [Å] and angles [°]: C1–N2 1.339(11), C1–N1 1.376(11), C5–N2 1.337(11), C6–N1 1.438(11), C15–N3 1.391(10), C15–N4 1.352(12), C19–N4 1.337(11), C20–N3 1.422(11), N1–Ta1 2.072(8), N2–Ta1 2.264(8), N3–Ta1 2.098(7), N4–Ta1 2.263(7), Cl1–Ta1 2.352(2), Cl2–Ta1 2.349(2), Cl3–Ta1 2.376(2); C1–N1–Ta 100.45(6), C1–N2–Ta 92.92(5), C1–N2–C5 118.55(8), C15–N4–C19 118.13(8), C15–N3–Ta 99.66(6), C15–N4–Ta 93.42(5), N1–Ta–N2 60.05(3), N3–Ta–N4 60.38(3), N2–C1–N1 106.52(8), N4–C15–N3 106.53(8), Cl1–Ta–Cl3 160.49(8), Cl1–Ta–Cl2 99.87(9), Cl2–Ta–Cl3 99.63(9).

In **8** methyl ligands adopt the same coordination sites as the chloro ligands in **7**. A distortion is caused by the small N-Ta-N angles due to the strained binding mode of the aminopyridinato ligands. In **7** they are 60.1(3) and 60.4(3)° and in **8**, 59.25(2)°. Both lead to a situation in which all other angles in the pentagonal plane are over 72°. In **7** N-Ta-Cl(2) *cis*-angles are 77.9(2) and 77.3(2)° and in **8** the N-Ta-C(1) *cis*-angles are 77.43(10)°. N-Ta-N angles

involving the amido bonds of the aminopyridinato ligands are the widest, 84.4(3)° in **7** and 86.65(18)° in **8**. The Cl_{ax}-Ta-Cl_{eq} angles for **7** are 99.87(9)° and 99.64(9)° and the C_{ax}-Ta-C_{eq} angles for **8** are 94.02(15)° and 93.23(16)°. Details of the X-ray crystal structure analyses of **7** and **8** are summarized in Table 3. The ^{1}H NMR shows two different sets of signals for methyl protons. The two methyl groups present above and below the pentagonal plane (axial positions) show a resonance at 1.26 ppm and the in plane methyl ligand at 0.63 ppm. Similar observations have been made for **6**. The trimethyl complex **8** was found to be stable towards elevated temperatures in terms of the formation of mixed methyl methylidene species. Heating of **8** in toluene at 80 °C for 40 minutes did not affect the structure of the compound. When harsher conditions were employed, i.e., heating to 120 °C for 30 minutes **8** started to decompose slowly without any signs of methylidene formation.

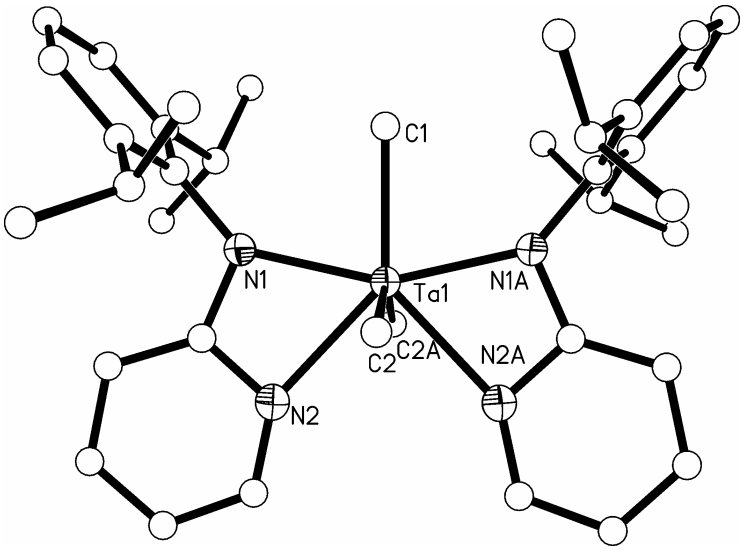
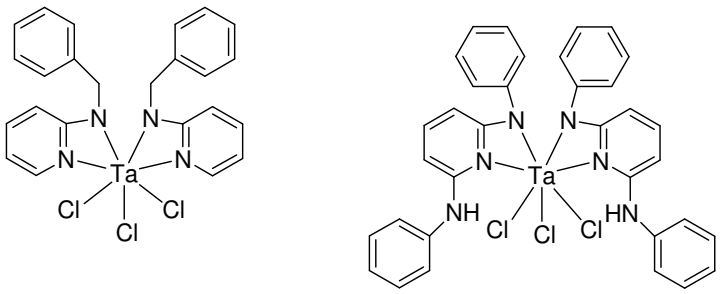


Figure 4. Molecular structure of **8**; selected bond lengths [Å] and angles [°]: C1–Ta1 2.190(6), C2–Ta1 2.203(4), N1–Ta1 2.105(3), N2–Ta1 2.332(4), N1–Ta1–N1A 154.86(19), C1–Ta1–C2 106.89(12), N1–Ta1–C2 93.23(16), C2A–Ta(1)–C2 146.2(2), N1–Ta1–N2 145.88(13), N1–Ta1–N2 59.25(13), C1–Ta1–N2 136.67(9), C2–Ta1–N2 77.25(16), N2–Ta1–N2A 86.65(18).

Formation of Organocations and their Application in Ethylene Polymerization

Because of the high ethylene polymerization activity observed for the tantalum complexes **9** and **10**[12] (Scheme 7) we became interested in exploring the polymerization behaviour of some of the complexes discussed in this study.



Scheme 7. Structure of **9** and **10**

Ethylene polymerization studies were performed using **7** (Table 1) and **8** (Table 2) as precatalysts.

Table 1. Ethylene polymerization result, activation of **7** using PMAO (PMAO = polymethylaluminoxane $([AlOMe]_x)$[a]

Pre-cat. [μmol]	PMAO [mmol]	PE [g]	Activity [kg(PE)mol(Ta)$^{-1}$h^{-1}bar^{-1}]
10	5	0.2	16

[a] 260 mL toluene solvent, 5 bar ethene, 50 ºC, 15 min run time, Ta:Al = 1:500 (m/m).

Table 2. Ethylene polymerization results, activation of **8** using trialkylammonium tetrakis(pentafluorophenyl)borate

Run no.	Pre-cat. [μmol]	$B(C_6F_5)_4^-$ [μmol]	TIBAO [mmol]	PE [g]	Activity [kg(PE)mol(Ta)$^{-1}$h^{-1}bar^{-1}]
1	-	11	0.1	0.05	-
2	10	11	0.1	0.06	5
3	10	22	0.1	0.16	13

260 mL toluene solvent, 5 bar ethene, 80 ºC, 15 min run time, Ta:Al = 1:20 (m/m); TIBAO = tetra-*iso*-butylaluminoxane ($[i\text{-}Bu_2Al]_2O$).

Ethylene polymerization activity of **7** after activation with PMAO is low. This is in contrast to what was observed for **9** and **10**. Thus, we expected to see a significantly better catalyst performance when starting from the methyl complex **8** and activating with trialkylammonium tetrakis(pentafluorophenyl)borate. No significant improvement in terms of activity was found by changing the activation procedure. Because of the low activity no molecular weight analysis of the polymers was accomplished. The generation of cationic complexes was studied in an NMR scale reaction. Reaction of **8** with 1 equiv of $B(C_6F_5)_3$ in CD_2Cl_2 results in the abstraction of one of the axial methyl group. A new resonance at 1.86 ppm was observed for

this methyl group in ^{1}H NMR spectra. The resulting organocation is not stable in solution and decomposes rapidly into unidentified species.

4.3. Conclusions

Trialkyltantalum complexes stabilized by aminopyridinato ligands can be synthesized by salt metathesis or toluene elimination. They adopt the coordination of either a capped octahedron or a pentagonal bipyramid depending on the steric demand of the aminopyridinato ligand. These trialkyltantalum complexes are thermally unusually stable towards α-H-elimination. They form rather unstable organocations and the instability of these cations might be the reason for the low activity in ethylene polymerization.

Table 3. Details of the X-ray crystal structure analyses.

Compound	**4**	**5**	**7**	**8**
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	C2/c	$P2_1/n$	P-1	C2/c
a [Å]	23.279(3)	13.955(3)	10.3627(9)	14.1240(10)
b [Å]	18.761(2)	14.704(3)	19.7101(18)	12.5620(10)
c [Å]	20.204(3)	18.617(3)	21.343(2)	22.694(2)
α [°]			96.120(7)	
β [°]	117.557(8)	91.680(2)	103.540(7)	93.375(5)
γ [°]			90.410(7)	
V [Å^3]	7823(3)	3818(2)	4211.6(7)	4019.5(6)
Crystal size [mm^3]	0.12 x 0.1 x 0.08	0.12 x 0.11 x 0.06	0.16 x 0.1 x 0.05	0.99 x 0.34 x 0.44
ρ_{calcd} [g cm^{-3}]	1.381	1.414	1.434	1.333
μ [mm^{-1}] (Mo Kα)	0.7107	0.7107	0.7107	0.7107
T [K]	193(2)	193(2)	193(2)	193(2)
θ range, [°]	1.47–26.19	1.77–26.21	1.35–25.83	1.80–25.68
No. of unique refl.	7732	7506	15909	3604
No. of obsd. refl. [I > 2σ(I)]	4508	2470	9228	3508
No. of parameters	415	409	880	214
wR^2 (all data)	0.1282	0.1033	0.1018	0.0924
R value [I>2σ (I)]	0.0755	0.0542	0.0632	0.0312

4.4. Experimental Section

General Procedures

Synthesis and Structure Analysis: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenktype glassware on a dual manifold Schlenk line or in an argonfilled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1 ppm O_2). Non-halogenated solvents were dried by distillation from sodium wire/benzophenone. Commercial $TaCl_5$ (Lancaster) was used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled prior to use. NMR spectra were recorded with a Bruker ARX at 250 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. X-ray crystal structure analyses were performed by using a STOE-IPDS II diffractometer equipped with an Oxford Cryostream low-temperature unit. Crystal structure data are presented in Table 3. Structure solution and refinement was accomplished using SIR97, [21] SHELXL97, [22] and WinGX. [23] CCDC-297697 (**4**), -297698 (**5**), -297699 (**7**), and -297700 (**8**) 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.

Polymerization: Toluene (Aldrich, anhydrous, 99.8%) was passed through columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger, and molecular sieves (4 Å, Aldrich). Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (4 Å, Aldrich). PMAO (4.9 wt.-% Al in toluene, Akzo Nobel), *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)borate [6.2 wt.-% $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals], and TIBA (Witco) were used as received. TIBAO was prepared according to published procedures.[24]

Synthesis of 3:[25] Toluene (25 mL) was added to a Schlenk vessel charged with tris(dibenzylideneacetone)dipalladium (0.082 g, 0.09 mmol), NaO^tBu (0.750 g, 7.8 mmol), and 1,3-bis(diphenylphosphanyl)propane (0.074 g, 0.18 mmol). To the resulting suspension 2-bromopyridine (0.57 mL, 6 mmol) and 2,6-diisopropylaniline (1.47 mL, 7.8 mmol) was added. The solution was stirred and heated to 90 °C for 48 h. On cooling to room temperature, water and diethyl ether were added to the resulting red solution. The organic phase was extracted and the remaining inorganic phase was further washed with diethyl ether (3×20 mL). The combined organic phases were washed with a saturated sodium chloride solution

and dried with sodium sulfate. The solvent was removed under reduced pressure and the resulting reddish solid was purified using silica gel chromatography (eluent: dichloromethane). The solvent was removed under reduced pressure and the product was recrystallized from pentane as a white crystalline material. Yield 1.07 g (70%). $C_{17}H_{22}N_2$ (254.37): calcd. C 80.27, H 8.72, N 11.01; found C 80.30, H 8.75, N 10.82. ^{1}H NMR (C_6D_6, 298 K): δ = 1.10 [d, 12 H, $CH(CH_3)_2$], 3.39 [sept, 2 H, $CH(CH_3)_2$], 5.88 (d, 1 H, Py-3-H), 6.20 (dd, 1 H, Py-5-H), 6.89 (t, 1 H, Py-4-H), 7.17–7.29 (m, 3 H, Ar-CH), 7.99 (dd, 1 H, Py-6-H), 8.34 (br. s, 1 H, NH) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 23.98 [4 CH_3, $CH(CH_3)_2$], 28.67 [2 CH, $CH(CH_3)_2$], 105.62 (CH, Py-C-5), 112.94 (CH, Py-C-3), 124.22 (2 CH, Ar-C-9,11), 134.69 (CH, Py-C-4), 137.68 (2 CH, Ar-C-8,12), 148.45 (1 C, Ar-C-7), 148.57 (1 CH, Py-C-6), 160.51 (1 CH, Py-C- 2) ppm.

Synthesis of 4: Compound **1** (0.380 g, 2 mmol, 425 µL) in hexane (5 mL) was added slowly to a stirred solution of [$Ta(CH_2C_6H_5)_5$] (0.636 g, 1 mmol) in hexane (15 mL) at –33 °C. The mixture was warmed to room temperature and was further heated at 60 °C for 2 h as a color change was observed from brown to deep red. The mixture was filtered and the volume of the solvent was reduced in vacuo. The solution was cooled at –25 °C overnight to afford a yellow crystalline material. Yield 0.365 g (43%). $C_{39}H_{51}N_4Si_2Ta$ (812.97): calcd. C 57.62, H 6.32, N 6.89; found C 57.36, H 6.62, N 6.29. ^{1}H NMR (C_6D_6, 298 K): δ = 0.40 [s, 18 H, $Si(CH_3)_3$], 1.61 (s, 6 H, CH_3), 2.96 (br. d, 6 H, CH_2), 5.76 (d, 2 H, Py-5-H), 5.88 (s, 2 H, Py-3-H), 6.74 (t, 3 H, Ar-4-H), 6.89–7.10 (m, 14 H, Py-6-H, Ar-2, 3, 5, 6 H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 2.45 (6 C, 6 CH_3), 21.6 (2 C, 2 CH_3), 99.40 (br. and flat s, 3 CH_2), 111.87 (2 CH, Py-C-3/5), 114.05 (2 CH, Py-C-3/5), 122.49 (3 CH, Benz-C-4), 126.83 (6 CH, Benz-C-3,5), 128.20 (6 CH, Benz-C-2,6), 141.51 (3 C, Benz-C-1), 151.53 (2 C, Py-C-4), 153.26 (2 CH, Py-C-6), 164.91 (2 C, Py-C-2) ppm.

Synthesis of 5: Compound **2** (0.463 g, 2.57 mmol, 546 µL) in hexane (5 mL) was added slowly to a stirred solution of [$Ta(CH_2C_6H_5)_5$](0.817 g, 1.28 mmol) in hexane (15 mL) at –33 °C. The mixture was warmed to room temperature and further heated at 60 °C for 2 h. The mixture was filtered and the volume of the solvent was reduced in vacuo. The solution was cooled at –25 °C overnight to afford a yellow crystalline material. Yield 0.460 g (44%). $C_{39}H_{51}N_4Si_2Ta$ (812.97): calcd. C 57.62, H 6.32, N 6.89; found C 56.73, H 6.24, N 6.54. ^{1}H NMR (C_6D_6, 298 K): δ = 0.27 [s, 18 H, $Si(CH_3)_3$], 1.92 (s, 6 H, CH_3), 3.15–2.96 (2 d, 6 H, CH_2), 5.65 (d, 2 H, Py-5-H), 5.83 (d, 2 H, Py-3-H), 6.69 (dd, 6 H, Benz-2,6-H), 7.00 (t, 6 H,

Benz- 3,5-H), 7.44 (t, 2 H, Py-4-H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 2.57 (6 C, 6 CH_3), 21.56 (2 C, 2 CH_3), 100.34 (3 CH_2), 108.34 (2 CH, Py-C-3/5), 113.95 (2 CH, Py-C-3/5), 122.66 (3 CH, Benz-C-4), 126.67 (6 CH, Benz-C-3,5), 129.42 (6 CH, Benz-C-2,6), 138.32 (3 C, Benz-C-1), 151.97 (2 CH, Py-C-4), 153.17 (2 C, Py-C-6), 161.49 (2 C, Py-C-2) ppm.

Synthesis of 6: To a stirred solution of **3** (0.557 g, 2.14 mmol) in diethyl ether (10 mL), nBuLi (1.34 mL, 1.6 M, 2.14 mmol) was added at 0 °C. This "ligand solution" was warmed slowly to room temperature and stirred for 2 h. This solution was slowly added to [$TaCl_2(CH_2C_6H_5)_3$] (0.562 g, 1.07 mmol) in hexane (10 mL) at room temperature. The mixture was stirred overnight and a color change from red to dark brown was observed. LiCl was filtered off and the volume of the solvent was reduced in vacuo. The solution was cooled at –25 °C overnight to afford an orange crystalline material. Yield 0.564 g (55%). $C_{55}H_{63}N_4Ta$ (961.06): calcd. C 68.74, H 6.61, N 5.83; found C 67.44, H 6.64, N 5.51. ^{1}H NMR (C_6D_6, 298 K): δ = 1.17 [d, 12 H, $CH(CH_3)_2$], 1.25 [d, 12 H, $CH(CH_3)_2$], 2.79 (s, 2 H, CH_2), 3.60 (s, 4 H, 2 CH_2), 3.85 [sept, 4 H, 4 $CH(CH_3)_2$], 5.52 (d, 2 H, Py-3-H), 5.81 (t, 2 H, Py-5-H), 6.22 (d, 4 H, Ar-H), 6.27 (d, 2 H, Py-4-H), 6.62 (dd, 2 H, Py-6-H), 6.78–6.67 (m, 5 H, Ar-H), 6.94–6.86 (m, 6 H, Ar-H), 7.19–7.16 (m, 6 H, Ar-CH) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 23.22 [8 CH_3, $CH(CH_3)_2$], 26.28 [2 CH, $CH(CH_3)_2$], 28.80 [2 CH, $CH(CH_3)_2$], 83.50 (3 C, CH_2), 106.53 (2 CH, Py-C-3/5), 112.39 (2 CH, Py-C-3/5), 123.18 (4 CH, Ar-C-9,11), 125.31 (6 CH, Benz-C-3,5), 126.57 (6 CH, Benz-C-2,6), 127.09 (3 CH, Benz-C-4), 129.96 (4 CH, Ar-C-8,12), 139.55 (2 CH, Ar-C- 10), 141.87 (2 CH, Py-C-4), 143.08 (2 C, Ar-C-7), 146.36 (3 C, Benz-C-1), 148.46 (2 CH, Py-C-6), 169.21 (2 CH, Py-C-2) ppm.

Synthesis of 7: Method I: $TaCl_5$ (1.432 g, 4 mmol) and **3** (2.035 g, 8 mmol) were heated at 110 °C. The melt started to turn dark brown immediately. During the reaction gas formation was observed. After 1 h, toluene (30 mL) was added and the dark-red reaction mixture was further refluxed for 2 h. The solution was filtered while hot and the volume was reduced until red crystals began to appear. The solution was cooled and a red crystalline material was obtained overnight. Yield 1.103 g (35%). $C_{34}H_{42}Cl_3N_4Ta$ + 0.5 C_7H_8 (840.10): calcd. C 53.61, H 5.51, N 6.67; found C 53.67, H5.54, N 6.08. ^{1}H NMR (C_6D_6, 298 K): δ = 1.15 [d, 12 H, $CH(CH_3)_2$], 1.46 [d, 12 H, $CH(CH_3)_2$], 2.10 (s, 3 H, toluene) 3.86 [sept, 4 H, $CH(CH_3)_2$], 5.74 (d, 2 H, Py-3-H), 6.05 (t, 2 H, Py-5-H), 6.83 (t, 2 H, Py-4-H), 7.28–7.16 (m, 6 H, Ar-H), 8.06 (d, 2 H, Py-6-H) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 24.73 [4 CH_3, $CH(CH_3)_2$], 24.95 [4 CH_3, $CH(CH_3)_2$], 28.22 [4 CH, $CH(CH_3)_2$], 107.56 (2 CH, Py-C-3/5), 113.50 (2 CH, Py-C-3/5),

124.46 (4 CH, Ar-C-9,11), 140.19 (2 CH, Ar-C-10), 140.66 (CH, Py-C-4), 141.15 (2 C, Ar-C-7), 147.37 (4 C, 2 CH, Ar- C-8,12, Py-C-6), 169.86 (2 C, Py-C-2) ppm. **Method II:** Lithiated **3** (1.041 g, 4 mmol) in diethyl ether (20 mL) was added to $TaCl_5$ (0.716 g, 2 mmol) in toluene (5 mL) at room temperature and the reaction mixture was stirred at room temperature overnight. The solution was filtered and the solvent was removed in vacuo. The red residue was washed with hexane (5 mL) and dried under vacuum. Yield 0.92 g (58%).

Synthesis of 8: LiMe (1.88 mL, 1.6 M, 3 mmol) was added to a stirred suspension of **7** (0.794 g, 1 mmol) in hexane (20 mL) at –40 °C. The red suspension was warmed to room temperature as the color started changing from red to yellow. The suspension was further stirred for 2 h. The brown solution was filtered and the residue washed with diethyl ether (5 mL). The volume was reduced in vacuo and the solution was cooled at –25 °C overnight to afford a yellow crystalline material. Yield 0.432 g (59%). $C_{37}H_{51}N_4Ta$ (732.78): calcd. C 60.65, H 7.02, N 7.65; found C 60.37, H 7.04, N 7.50. ^{1}H NMR (C_6D_6, 298 K): δ = 0.63 (s, 3 H, CH_3), 1.13 [d, 12 H, $CH(CH_3)_2$], 1.26 (s, 6 H, 2 CH_3),1.34 [d, 12 H, $CH(CH_3)_2$], 3.61 [sept, 4 H, $CH(CH_3)_2$], 5.54 (d, 2 H, Py-3-H), 6.18 (dd, 2 H, Py-5- H), 6.86 (t, 2 H, Py-4-H), 7.24–7.17 (m, 6 H, Ar-8,9,10-H) ppm.^{13}C NMR (C_6D_6, 298 K): δ = 24.10 [4 CH_3, $CH(CH_3)_2$], 24.18 [4 CH_3, $CH(CH_3)_2$], 25.10 (3 CH_3), 27.75 [2 CH, $CH(CH_3)_2$], 27.93 [2 CH, $CH(CH_3)_2$], 105.67 (2 CH, Py-C-3/5), 113.36 (1 CH, Py-C-3/5), 113.56 (1 CH, Py-C-5), 124.45 (4 CH, Ar-C-9,11), 127.09 (1 CH, Ar-C-10), 127.14 (1 CH, Ar-C-10), 138.91 (1 CH, Py-C-4), 139.11 (1 CH, Py-C-4), 141.32 (4 CH, Ar-C-8,12), 146.09 (4 CH, Py-C-6, 2 C, Ar-C-7), 168.32 (1 C, Py-C-2) ppm.

General Description of Polymerization Experiments: The catalytic ethylene polymerization reactions were performed in a stainless steel 1-L autoclave (Medimex) 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 and a sample outlet for continuous reaction monitoring. At 5 bar of ethylene pressure multiple injection of the catalyst with a pneumatically operated catalyst-injection system was used. During a polymerization run the pressure, ethylene flow, inner and outer reactor temperature, and the stirrer speed were monitored continuously. In a typical semi-batch experiment, the autoclave was evacuated and heated at 125 °C for 1 h prior to use. The reactor was then brought to the desired temperature with stirring at 600 rpm and charged with 230 mL of toluene together with either the required

amount of PMAO [2.76 g, Ta/Al = 1:500 (m/m)] or TIBAO scavenger [1 mL of a 0.1 M stock solution in toluene, Ta/Al = 1:20 (m/m)]. After pressurizing with ethylene to reach 5 bar total pressure the autoclave was equilibrated for 5 min. Subsequently 1 mL of a 0.01 M stock solution of the tantalum complex in toluene was injected together with 30 mL of toluene, to start the reaction. In the case where trialkylammonium tetrakis(pentafluorophenyl)borate was the activator, 1 mL of the tantalum complex stock solution and the appropriate amount of borate [0.12 g, Ta/B = 1:1.1 (m/m)] were premixed before injection. During the run the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing flow. After the desired reaction time, the reactor was vented and the residual PMAO/TIBAO was destroyed by addition of 20 mL of ethanol. Polymeric product was collected, stirred in acidified ethanol for 30 min, and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and subsequently in vacuo at 80 °C.

Acknowledgments

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5. Highly Active/Selective and Adjustable Zirconium Polymerization Catalysts Stabilized by Aminopyridinato Ligands

Dedicated to Prof. Gerhard Erker

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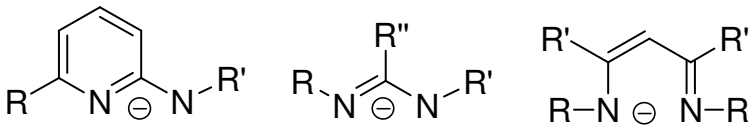
Abstract: This paper describes a substantial enhancement of the aminopyridinato ligand stabilized early transition metal chemistry by introducing the sterically very demanding 2,6-dialkylphenyl substituted aminopyridinato ligands derived from (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridin-2-yl]-amine (**1a**–H, ApH) and (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridin-2-yl]- amine (**1b**–H, Ap*H). The corresponding bis(aminopyridinato) zirconium dichloro complexes, [Ap_2ZrCl_2] (**3a**) and [$Ap^*_2ZrCl_2$] (**3b**) and the dimethyl analogues, [Ap_2ZrMe_2] (**4a**) and [$Ap^*_2ZrMe_2$] (**4b**) (Me = methyl) were synthesized, using standard salt metathesis routes. Single-crystal X-ray diffraction was carried out for the dichloro derivatives. Both zirconium metal centres have a distorted octahedral environment with a cis-orientation of the chloride ligands in **3a** and a closer to trans-arrangement in **3b**. The dimethyl derivatives are proven to be highly active ethylene polymerization catalysts after activation with [$R_2N(Me)H][B(C_6F_5)_4$] (R=$C_{16}H_{33}$–$C_{18}H_{37}$). During attempted co-polymerizations of α-olefins (propylene) and ethylene high activity and selectivity for ethylene and nearly no co-monomer incorporation was observed. Increasing the steric bulk of the ligand going from (2,6-dimethylphenyl) to (2,4,6-triisopropylphenyl) substituted pyridines, switches the catalyst system from producing long chain a-olefins to polymerization of ethylene in a living fashion. In contrast to the dimethyl complexes only [$Ap^*_2ZrCl_2$] in the presence of MAO at elevated temperature gave decent polymerization

activity. NMR investigations of the reaction of dichloro complexes with 25 equiv. of MAO or $AlMe_3$ at room temperature revealed, that [Ap_2ZrCl_2] decomposes under ligand transfer to aluminium and formation of [$ApAlMe_2$], while [$Ap^*_2ZrCl_2$] remains almost unreacted under the same conditions. The aminopyridinato dimethyl aluminum complexes, [$ApAlMe_2$] (**5a**) and [Ap^*AlMe_2] (**5b**) were synthesized independently and structurally characterized. The aluminium complexes **5a** and **b** show no catalytic activity towards ethylene, when ''activated'' with [$R_2N(Me)H$][$B(C_6F_5)_4$].

5.1. Introduction

In recent years the organo zirconium chemistry of the ancillary aminopyridinato ligands (Scheme 1, left)[1] has been increased rapidly. Relatively simple and high yield synthesis, combined with easy modification of steric and electronic properties of the precursor aminopyridines have led to a wide variety of mono, bis, tris- and tetrakis(aminopyridinato) derivatives. In general, aminopyridinato ligands are interesting non-symmetric versions of bidentate monoanionic N-Ligands suited to stabilize early and late transition metals and can be considered as related to amidinates[2] or NacNac[3] ligands (Scheme 1, middle and right, respectively).

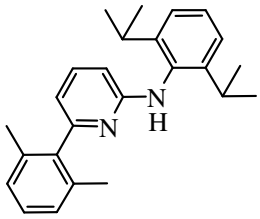


Scheme 1. Aminopyridinato ligands (left) and other related bidentate monoanionic N-Ligands (R, R' and R'', for instance, alkyl or aryl substituents).

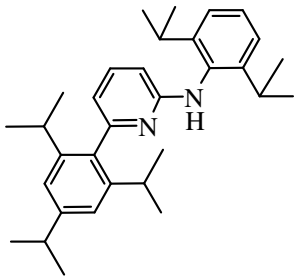
However, comparing with the literature only a few aminopyridinato ligand based zirconium olefin polymerization catalyst systems, with low or moderate activity have been reported. It seems that the olefin polymerization chemistry of the aminopyridinato zirconium complexes has been limited so far since no ligands were available that could avoid ligand redistribution to tris- or tetrakis(aminopyridinato) complexes independent from the ''remaining'' ligands [4]. Contributions by Scott and co-workers emphasize the importance of the introduction of steric bulk at the pyridine ring[4f,4g]. Thus, we concluded that the bulky aminopyridinato ligands containing 2,6-disubstituted phenyl substituents at the amido N-atom and at the pyridine ring introduced by us recently[5] could address this problem.

In this contribution, we report the synthesis of zirconium polymerization catalysts based on sterically very demanding aminopyridines (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-

pyridin-2-yl]-amine (**1a**–H, ApH) and (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridin-2-yl]- amine (**1b**–H, Ap*H) (Scheme 2). It is shown that such zirconium aminopyridinato complexes are thermally robust and highly active ethylene polymerization catalysts. Furthermore, a selective discrimination of propylene in ethylene/propylene-copolymerization is observed. Such monomer selectivity especially in combination with high temperature stability could be of relevance for instance in chain shuttling polymerizations.[6] Furthermore, the increase of steric bulk going from Ap to Ap* switches the catalyst system from producing long chain α-olefins to polymerization of ethylene in a living fashion, if no chain transfer agents are present. The introduction of bulkiness does not necessarily lead to very high polymerization activity of the corresponding metal complexes. For related, sterically demanding amidinate-based zirconium catalysts only low activities were observed.[7]



1a-H, Ap-H



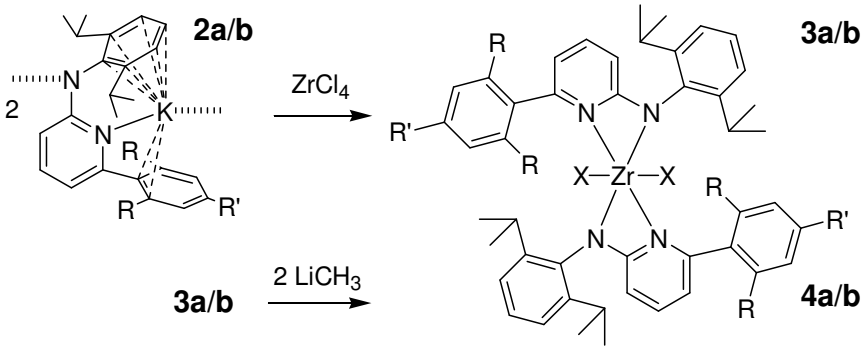
1b-H, Ap*-H

Scheme 2. 2,6-dialkylphenyl substituted amino pyridines.

5.2. Results and Discussion

Synthesis and characterization of the zirconium dichloride and dimethyl complexes

The reaction of the potassium salts **2a/b**[5a] with $ZrCl_4$ leads to the zirconium dichlorides **3a/b** which on reacting with methyl lithium convert selectively to the bisalkyls **4a/b** (Scheme 3).



Scheme 3. Synthesis of **3a/b** and **4a/b** (**3**: X = Cl, **4**: X = CH_3; **a**: R = Me, R' = H; **b**: R, R' = *i*-Pr)

The molecular structures of **3a/b** were determined via X-ray crystal structure analysis (for experimental details see Table 1) and are shown in Fig. 1. The space filling model clearly indicates a well protected active site of **3b** compared to **3a**.

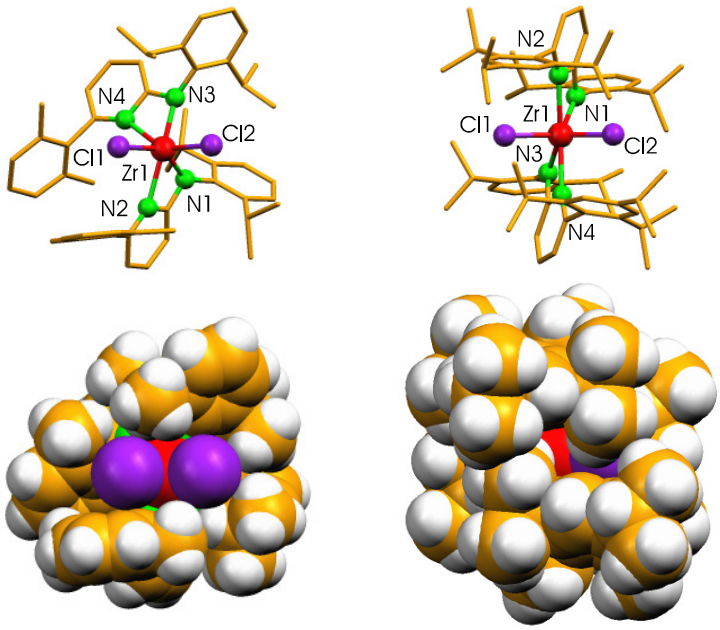


Figure 1. Molecular structures of **3a** (left) and **3b** (right). Selected bond lengths [Å] and angles [°]: **3**[a]) Zr1 N3 2.123(3), Zr1 N1 2.145(3), Zr1 N4 2.348(3), Zr1 N2 2.355(3); N3 Zr1 N4 60.04(11), N1 Zr1 N2 59.44(11), Cl2 Zr1 Cl1 96.47(4); **3b**) N1 Zr1 2.154(4), N2 Zr1 2.358(4), N3 Zr1 2.184(4), N4 Zr1 2.338(4); N3 Zr1 N4 59.40(14), N1 Zr1 N2 59.52(14), Cl1 Zr1 Cl2 123.08(6).

The overall coordination environment of complexes **3a/b** can best be described as distorted octahedron with *cis* orientated chlorides for **3a** [96.47(4)°], while the Cl–Zr–Cl angle of **3b** is significantly closer to a transoide arrangement [123.08(6)°]. The differences in the Zr–N_{amido}/Zr–$N_{pyridine}$ bond lengths indicate a localized binding mode. The anionic charge of the N ligand is localized at the N_{amido} atom which means a classic donor functionalized amido metal bond rather than an aminopyridinate is observed.[8]

Despite the bulk of the ligands and their crowded metal environment the aminopyridinato complexes **3a/b** and **4a/b** show a dynamic behaviour in solution. In the ^{1}H and ^{13}C NMR spectra at room temperature for all four complexes only one set of resonances for both ligands is observed (see for instance Fig. 2a).

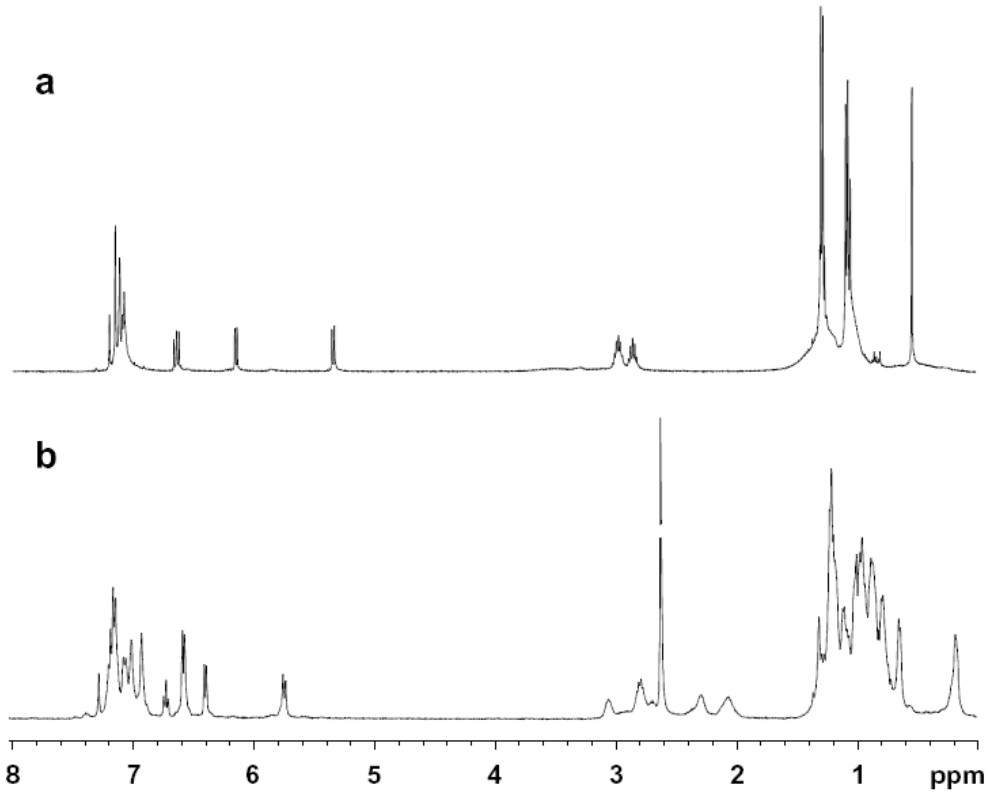
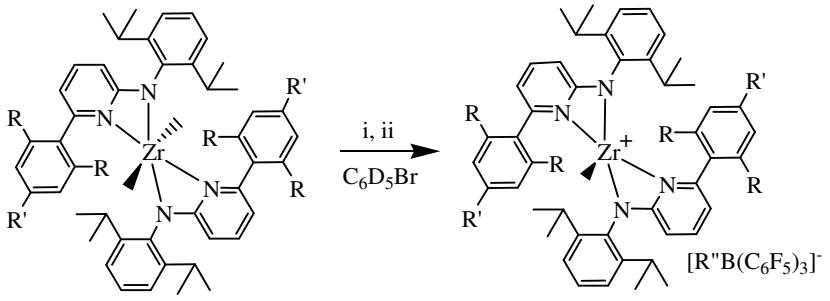


Figure 2. ^{1}H NMR spectrum of [Ap*$_2$ZrMe$_2$] a) (C_6D_6, 20 °C) and after addition of 1 equiv. [PhNMe$_2$H][B(C_6F_5)$_4$] b) (C_6D_5Br, 20 °C).

These together with the splitting of the methyl resonances for each isopropyl group in a doublet of doublets indicates, there is a chemically difference for the upper and lower site of the aromatic rings while the right and left is equal. This observation indicates a fast inter-conversion of the ligands on NMR time scale at room temperature. Reaction of **4b** with N,N-dimethylanilinium-tetra(pentafluorophenyl)borate ([PhNMe$_2$H][B(C_6F_5)$_4$]) in bromobenzene leads to the corresponding [Ap*$_2$ZrMe]$^+$ cation (Scheme 4).



4b (R = R' = *i-Pr)* (R" = Me, C_6F_5)

Scheme 4. Formation of the alkyl zirconium cations through reaction with i) B(C_6F_5)$_3$ and ii) [PhNMe$_2$H][B(C_6F_5)$_4$].

Despite the increase in space around the metal (abstraction of one of the alkyl functions) the increase in electrostatic interaction between the cationic metal centre and the pyridine fragment most likely prevents the dissociation and leads to five chemically unequal isopropyl groups (Fig. 2b). This observation is indicative of a dissociative mechanism of the exchange process observed for **3a/b** and **4a/b** (Fig. 3).

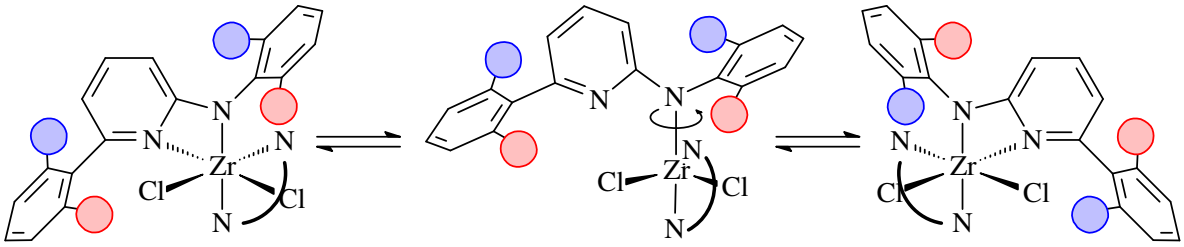


Figure 3. Proposed reaction mechanisms for the dissociative inter-conversion.

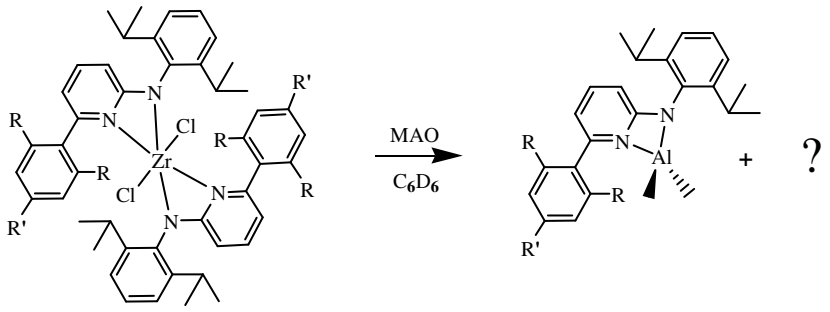
It is notable that reaction of **4b** with tris(pentafluorophenyl)borane give identical ^{1}H and ^{13}C NMR spectra in bromobenzene except the resonances for the dimethylaniline and the different anions. The formation of solvent separated cation-anion-pairs through smooth methyl abstraction was also reflected by the small value of $\Delta\delta$[(*p*-F)-(*m*-F)] of 2.4 ppm.[9]

Table 1. Details of the X-ray crystal structure analyses of **3a***2C_6D_6, **3b***C_6H_{14}, **5a** and **5b**.

Compound	**3a***2C_6D_6	**3b***C_6H_{14}	**5a**	**5b**
Formula	$C_{59}H_{67}Cl_2N_4Zr$	$C_{67}H_{93}Cl_2N_4Zr$	$C_{27}H_{35}AlN_2$	$C_{34}H_{49}AlN_2$
Molecular weight	994.29	1116.57	414.55	512.73
Crystal system	triclinic	triclinic	orthorhombic	triclinic
Space group	P-1	P-1	Pbca	P-1
a [Å]	10.620(1)	12.191(1)	15.3010(12)	10.9320(10)
b [Å]	12.217(1)	13.561(2)	17.4760(13)	12.0050(10)
c [Å]	20.789(2)	20.431(2)	18.9130(17)	13.4470(11)
α [°]	91.276(5)	106.085(5)	90.000(7)	75.446(7)
β [°]	97.303(6)	91.940(5)	90.000(7)	81.462(7)
γ [°]	95.911(5)	91.558(5)	90.000(6)	70.393(7)
V [$Å^3$]	2659.4(8)	3241(1)	5057.3(7)	1605.1(2)
Z	2	2	8	2
Crystal size [mm^3]	0.15 x 0.12 x 0.1	0.24 x 0.09 x 0.06	0.42 x 0.35 x 0.23	0.45 x 0.36 x 0.25
Habit	Prism	Needle-like	Prism	Prism
Colour	Yellow	Yellow	Yellow	Colorless
ρ_{calcd} [g cm^{-3}]	1.242	1.144	1.089	1.061
T [K]	193(2)	193(2)	193(2)	193(2)
θ range [°]	1.68-25.84	1.56-26.35	1.33-26.03	1.57-26.06
Refl. unique	10196	12821	4813	6076
Refl. Obsd. [$I > 2\sigma(I)$]	6736	3466	2908	3733
Number of parameters	595	652	271	334
wR^2 (all data)	0.1381	0.0918	0.1537	0.1113
R value [$I > 2\sigma(I)$]	0.0543	0.0414	0.0705	0.0507

Olefin polymerization and formation of Aluminium aminopyridinates

Despite the fact that the difference in the aminopyridinato ligands Ap and Ap* is quite small, the influence on the polymerization activity of their complexes **3a** and **b** if activated with MAO was found to be huge. As shown in Table 2, **3b** polymerizes ethylene highly actively[10] at elevated temperature. Ethylene consumption was observed over the whole time period (15 min). Complex **3a** was almost inactive after a few minutes under the same conditions.



3a (R' = H, R = Me)
3b (R = R' = *i-Pr)*

5a (R' = H, R = Me)
5b (R = R' = *i-Pr)*

Scheme 5. MAO assisted aminopyridinato ligand transfer from Zr to Al.

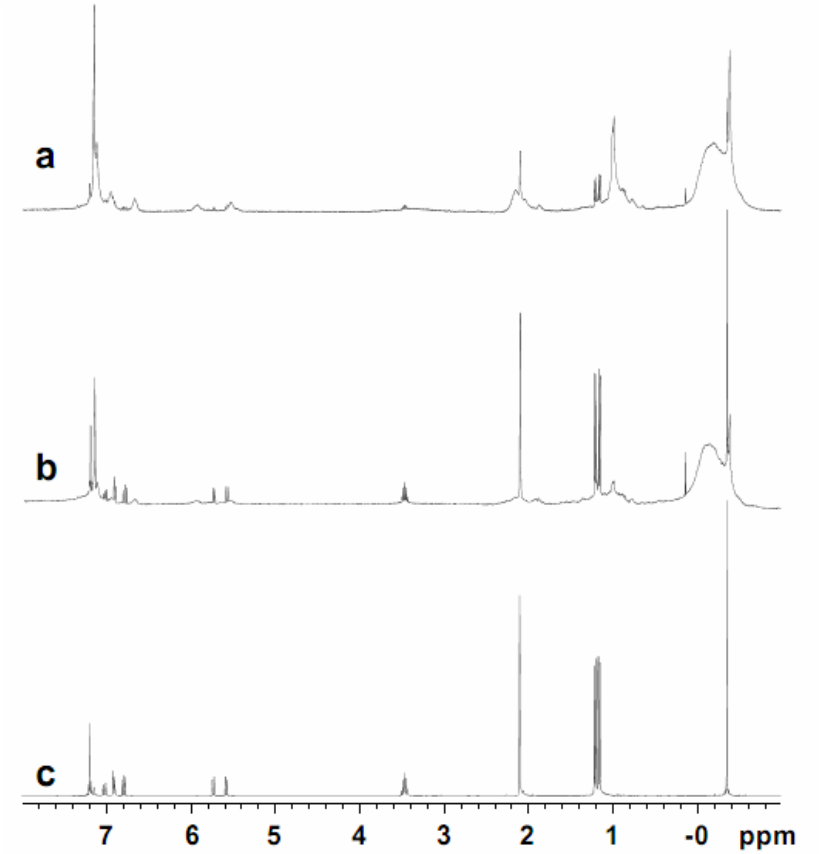
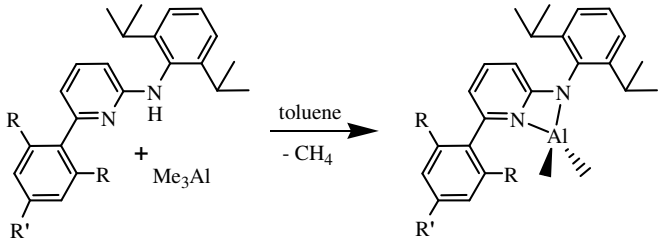


Figure 4. ^{1}H NMR spectra (C_6D_6, 20 °C) of [Ap_2ZrCl_2] + 25 equiv. d-MAO a) after 5 min and b) after 6 h. c) ^{1}H NMR spectrum (C_6D_6, 20 °C) of [$ApAlMe_2$].

To gain more insight into this different behaviour we studied the stability of **3a** and **3b** against d-MAO ("dry methylalumoxane") in NMR tube experiments. NMR tubes were charged with 10 µmol of dichloride **3a/b** in 0.5 mL of deutero-benzene before 25 equiv. of d-MAO were added. While **3b** reacts very smoothly (50% in 24 h) with MAO to form the corresponding methyl complex, compound **3a** shows a fast decomposition to insoluble products and ligand

transfer to aluminium (Scheme 5, Figure 4). After 5 min an NMR detectable amount of [ApAlMe$_2$] (**5a**) was found. After 6 h **5a** seems to be the only Ap containing species present. To prove this observation we independently synthesized the aminopyridinato containing dimethyl alumino complexes [ApAlMe$_2$] (Scheme 6, **5a**) and [Ap*AlMe$_2$] (**5b**), by reaction of the aminopyridines **1a-H** and **1b-H** with TMA (trimethylaluminium) in toluene. Removal of all volatiles under reduced pressure gives the spectroscopically pure products as colorless oils, which could be crystallized by very slow evaporation of hexane solutions. The crystal structures are presented in Figure 5.



5a (R' = H, R = Me)

5b (R = R' = *i-Pr)*

Scheme 6. Synthesis of **5a/b**.

Experimental details of the analyses can be found in Table 1. Both structures are mononuclear involving a strained η^2-coordination of the Ap ligand. The Al–N bond distances are quite similar and thus indicative of a binding mode with a high degree delocalization of the anionic function of the Ap ligands. η^2-coordinated Ap aluminium complexes are rare[5c,11,12]. The first compound of this kind was published by Wang and coworkers.[12] The temperature dependence of the polymerization activity of **3a/b** if activated with MAO is shown in Table 2.

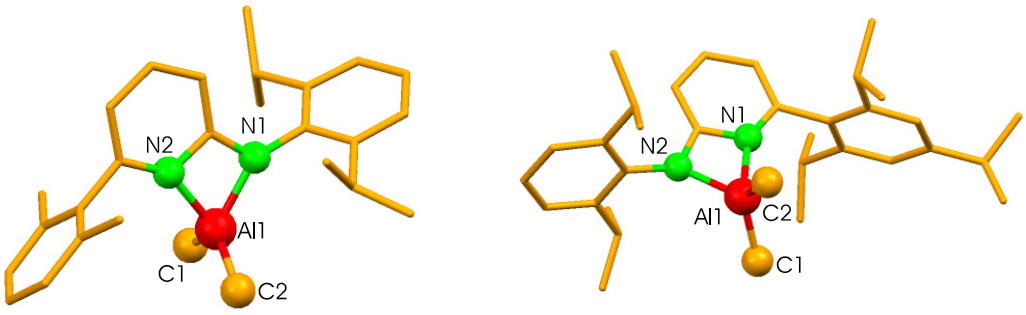


Figure 5. Molecular structures of **5a** (left) and **5b** (right). Selected bond lengths [Å] and angles [°]: **5a**) Al1 N1 1.922(2), Al1 N2 1.959(2), Al1 C1 1.944(3), Al1 C2 1.954(3); N1 Al1 N2 68.87(10), C1 Al1 C2 120.69(16); **5b**) Al1 N1 1.9212(18), Al1 N2 1.9855(17), Al1 C1 1.941(2), Al11 C2 1.943(2); N1 Al1 N2 68.63(7), C1 Al1 C2 119.98(12).

Complex **3b** activated with MAO gives rise to a highly active single site catalyst. No ligand redistribution which can give rise to additional polymerization active species seems to occur during the polymerization process as can be seen from the narrow molecular weight distributions. The low activity at low temperature results mainly from a very slow alkylation due to the poor accessibility of the two chloro ligands (Fig. 1) which was also reflected in the decrease of the induction periods with increasing temperature. Induction periods (time between injection of the pre-catalyst and start of the ethylene uptake) of about 120 s at 30 °C, 75 s at 50 °C and 25 s at 80 °C were observed. The slow alkylation, especially at low temperatures, is also in accordance with the rather broad polydispersity observed for the 30 °C run in comparison to the higher temperature runs. A possibility to overcome the slow alkylation problem is the premixing of **3b** with an excess of MAO prior to injection (Table 2, entry 7). It is also notable that the catalyst system is very robust at elevated temperatures since a very high activity is observed even at 100 °C as well. Ethylene consumption for this run had been observed during the entire polymerization process (15 min) (Table 2, entry 6).

Table 2. Temperature dependence of the ethylene polymerization catalyzed by **3a/b** (activation with MAO).[a]

pre-cat.	**T**	**activator**	$\mathbf{m_{Pol.}}$	**Activity**	$\mathbf{M_w}$	$\mathbf{M_w/M_n}$
	[°C]		[g]	$[kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}]$	$[gmol^{-1}]$	
3a	50	MAO	0.7	280	790000	35.3
3a	80	MAO	0.8	320	675000	14.6
3b	30	MAO	0.4	160	890800	15.1
3b	50	MAO	1.7	680	835200	3.1
3b	80	MAO	6.9	2760	535500	2.0
3b	100	MAO	6.7	2680	392300	2.2
3b[b]	50	MAO	5.9	2360	541500	1.9

[a] pre-cat.: 2 μmol, Zr/Al = 1/500, 260 ml toluene, pressure: 5 bar, t: 15 min.[b] Ten min of premixing of **3b** with 250 equiv. of MAO in 2 ml of toluene (over all Zr/Al = 1/500).

Since ligand transfer processes seems to interfere while alkylation seems to be rate limiting, we became interested in perfluoroarylborate activation protocols. The abstraction of one of the two methyl groups of **4a/b** by ammonium perfluorotetraphenylborate leads to highly active polymerization catalyst systems. Again a notable difference was found between the Ap and Ap* containing catalysts. In contrast to the **3a**/MAO catalyst system **4a** (after activation

with ammonium perfluorotetraphenylborate) was found to be highly active in the formation of long chain α-olefins (Fig. 6) indicating a rather fast β-H-elimination/transfer. Molecular weight distribution clearly shows the presence of a single site catalyst, while no ligand transfer to scavenger was observed. The more crowded pre-catalyst **4b**[13] instead gives high molecular weight polyethylene most likely due to sterically disfavoured direct β-H transfer.[14,15] However, under the applied conditions only multimodal distributed polymers were found (Fig. 7).

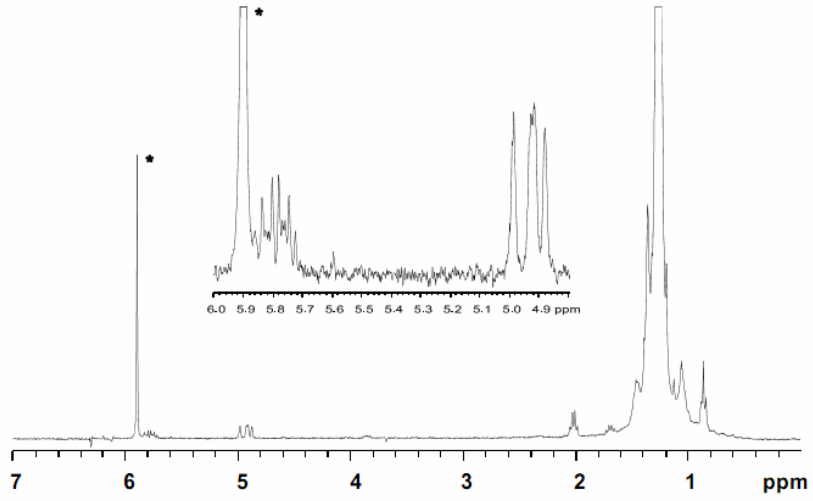


Figure 6. ^{1}H NMR spectrum (*$C_2D_2Cl_4$, 120 °C) of PE (Table 3, entry 3).

The GPC data are also indicative of a rather narrowly distributed main peak. The rapid precipitation of the polymers may lead to a diffusion controlled process and thus to the broad molecular weight distribution. This problem could be addressed by a reduction of the catalyst concentration. Consequently, under a regime which avoids diffusion controlled circumstances a "living" polymerization process (Table 4, Fig. 8) is observed.[16] As long as the living chains stay in solution very fast chain growing (for the first seconds) was evidenced by high ethylene consumption. At some stage the polymer precipitates, ethylene consumption drops down and we observe further chain growing of the precipitated polymer. This part of the chain growing process is shown in Table 4, Fig. 8.

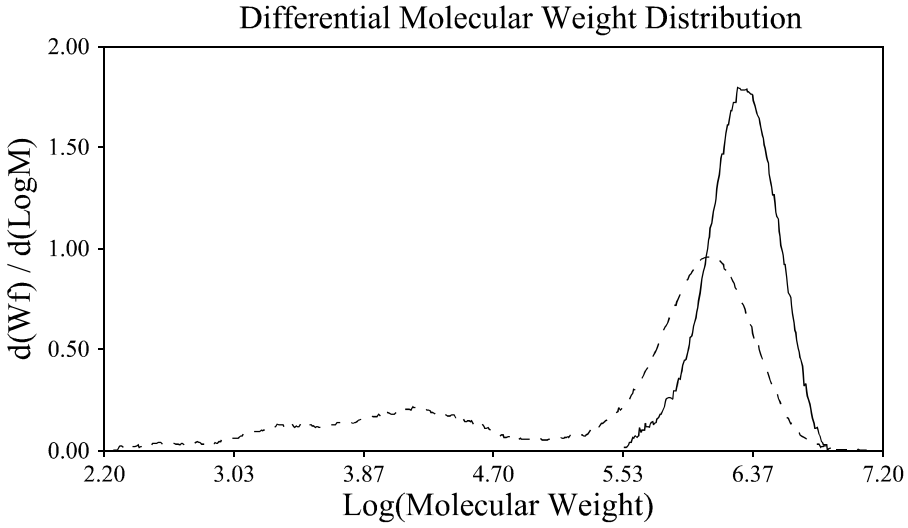


Figure 7. Molecular weight distribution (SEC) of the polymerization experiments listed in Table 3 entry 6 and Table 4 entry 3.

The catalyst systems based on **3a/b** (activation with MAO) or **4a/b** (borate activation) are not active towards α-olefins (for instance propylene).[17] Catalysts that polymerize ethylene and for which olefin insertion is blocked in the presence of α-olefins are well documented. Such a behaviour is observed for instance for lanthanide catalysts.[18] A variety of transition metal complexes get into a dormant state in the presence of α-olefins. Ethylene is able to reactivate the catalyst which leads to specific insertion sequences.[19] Both mechanisms are not valid for the catalysts systems described here as can be seen from experiments in which the catalysts are exposed to a mixture of ethylene and propylene (Table 3, entry 9 and 10).

Table 3. Temperature dependence of the ethylene polymerization catalyzed by **4a/b** (activation with ammonium perfluorotetraphenylborate).[a]

pre-cat.	**T**	**$m_{Pol.}$**	**Activity**	**M_w**	**M_w/M_n**
	[°C]	[g]	[$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]	[$gmol^{-1}$]	
4a	30	1.9	760	12070	2.3
4a	50	4.9	1960	10900	2.1
4a	80	11.1	4440	9670	1.9
4a	100	7.0	2800	9000	2.0
4b	30	3.5	1400	1833000	22.5[b]
4b	50	6.3	2520	1371000	29.8[b]
4b	80	7.9	3160	1063000	393.7[b]
4b	100	9.4	3760	1009000	176.7[b]
4a[c]	80	27.0	54000[c]	8960	2.2
4b[c]	80	28.5	57000[c]	755700	113.1[b]

[a] **pre-cat.**: 2 µmol, ammoniumborate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$ – $C_{18}H_{37}$), Zr/B = 1/1.1, **4** and borate were mixed prior to the injection, scavenger: TIBAO (tetra-*iso*-butyl-alumoxane), Zr/Al = 1/50, 260 ml toluene, pressure: 5 bar, t: 15 min.

[b] multimodal. [c]co-polymerization, pressure: 5 bar propylene, 15 bar total. [c]$kg_{PE}mol_{Kat}^{-1}h^{-1}$.

Even at relatively high partial propylene pressure ethylene is polymerized selectively. NMR spectroscopy of the obtained polymers revealed a propylene insertion of less than 1 mol%. Polymer data are quite similar if carried out in the absence or presence of propylene (Table 3, entries 3 and 9). A highly selective polymerization of ethylene out of an ethylene/propylene mixture seems to be possible. Such a behaviour can result from steric or electronic characteristics. If steric reasons dominate one could describe it as shape selectivity as documented for micro porous materials like zeolites.[20] We concluded that the electronic situation at the metal centre caused by the Ap ligands is dominating the responsibility for such a behaviour since the selectivity is observed for **3/4a** and **b** and not just for the significantly higher crowded zirconium moieties (Fig. 1). Steric reasons are most likely responsible for the product selectivity–the selective formation of either α-olefines (Ap_2Zr alkyl cations) or saturated products attached at the Zr centre in a living fashion or chain transferred to Al if aluminium alkyls are present (in case of Ap^*_2Zr alkyl cations).

Table 4. Living ethylene polymerization at 50 °C.

t	$m_{Pol.}$	Activity	M_w	M_w/M_n
[min]	[g]	[$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]	[$gmol^{-1}$]	
3	0,46	9200	1745000	1.26
9	0,67	4467	1996000	1.33
15	0,88	3520	2301000	1.30

4b: 200 nmol, ammoniumborate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$ – $C_{18}H_{37}$), Zr/B = 1/1.1, **4b** and borate were pre-mixed prior the injection, scavenger: TPPAO {tetra-(2-phenyl-1-propyl)alumoxan}, Zr/Al = 1/500, 260 ml toluene, pressure: 5 bar, T: 50 °C.

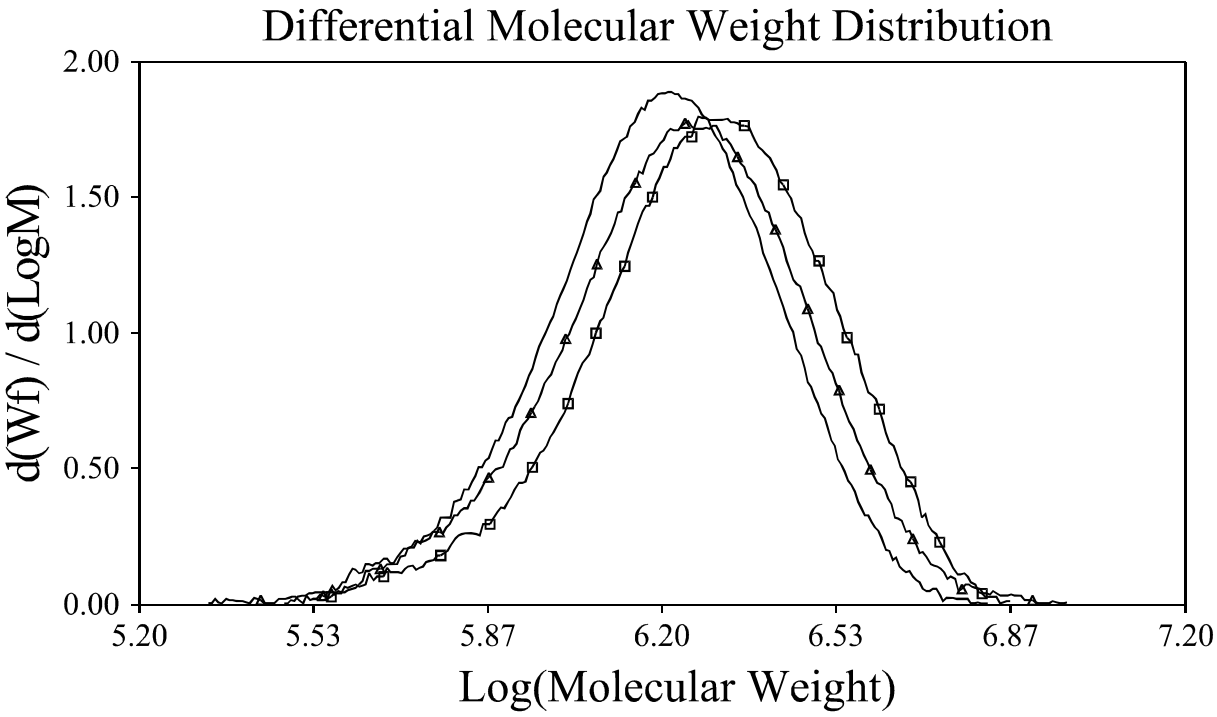


Figure 8. Molecular weight distribution (SEC) of the polymerization experiments listed in Table 4.

5.3. Conclusions

Several conclusions can be drawn from this study. First, the ligands used here namely Ap and Ap^* are able to avoid ligand redistribution to tris- or tetrakis(aminopyridinato) zirconium complexes independent from the "remaining" ligands due to steric demand. Second, the zirconium complexes are thermally robust, highly active and selective ethylene

polymerization catalysts. Out of a mixture of ethylene and propylene, ethylene is polymerized highly selectively. Third, slight changes in the steric demand of the bulky ligand periphery can be used to tune the nature of the formed polymers by maintaining the selectivity issue. Fourth, Ap^*_2Zr alkyl cations can polymerize ethylene in a living fashion even at 50 °C.

5.4. Experimental Section

General aspects

All reactions were carried out under inert atmosphere using standard glove box and Schlenk line techniques. The solvents toluene, pentane, hexane, diethyl ether, and tetrahydrofurane were dried by refluxing over sodium/benzophenone. Benzene-d_6 was dried over sodium/potassium alloy and bromobenzene-d_5 over molecular sieves. Toluene for polymerization (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). *N*,*N*,*N*-Trialkylammonium(tetrapentafluorophenyl)borate ($[R_2NmeH][B(C_6F_5)_4]$, R = $C_{16}H_{33}$–$C_{18}H_{37}$, 6.2 wt.% $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals), trimethyl aluminum (TMA, 2.0 M in toluene, Aldrich), TIBA (Witco), and polymethylaluminoxane ($[MeAlO]_n$, PMAO, 4.9 wt.% in Al, Akzo) were used as received. Tetra-*iso*-butyl aluminoxane ($[i\text{-}Bu_2Al]_2O$, TIBAO) and tetra(2-phenyl-1-propyl) aluminoxane ($\{[CH_3CH(Ph)CH_2]_2Al\}_2O$, TPPAO) were prepared according to published procedure.[21] D-MAO was prepared by removal of all volatile from PMAO (4.9 wt.% in Al, Akzo). The synthesis of **1a**–**H**, **1b**–**H**, **2a** and **2b** has been described previously.[5a]

NMR spectra were recorded on a Varian Gemini 400 (^{1}H: 400 MHz, ^{13}C: 100.5 MHz) or Varian VXR-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) or a Bruker ARX 250 (^{1}H: 250 MHz, ^{13}C: 63 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 25 °C and 120 °C, were referenced internally using the residual solvent resonances, and the chemical shifts (δ) reported in ppm. The polymer samples 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 Polymer Laboratories Ltd. (PL-GPC210) chromatograph, equipped with a capillary differential viscometer (Viscotek), a refractive index (RI) detector and a two-angle (15° and 90°) light scattering photometer at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer

(0.1% weight/volume) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (M_w = 50 000 g/mol) and polystyrene (M_w = 100 000–500 000 g/mole) 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.

General description of ethylene polymerization experiments with MAO

The catalytic ethylene polymerization reactions were performed in a stainless steel 1 L autoclave (Medimex) 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 co-catalyst injection systems and a sample outlet for continuous reaction monitoring. Up to 15 bar of ethylene pressure multiple injections of the catalyst with a pneumatically operated catalyst injection system were used. 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 125 °C prior to use. The reactor was then brought to desired temperature, stirred at 600 rpm and charged with 230 ml of toluene together with PMAO (550 mg of a toluene solution, 4.9 wt.% Al, 1 mmol), if not mentioned different in the text. After pressurizing with ethylene to reach 5 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 together with 30 ml of toluene, to start the reaction. During the run the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing flow. After 15 min reaction time the reactor was vented and the residual aluminium alkyls were destroyed by addition of 100 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 on air and subsequently in vacuum at 80 °C.

Description of ethylene polymerization experiments with ammonium borate activator

The general procedure and conditions as described above were followed, using 1 ml of a 0.05 M solution of TIBAO (tetra-*iso*-butyl-aluminoxan, Zr/Al = 1/50) in toluene instead of PMAO to charge the reactor and a catalyst mixture instead of the stock solution to start the reaction. The catalyst mixture was prepared by successively adding 1 ml of toluene and 1 ml of a 0.002 M catalyst stock solution in toluene to 25 mg of $[R_2NmeH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–

$C_{18}H_{37}$, 6.2 wt.% $B(C_6F_5)_4^-$ in Isopar, Zr/B = 1/1.1). After shaking for 1 min the mixture was injected, to start the reaction.

Alternatively, 1 ml of a 0.05 M solution of TPPAO (tetra(2-phenyl-1-propyl)aluminoxane, Zr/Al = 1/500) in toluene instead of TIBAO and a catalyst mixture prepared by successively adding 1 ml toluene and 100 µl of a 0.002 M catalyst stock solution toluene to 2.5 mg of $[R_2NmeH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$, 6.2 wt.% $B(C_6F_5)_4^-$ in Isopar, Zr/B = 1/1.1) were used.

Description of ethylene/propylene co-polymerization experiments

The general procedure and conditions as described above were followed, using successively 5 bar propylene and 15 bar ethylene to pressurize the reactor.

Synthesis of the metal complexes

Synthesis of 3a.THF (40 mL) was added to $[ZrCl_4(thf)_2]$ (0.38 g, 1.00 mmol) and **2a** (0.80 g, 2.00 mmol), in a Schlenk vessel and the mixture was stirred for 15 h. The solvent was removed in vacuum and hexane (30 mL) was added. The bright yellow reaction mixture was filtered and the filtrate was allowed to stand at room temperature for 24 h to afford yellow crystals. Yield: 0.52 g (54%). Elemental analyses for $C_{50}H_{58}Cl_2N_4Zr$ (877.15): C, 68.5; H, 6.7; N, 6.4. Found: C, 68.1; H, 7.1; N, 6.4%. ^{1}H NMR: (250 MHz, C_6D_6, 298 K): δ = 0.87–1.21 (m, 24H, $H^{24,25,26,27}$), 2.09 (v br s, 12H, $H^{13,14}$), 3.28 (br m, 4H, $H^{21,22}$), 5.52 (br d, 2H, H^3), 5.87 (br d, 2H, H^5), 6.67 (t, 2H, H^4), 6.98–7.13 (m, 12H, $H^{9,10,11,17,18,19}$). ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 20.50 ($C^{13,14}$), 23.83 ($C^{21,22}$), 28.72 ($C^{23,24/25,26}$), 30.18 ($C^{23,24/25,26}$), 103.73 (C^3), 114.55 (C^5), 124.19 ($C^{9,11}$), 126.88 ($C^{18/10}$), 127.78 ($C^{17,19}$), 134.70 ($C^{8/10}$), 135.88 ($C^{8,12}$), 137.86 (C^7), 141.85 (C^4), 144.84 (C^{15}), 148.03 ($C^{16,20}$), 159.30 (C^6), 159.90 (C^2) ppm.

Synthesis of 3b. This compound was obtained in the same way as **3a**, with **2b** (0.99 g, 2.00 mmol) instead of **2a**. Yield: 0.60 g (56%). Elemental analyses for $C_{64}H_{86}Cl_2N_4Zr$ (1073.52): C, 71.6; H, 8.1; N, 5.2. Found: C, 71.4; H, 8.2; N, 4.7%. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.99–1.37 (m, 60H, $H^{24,25,26,27,28,29,30,31,32,33}$), 2.89–3.05 (m, 6H, $H^{13,14,15}$), 3.34 (sep, 4H, $H^{22,23}$), 5.39 (d, 2H, H^3), 6.27 (d, 2H, H^5), 6.65 (dd, 2H, H^4), 7.10–7.24 (m, 10H, $H^{9,11,18,19,20}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 23.0 ($C^{22,23}$), 24.5 ($C^{28,29,30,31,32,33}$), 28.8 ($C^{13,14}$), 31.2 ($C^{24,25,26,27}$), 34.9 (C^{15}), 105.5 (C^3), 116.6 (C^5), 120.8

($C^{9,11}$), 125.0 (C^{19}), 127.2 ($C^{18,20}$), 133.5 (C^{7}), 140.3 (C^{4}), 143.1 (C^{16}), 145.1 ($C^{8,12}$), 146.8 ($C^{17,21}$), 149.4 (C^{10}), 155.9 (C^{6}), 169.1 (C^{2}) ppm.

Synthesis of 4a. CH_3Li (0.71 mL, 1.6 M, 1.13 mmol) was added slowly to **3a** (0.44 g, 0.57 mmol) in hexane (20 mL) at −30 °C. The yellow reaction mixture was allowed to warm up to room temperature and was stirred overnight as color turned into brown. LiCl was filtered off and volume of the filtrate was reduced in vacuum. Yellow crystals were obtained at room temperature after standing for 24 h. Yield: 0.32 g (52%). Elemental analyses for $C_{52}H_{64}N_4Zr$ (836.32): C, 74.7; H, 7.7; N, 6.7. Found: C, 74.0; H, 7.8; N, 6.4%. ^{1}H NMR (250 MHz, C_6D_6, 298 K): $\delta = 0.47$ (s, 6H, CH_3), 0.92 (br d, 12H, $H^{23,24/25,26}$), 1.21 (d, 12H, $H^{23,24/25,26}$), 2.15 (s, 12H, $H^{13,14}$), 3.29 (br m, 4H, $H^{21,22}$), 5.39 (d, 2H, H^{3}), 5.89 (d, 2H, H^{5}), 6.67 (dd, 2H, H^{4}), 7.00–7.16 (m, 12H, $H^{9,10,11,17,18,19}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): $\delta = 20.48$ ($C^{13,14}$), 23.61 ($C^{21,22}$), 28.80 ($C^{23,24/25,26}$), 28.67 ($C^{23,24/25,26}$), 54.38 (2 CH_3), 105.04 (C^{3}), 112.20 (C^{5}), 124.50 ($C^{9,11}$), 126.10 ($C^{18/10}$), 127.84 ($C^{17,19}$), 135.89 ($C^{18/10}$), 136.30 ($C^{8,12}$), 139.10 (C^{7}), 140.91 (C^{4}), 143.24 (C^{15}), 144.58 ($C^{16,20}$), 155.88 (C^{6}), 170.31 (C^{2}) ppm.

Synthesis of 4b. This compound was obtained in the same way as **4a**, with CH_3Li (0.98 mL, 1.6 M, 1.56 mmol) and **3b**, (0.84 g, 0.78 mmol) instead of **3a**. Yield: 0.49 g (61%). Elemental analyses for $C_{69}H_{99}N_4Zr$ (1075.78): C, 77.0; H, 9.3; N, 5.2. Found: C, 77.1; H, 9.2; N, 5.2%. ^{1}H NMR (250 MHz, C_6D_6, 298 K): $\delta = 0.57$ (s, 6H, CH_3), 1.11(d, 24H, $H^{24,25,26,27,28,29,30,31,32,33}$), 1.32 (d, 24H, $H^{24,25,26,27,28,29,30,31,32,33}$), 2.80–3.06 (m, 10H, $H^{13,14,15,22,23}$), 5.38 (d, 2H, H^{3}), 6.18 (d, 2H, H^{5}), 6.65 (dd, 2H, H^{4}), 7.11–7.19 (m, 10H, $H^{9,11,18,19,20}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): $\delta = 23.4$ ($C^{22,23}$), 24.4 ($C^{28,29,32,33}$), 24.8 ($C^{30,31}$), 26.6 ($C^{13,14}$), 31.0 ($C^{24,25,26,27}$), 34.9 (C^{15}), 55.3 (2 CH_3), 105.0 (C^{3}), 114.3 (C^{5}), 120.7 ($C^{9,11}$), 124.6 ($C^{18,20}$), 126.2 (C^{19}), 134.8 (C^{4}), 139.8 (C^{7}), 143.5 ($C^{8,12}$), 144.7 ($C^{17,21}$), 146.8 (C^{10}), 149.3 (C^{16}), 155.8 (C^{6}), 170.5 (C^{2}) ppm.

Synthesis of 5a. A Schlenk vessel was charged with amino pyridine ligand **1a**–**H** (0.106 g, 0.3 mmol) in toluene (2 mL) before trimethylaluminium solution (0.5 mL, 2.0 M Me_3Al in toluene, 1.0 mmol) was added. After stirring for 30 min all volatile was removed, to yield the corresponding, spectroscopic pure [$ApAlMe_2$] (based on ^{1}H NMR) as colorless oil in almost quantitative yield. For X-ray analysis of **5a** the residue was dissolved in 3 mL hexane. Slow evaporation of the solvent over a period of 5 days leave colorless crystals in quantitative yield. Elemental analyses for $C_{27}H_{35}AlN_2$ (414.6): C, 78.2; H, 8.5; N, 6.8. Found: C, 78.1; H, 8.6; N, 6.6%. ^{1}H NMR (400 MHz, C_6D_6, 298 K): $\delta = -0.35$ (s, 6H, H^{AlMe2}), 1.17 (d, 6H,

^3J(H,H) = 6.6 Hz, H^{23-26}), 1.21 (d, 6H, ^3J(H,H) = 6.9 Hz, H^{23-26}), 2.11 (s, 6H, $H^{13,14}$), 3.48 (sept, 1H, ^3J(H,H) = 6.9 Hz, $H^{21,22}$), 5.58 (dd, 1H, ^3J(H,H) = 8.8 Hz,^4J(H,H) = 0.8 Hz, H^3), 5.73 (dd, 1H, ^3J(H,H) = 7.0 Hz,^4J(H,H) = 0.8 Hz, H^5), 6.80 (dd, 1H, ^3J(H,H) = 8.8 Hz, ^3J(H,H) = 7.0 Hz, H^4), 6.91 (d, 2H, ^3J(H,H) = 7.7 Hz, $H^{9,11}$), 7.03 (t, 1H, ^3J(H,H) = 7.7 Hz, H^{10}), 7.12–7.23 (m, 3H; H^{17-19}). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = −10.2 (br, C^{AlMe2}), 19.7 (s, $C^{13,14}$), 24.2 (s, C^{23-26}), 24.7 (s, C^{23-26}), 28.5 (s, $C^{21,22}$), 104.2 (s, C^3), 108.9 (s, C^5), 124.2 (s, $C^{17,19}$), 126.3 (s, C^{18}), 127.6 (s, $C^{9,11}$), 129.0 (s, C^{10}), 135.8 (s, $C^{8,12}$), 137.6 (s, C^7), 138.2 (s, C^{15}), 142.5 (s, C^4), 145.8 (s, $C^{16,20}$), 154.6 (s, C^6), 166.9 (s, C^2) ppm.

Synthesis of 5b. This compound was obtained in the same way as **5a**, with trimethylaluminium (0.2 mL, 2.0 M Me_3Al in toluene, 0.4 mmol) and amino pyridine ligand **1b–H** (0.046 g, 0.1 mmol) instead of **1a–H**. Yield: quantitative. Elemental analyses for $C_{34}H_{49}AlN_2$ (512.8): C, 79.6; H, 9.6; N, 5.5. Found: C, 79.4; H, 9.6; N, 5.4%. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = −0.24 (s, 6H, H^{AlMe2}), 1.07 (d, 6H, ^{3}J(H,H) = 6.6 Hz, H^{24-33}), 1.14 (d, 6H, ^{3}J(H,H) = 6.6 Hz, H^{24-33}), 1.16 (d, 6H, ^{3}J(H,H) = 6.6 Hz, H^{24-33}), 1.21 (d, 6H, ^{3}J(H,H) = 6.6 Hz, H^{24-33}), 1.39 (d, 6H, ^{3}J(H,H) = 6.6 Hz, $H^{28,29,32,33}$), 2.76 (sept, 1H, ^{3}J(H,H) = 6.6 Hz, H^{15}), 2.90 (sept, 2H, ^{3}J(H,H) = 6.6 Hz, $H^{13,14}$), 3.49 (sept, 2H, ^{3}J(H,H) = 6.6 Hz, $H^{22,23}$), 5.61 (d, 1H, ^{3}J(H,H) = 8.8 Hz, H^3), 6.02 (d, 1H, ^{3}J(H,H) = 7.3 Hz, H^5), 6.79 (dd, 1H, ^{3}J(H,H) = 8.8 Hz, ^{3}J(H,H) = 7.3 Hz, H^4), 7.16 (br, 2 H, $H^{18,20}$), 7.19 (br, 3H, $H^{9,11,19}$). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = −9.6 (br, C^{AlMe2}), 23.1 ($C^{28,29,32,33}$), 24.1 (br, $C^{24-29,32,33}$), 24.2 ($C^{24,25,26,27}$), 26.1 ($C^{30,31}$), 28.5 ($C^{22,23}$), 30.9 ($C^{13,14}$), 34.7 (C^{15}), 104.3 (C^3), 111.1 (C^5), 121.0 ($C^{9,11}$), 124.2 ($C^{18,20}$), 126.3 (C^{19}), 133.1 (C^7), 138.1 (C^4), 141.6 ($C^{17,21}$), 145.7 (C^{16}), 146.9 ($C^{8,12}$), 150.1 (C^{10}), 154.9 (C^6), 167.0 ppm (C^2).

Generation of the cationic zirconium alkyl complexes

(a) Reaction with *N*,*N*-dimethylanilinium-tetra(pentafluorophenyl)borate ([$PhNMe_2H$]-[$B(C_6F_5)_4$]): A NMR tube was charged with **4b** (0.022 g, 20 μmol), deutero-bromobenzene (0.5 mL) together with [$PhNMe_2H$][$B(C_6F_5)_4$] (0.016 g, 20 μmol). Afterwards the tube was sealed and shaken for 5 min to become a clear solution before measured. ^{1}H NMR (250 MHz, C_6D_5Br, 298 K): δ = 0.21 (s, 3H, CH_3) 0.60–1.40 (m, 63H, $CH(CH_3)_2$), 2.00–3.20 (m, 10H, $CH(CH_3)_2$), 2.60 (s, 6H, $N(CH_3)_2$), 5.72 (d, 2H, H-3), 6.37 (d, 2H, H-5), 6.59 (d, 2H, PhN), 6.73 (t, 1H, PhN), 7.00–7.20 (m, 13H, H-9,11, 18, 19, 20) ppm. ^{13}C NMR (C_6D_5Br, 298 K): δ = 22.0 ($CH(CH_3)_2$,C-22), 22.5 ($CH(CH_3)_2$,C-23), 23.1 ($CH(CH_3)_2$,C-28), 23.5 ($CH(CH_3)_2$,C-29), 24.1 ($CH(CH_3)_2$, C-30), 24.8 ($CH(CH_3)$, C-31), 25.8 ($CH(CH_3)_2$,C-32,33),

26.2 ($CH(CH_3)$, C-13), 28.7 ($CH(CH_3)_2$,C-14), 31.1 ($CH(CH_3)_2$, C-26,27), 31.3 ($CH(CH_3)_2$, C-24,25), 34.7 ($CH(CH_3)_2$, C15), 54.0 ($N(CH_3)_2$), 73.3 (CH_3), 107.1 (CH, C-3/5), 118.6 (CH, C-3/5), 121.4 (CH, C-9,11), 122.8 (CH, C-18,20), 126.0 ($B(C_6F_5)_4$), 126.2 (CH, C-19), 135.5 ($B(C_6F_5)_4$), 136.7 (CH, C-4), 138.9 ($B(C_6F_5)_4$), 139.0 (C, C-7), 142.6 (C, C-8,12), 144.6(C, C-17,21), 146.5 (C, C-10), 148.0 (C, C-16), 150.6 ($B(C_6F_5)_4$), 155.5 (C, C-6), 165.2 (C, C-2) ppm. ^{19}F NMR (C_6D_5Br, 298 K): δ = 132.1 (*o*-F), 162.6 (*p*-F), 166.5 (*m*-F).

(b) Reaction with tris(pentafluorophenyl)borane ($B(C_6F_5)_3$). A NMR tube was charged with **4b** (0.022 g, 20 µmol), deutero-benzene (0.5 mL) together with $B(C_6F_5)_3$ (0.012 g, 22 µmol) to give a red oil, which was separated from the solvent and dissolved in deutero-bromobenzene (0.5 ml) before measured. ^1H NMR (250 MHz, C_6D_5Br, 298 K): δ = 0.21 (s, 3H, CH_3) 0.60-1.40 (m, 63H, $CH(CH_3)_2$, CH_3B), 2.00–3.20 (m, 10H, $CH(CH_3)_2$), 5.72 (d, 2H, H-3), 6.37 (d, 2H, H-5), 6.96 (dd, 2H, H-4), 7.00–7.20 (m, 10H, H-9,11, 18, 19, 20) ppm. ^{13}C NMR (C_6D_5Br, 298 K): δ = 11.1 (br, $CH_3B(C_6F_5)_3$), 22.0 ($CH(CH_3)_2$,C-22), 22.5 ($CH(CH_3)_2$,C-23), 23.1 ($CH(CH_3)_2$,C-28), 23.5 ($CH(CH_3)_2$,C-29), 24.1 ($CH(CH_3)_2$, C-30), 24.8 ($CH(CH_3)$, C-31), 25.8 ($CH(CH_3)_2$,C-32,33), 26.2 ($CH(CH_3)$, C-13), 28.7 ($CH(CH_3)_2$,C-14), 31.1 ($CH(CH_3)_2$, C-26,27), 31.3 ($CH(CH_3)_2$, C-24,25), 34.7 ($CH(CH_3)_2$, C15), 73.3 (CH_3), 107.1 (CH, C-3/5), 118.6 (CH, C-3/5), 121.4 (CH, C-9,11), 122.8 (CH, C-18,20), 125.8 ($CH_3B(C_6F_5)_3$), 126.2 (CH, C-19), 135.7 ($CH_3B(C_6F_5)_3$), 136.7 (CH, C-4), 138.6 ($CH_3B(C_6F_5)_3$), 139.0 (C, C-7), 142.6 (C, C-8,12), 144.6(C, C-17,21), 146.5 (C, C-10), 148.0 (C, C-16), 150.1 ($CH_3B(C_6F_5)_3$), 155.5 (C, C-6), 165.2 (C, C-2) ppm. ^{19}F NMR (C_6D_5Br, 298 K): δ = 132.2 (*o*-F), 164.9 (t, *p*-F), 167.2 (*m*-F).

NMR tube reaction with d-MAO

(a) A NMR tube was charged with **3a** (0.020 g, 20 µmol), deutero-bromobenzene (0.5 mL) together with d-MAO (0.029 g, 500 µmol). Afterwards the tube was sealed, shaken for 5 min and measured.

(b) A NMR tube was charged with **3b** (0.023 g, 20 µmol), deutero-bromobenzene (0.5 mL) together with d-MAO (0.029 g, 500 µmol). Afterwards the tube was sealed, shaken for 5 min and measured.

Supplementary material

CCDC 289175, 289174, 640085, and 640086 contain the supplementary crystallographic data for **3a**, **3b**, **5a**, and **5b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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6. Synthesis and Structure of Zirconium and Hafnium Complexes Stabilized by very Bulky Aminopyridinato Ligands

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Keywords: Aminopyridinato ligands / N-ligands / Hafnium / Zirconium / Zwitterionic complexes

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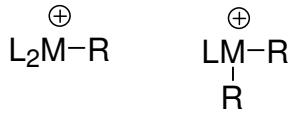
Abstract: Mono(aminopyridinato) complexes of the type [ApM($CH_2C_6H_5$)$_3$] [M = Zr, Hf and Ap = Aminopyridinato] were prepared by reacting the three different sterically demanding aminopyridines with one equivalent of tetrabenzylzirconium or tetrabenzylhafnium in high yields. Single crystal structure X-ray analysis shows distorted geometry for these complexes where one of the three benzyls is η^2-coordinated in the solid state. However all of the three benzyls are equivalent in solution as evidenced by ^{1}H NMR spectrum. Treatment of these neutral complexes with B(C_6F_5)$_3$ afforded the corresponding zwitterionic dibenzyl complexes. η^6-coordination of the phenyl ring of the B-bounded benzyl group to the metal centre was supported by ^{1}H NMR and confirmed by single crystal analysis. These zwitterionic complexes show very low activity in ethylene polymerization at low temperature since the coordination site is blocked by η^6-coordinated phenyl ring. At elevated temperature a moderate activity with the formation of high molecular weight polyethylene (PE) was observed. An attempted abstraction of the second benzyl group failed when the zwitterionic complexes were reacted with an additional equivalent of B(C_6F_5)$_3$. Using one equivalent of [R_2(Me)NH][B(C_6F_5)$_4$] (R = $C_{16}H_{33}$–$C_{18}H_{37}$) instead of B(C_6F_5)$_3$ moderate activities in ethylene polymerization were observed. Treatment of the aminopyridinato metal tribenzyls with [R_2(Me)NH][B(C_6F_5)$_4$] (R = $C_{16}H_{33}$–$C_{18}H_{37}$) gave active ethylene polymerization catalysts, which produced low molecular weight PE in the case of zirconium complexes and higher molecular weight PE in

the case of the hafnium ones. Propylene polymerization under the same conditions failed, while ethylene-propylene copolymers with separated propene-units and alternating sequences were observed.

6.1. Introduction

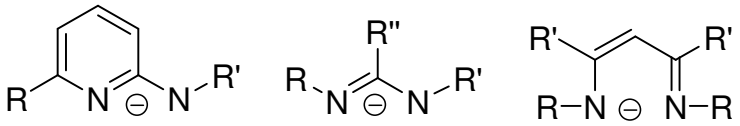
Group 4 metal alkyl cations possessing a weakly coordinating anion are one of the most important classes of compounds with regard to coordinative polymerization of olefins. The Zr/Hf chemistry of dialkyl cations stabilized by anionic polydentate N-ligands is rather unexplored but might be unique due to the presence of two metal-alkyl functionalities and the tuneable N-ligand environment (Scheme 1).



Scheme 1. Mono vs dialkyl cations (L = monoanionic N-ligand).

The starting material to generate such N-ligand stabilized dialkyl cations, Zr/Hf trialkyls stabilized by anionic N-ligands are well documented and known for amidinates,[1] guanidinates[2] diketiminate,[3] macrocyclic amides,[4] tropocoronands[5] and tris(pyrazolyl)borates.[6] Dialkyl cations have been generated from the corresponding tris(pyrazolyl)borates.[6] Unfortunately, these cations are unstable at temperatures above 0 °C and rearrange via ligand degradation.

In recent years the organometallic chemistry of the ancillary aminopyridinato ligands has been increased rapidly.[7] Relatively simple and high yield synthesis, combined with easy modification of steric and electronic properties of the precursor aminopyridines have led to a wide variety of mono, bis, tris- and tetrakis(aminopyridinato) Zr derivatives.[8] In comparison to zirconium, the hafnium chemistry of such ligands is much less developed and only homoleptic complexes have been reported so far.[9] In general, aminopyridinato ligands are interesting 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[10] or diketiminates[11] ligands Scheme 2 (middle and right, respectively).



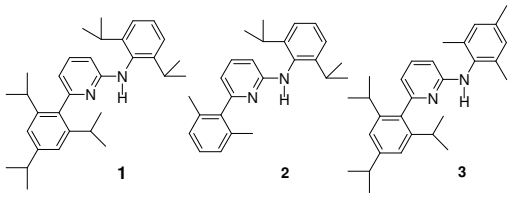
Scheme 2. Aminopyridinato ligands (left) and other related bidentate monoanionic N-Ligands (R, R' and R'', for instance, alkyl or aryl substituents).

We have recently reported that bis(aminopyridinato) zirconium catalysts show not only very high activity in olefin polymerization but also show selectivity in polymerizing ethylene out of ethylene/propylene mixture and exhibit living ethylene polymerization at elevated temperature.[8m] The bis(aminopyridinato) complexes discussed in this study were synthesized via salt metathesis. Since the overall yield was only moderate we became interested in toluene elimination chemistry and observed that the bulky aminopyridinates that gave selectively bis(aminopyridinato) complexes via salt metathesis lead selectively to mono(aminopyridinato) tribenzyl Zr/Hf complexes. Mono(aminopyridinates) of these metals are rare[8b,h,12] and the corresponding trialkyls are unknown. We report here on synthesis and structure of a series of tribenzyl Hf and Zr aminopyridinates and the corresponding dibenzyl zwitterions as well as some aspects of their ethylene and propylene polymerization behaviour.

6.2. Results and Discussion

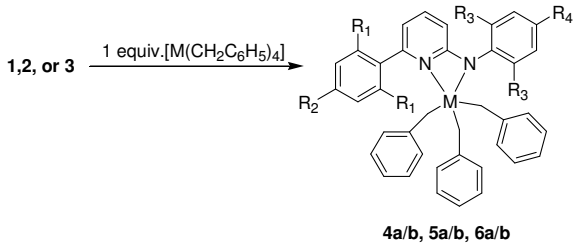
Synthesis and structure of the Zr and Hf tribenzyl complexes

The aminopyridine ligands **1**, **2**, and **3** (Scheme 3) can be synthesized according to the published procedures.[13,14,15]



Scheme 3. Used aminopyridines (**1** = Ap*-H, **2** = Ap^{+}-H and **3** = Ap^{9Me}-H).

Treatment of one equivalent of $[Zr(CH_2C_6H_5)_4]$ or $[Hf(CH_2C_6H_5)_4]$ with **1** in toluene leads to mono substituted complexes **4a** and **4b** respectively owing to clean elimination of one toluene molecule (Scheme 4).



Scheme 4. Syntheses of complexes (**4**: $R_1 = R_2 = R_3 = CH(CH_3)_2$, $R_4 = H$, **5**: $R_1 = CH_3$, $R_2 = R_4 = H$, $R_3 = CH(CH_3)_2$, **6**: $R_1 = R_2 = CH(CH_3)_2$, $R_3 = R_4 = CH_3$; **a**: M = Zr; **b**: M = Hf).

NMR scale reactions show complete conversion to the desired products. X-ray quality crystals of complex **4a** were grown from concentrated pentane solution. Details of the X-ray crystal structure analyses are summarized in Table 1. The molecular structure of **4a** is shown in Figure 1. Two of the benzyl groups are bound to the metal in η^1 manner [Zr1-C40-C41 = 116.4(3)° and Zr1-C47-C48 = 102.5(3)°] while the third displays an acute Zr-C-C_{ipso} angle consistent with η^2-coordination [Zr1-C33-C34 = 89.3(3)°]. Distances between the metal and the ipso carbons of the two benzyl groups are [2.921(4)) and (3.222(4) Å] while a short [2.664(4) Å] distance observed for the third is consistent with an η^2-coordinated benzyl group. The average Zr-CH_2 distance is 2.252 Å, which is slightly shorter than the corresponding distances in the closely related guanidinate [{CyNC[$N(SiMe_3)_2$]Ncy}$Zr(CH_2C_6H_5)_3$ (Cy = cyclohexyl) 2.273(6) Å][2] or diketiminate complexes [(TTP)$Zr(CH_2C_6H_5)_3$ (TTP = 2-*p*-tolylamino-4-*p*-tolylimino-2-pentenato) 2.290(5) Å].[3]

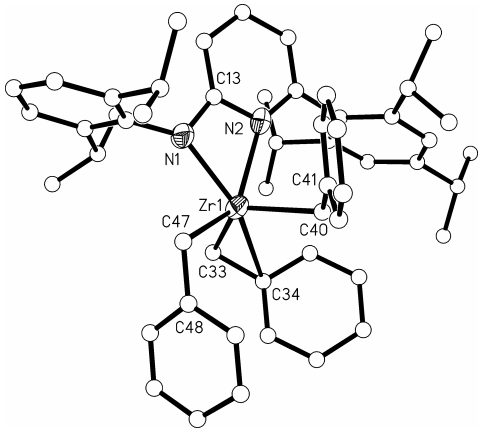


Figure 1. Molecular structure of **4a**, Hydrogen atoms have been omitted for clarity; selected bond lengths [A°] and angles [°]: C33-Zr1 2.243(5), C34-Zr1 2.664(4), C40-Zr1 2.275(5), C47-Zr1 2.236(5), N1-Zr1 2.167(3), N2-Zr1 2.379(4); C34-C33-Zr1 89.3(3), N1-Zr1-C47 82.81(17), C47-Zr1-C33 106.4(2), C47-Zr1-C40 96.7(2), C33-Zr1-C40 126.91(18), N1-Zr1-N2 58.37(12), C47-Zr1-C13 109.33(16), C33-Zr1-C13 109.32(16), C40-Zr1-C13 106.70(16).

Complex **4b** was crystallized from toluene solution along with a solvated toluene molecule and is the first structurally characterized heteroleptic Hf aminopyridinates known to date. The molecular structure is shown in Figure 2. The bonding pattern for the three benzyls is similar to that observed for **4a**, two of them being η^1-coordinated and the third one being η^2-bonded making an acute angle of [Hf1-C8-C9 = 88.06 (19)°] which is comparatively smaller than that of **4a**. This angle as well as η^1 or η^2 binding mode is quite sensitive to packing forces.[2b] The averaged Hf-C bond length [2.236 Å] is, as expected, slightly shorter than the corresponding bond length observed for the analogous Zr complex.[16]

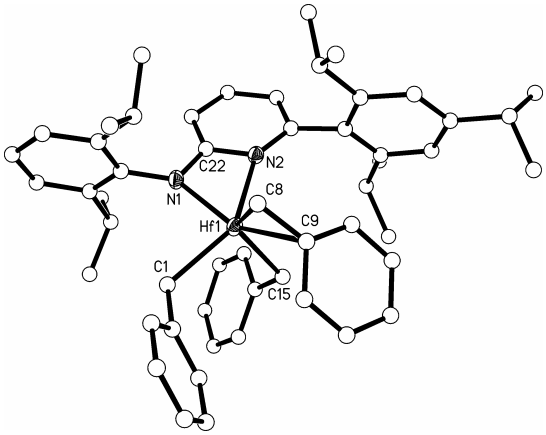


Figure 2. Molecular structure of **4b**, Hydrogen atoms and one toluene molecule have been omitted for clarity; selected bond lengths [Å] and angles [°]: C1-Hf1 2.236(3), C8-Hf1 2.228(3), C9-Hf1 2.632(3), C15-Hf1 2.245(3), N1-Hf1 2.132(2), N2-Hf1 2.360(2); C9-C8-Hf1 88.06(19), C8-Hf1-C1 102.91(13), C8-Hf1-C15 124.01(12), C1-Hf1-C15 96.73(13), N1-Hf1-N2 58.85(9), C15-Hf1-C9 89.93(11), C15-Hf1-C22 103.99(10).

The ^{1}H NMR spectra display single sharp peaks at 2.08 ppm and 1.85 ppm for all CH_2 protons of **4a** and **4b** respectively, and indicate the equivalency for all CH_2 protons in solution.

Addition of **2** to $[Zr(CH_2C_6H_5)_4]$ or $[Hf(CH_2C_6H_5)_4]$ in toluene leads to immediate precipitation of the desired mono(aminopyridinato) tribenzyl zirconium, (**5a)** or hafnium (**5b)** complexes (Scheme 4) in quantitative yield. X-ray quality crystals of **5a** were grown from C_6D_6 and that of **5b** were obtained from the cold solution of the filtered mother liquor. The molecular structure of **5a** is shown in Figure 3 and that of **5b** in Figure 4. Again, as in the case of **4a** one of the three benzyls is η^2-coordinated and the other two benzyl ligands show η^1-coordination.

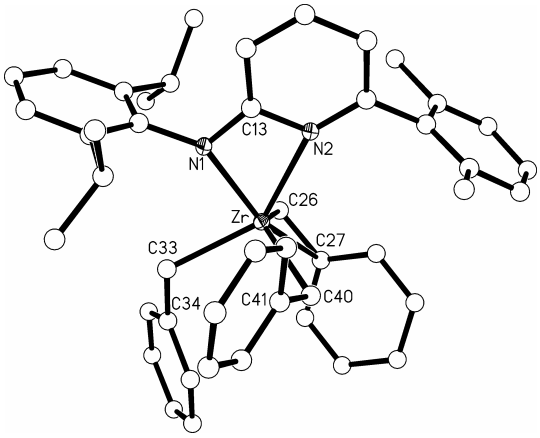


Figure 3. Molecular structure of **5a**; Hydrogen atoms and C_6D_6 molecule are omitted for clarity; selected bond lengths [A°] and angles [°]: N1-Zr 2.180(12), N2-Zr 2.359(11), C26-Zr 2.268(16), C27-Zr 2.629(15), C33-Zr 2.260(16), C40-Zr 2.273(15); N1-Zr-N2 58.70(4), C26-Zr-C33 101.16(6), C26-Zr-C40 125.85 (6), C33-Zr-C40 96.53 (6), C27-C26-Zr 86.74 (9).

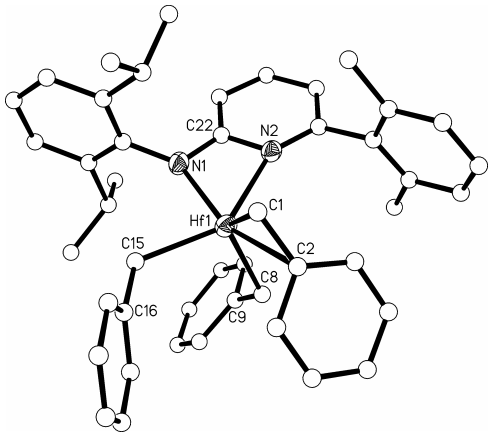


Figure 4**.** Molecular structure of **5b**; Hydrogen atoms are omitted for clarity; selected bond lengths [A°] and angles [°]: C1-Hf1 2.223(4), C2-Hf1 2.669(4) C8-Hf1 2.233(4), C15-Hf1 2.243(4), N1-Hf1 2.136(3), N2-Hf1 2.340(3); C2-C1-Hf1 90.2(2), C1-Hf1-C8 120.81(15), C1-Hf1-C15 99.24(18), C8-Hf1-C15 101.16(18), C1-Hf1-C22 117.43(13), C8-Hf1-C22 105.57(13), C15-Hf1-C22 111.02(14).

The η^2-coordinated benzyl group makes an acute angle of 86.74(9)° in **5a** which is smaller than the equivalent angle of **4a**. The same angle in **5b** is 90.2(2)° which is slightly larger than that of **4a**. The averaged Zr-CH_2 distance (2.267 Å) is comparable to **4a** (2.252 (5) Å) but Hf-CH_2 distance 2.233(4) Å is comparatively shorter than that of **4a**. Similarly the distance of Zr-C_{ipso} [2.629(15)] Å in **5a** is comparatively shorter than **5a** but Hf-C_{ipso} in **5b** of η^2-coordinated benzyl [2.669(4)] Å is comparable to [2.664(4)] Å of **4a**. The differences in Zr-N_{amido}

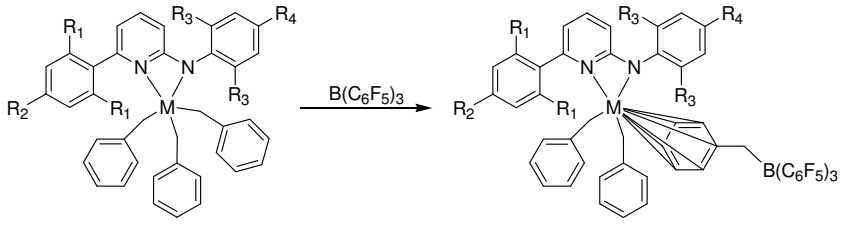
[2.167(3)/2.180(12)] Å and Zr-$N_{pyridine}$ [2.379(4)/2.359(11)] Å of **4/5a**, respectively, and Hf-N_{amido} [2.132(2)/2.136(3)] Å and Hf-$N_{pyridine}$ [2.360(2)/2.340(3)] Å in **4/5b**, respectively, indicate a localized binding mode. The anionic charge of the N ligand is localized at the N_{amido} atom which means a classic donor functionalized amido metal bond rather than an aminopyridinate is observed.[17]

Mono(aminopyridinato) tribenzyl zirconium or hafnium complexes **6a/b** could be obtained when **3** was reacted with an equimolar quantity of the corresponding tetrabenzyl complex in toluene (Scheme 4). Cooling of the reaction mixture leads to the desired complexes in good yields.

Table 1. Details of the X-ray crystal structure analyses.

Compound	**4a**	**4b+C_7H_8**	**5a+C_6D_6**	**5b**
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	Cc	P-1	P-1	P2(1)/n
a [Å]	18.2613(14)	11.6990(6)	11.1891(7)	12.8690(7)
b [Å]	16.9597(12)	31.2140(7)	12.6619(8)	14.3510(5)
c [Å]	15.8685(11)	18.4030(9)	15.981(1)	21.4180(10)
α [°]		110.893(4)	83.967(1)	
β [°]	111.438(6)	102.505(4)	72.555(1)	101.687(4)
γ [°]		92.733(4)	83.492(1)	
V [$Å^3$]	4574.5(6)	2570.4(2)	2140.0(2)	3873.5(3)
Crystal size [mm^3]	0.3 x 0.25 x 0.2	0.76 x 0.33 x 0.12	0.51 x 0.43 x 0.37	0.3 x 0.22 x 0.21
ρ_{calcd} [g cm^{-3}]	1.191	1.292	1.242	1.388
μ [mm^{-1}] (Mo-Kα)	0.276	2.068	0.294	2.726
T [K]	193(2)	133(2)	100(1)	173(2)
θ range [°]	1.70–25.75	1.65–25.69	2.40–29.60	1.71–25.75
No. of unique refl.	8615	9681	9153	7319
No. of obsd. refl. [$I > 2\sigma(I)$]	5454	8685	8604	5718
No. of parameters	505	569	720	448
wR_2 (all data)	0.0895	0.0699	0.0707	0.0664
R value [$I > 2\sigma(I)$]	0.0507	0.0245	0.0275	0.0326

Synthesis and structure of the zwitterionic complexes



Scheme 5. Synthesis of the zwitterionic complexes (**7**: $R_1 = R_2 = R_3 = CH(CH_3)_2$, $R_4 = H$, **8**: $R_1 = CH_3$, $R_2 = R_4 = H$, $R_3 = CH(CH_3)_2$, **9**: $R_1 = R_2 = CH(CH_3)_2$, $R_3 = R_4 = CH_3$, **a**: M = Zr; **b**: M = Hf).

The reaction of **4a** with one equivalent of $B(C_6F_5)_3$ in toluene (Scheme 5) at room temperature afforded a red-orange crystalline solid after the addition of pentane. It was identified by ^1H and ^{13}C NMR spectra as the zwitterionic complex, $[Ap^*Zr(CH_2Ph)_2]^+[B(CH_2Ph)(C_6F_5)_3]^-$ (**7a**). Noteworthy in the ^1H NMR spectrum are two doublets of an AB system observed at 2.42 and 2.80 ppm for non equivalent Zr-CH_2Ph methylene protons. The chemical shifts of the BCH_2Ph methylene moiety appears as broad singlet at 3.13 ppm. The *ortho*, *meta* and *para* hydrogens of the B-bonded benzyl group appear at 6.22, 5.89 and 5.77 ppm respectively, suggesting the coordination of the phenyl ring to Zr. An analogous reaction of **4b** with $B(C_6F_5)_3$ in the NMR tube led to similar ^1H NMR spectrum for **7b** (two doublets of an AB system observed at 2.12 and 2.24 ppm for non equivalent Zr-CH_2Ph methylene protons and a broad doublet at 3.31 ppm for BCH_2Ph methylene protons. The B-bound benzyl group shows a doublet-triplet-triplet pattern of resonances with chemical shifts of 5.85, 6.14 and 6.42 ppm for the *ortho*, *meta* and *para* hydrogen atoms, respectively, suggesting coordination of the phenyl ring of the borate moiety to Hf metal centre. The formation of these zwitterionic complexes through benzyl coordination was also reflected by the large value of $\Delta\delta$[(*p*-F)-(*m*-F)] 3.9 ppm.[18] Complexes **8a/b** were prepared in analogous way to **7a/b** by reacting **5a/b** with $B(C_6F_5)_3$ (Scheme 5). Complex **8a** was crystallized by layering toluene solution with pentane in good yield (81%). The molecular structure of **8a** was established by single crystal X-ray diffraction analysis of its toluene solvate. Details of the X-ray crystal structure analyses are summarized in Table 2. As shown in Figure 5, the molecular structure of **8a** consists of an $[Ap^+Zr(CH_2C_6H_5)_2]^+$ cation π-coordinated to the $BCH_2C_6H_5$ moiety of the $[B(CH_2C_6H_5)(C_6F_5)_3]^-$ anion. The two benzyl groups of the "cation" behave as normal, undistorted η^1 ligands, without significant Zr…C_{ipso} interactions. Zr-CH_2 distances [2.258(5)

and 2.267(5) Å], are in the typical range of values observed for Zr benzyl compounds. The six Zr-C metal-arene distances are slightly different. In particular, the *ipso* carbon is significantly further from Zr [2.844(5) Å], whereas the *m*, *p*-carbons are found closer to Zr. The four B-C bonds in $[B(CH_2C_6H_5)(C_6F_5)_3]^-$ are tetrahedrally arranged. ^{1}H NMR shows that the zwitterionic structure of **8a** found in the solid state is maintained in solution as well. An NMR tube reaction was carried out for **5b** with $B(C_6F_5)_3$ to form **8b** in C_6D_6. Noteworthy in the ^{1}H NMR spectrum are broad signals, especially two broad singlets at 2.10 and 2.21 ppm for the Zr-C*H*$_2$Ph protons, one broad singlet for the protons of the isopropyl group of the ligands and one broad singlet for B-CH_2 protons. The two broad singlets for C*H*$_2$Ph convert into two sharp doublets of an AB system if C_7D_8 solution is cooled to 253 K. This low temperature measurement also leads to well resolved septet for the protons of the isopropyl group and sharp signals for the aromatic protons of the aminopyridinato ligand. The large value of $\Delta\delta$[(*p*-F)-(*m*-F)] of 4.1 and 4.0 ppm found for **8a** and **8b** respectively, are indicative of the formation of zwitterionic complexes.[18]

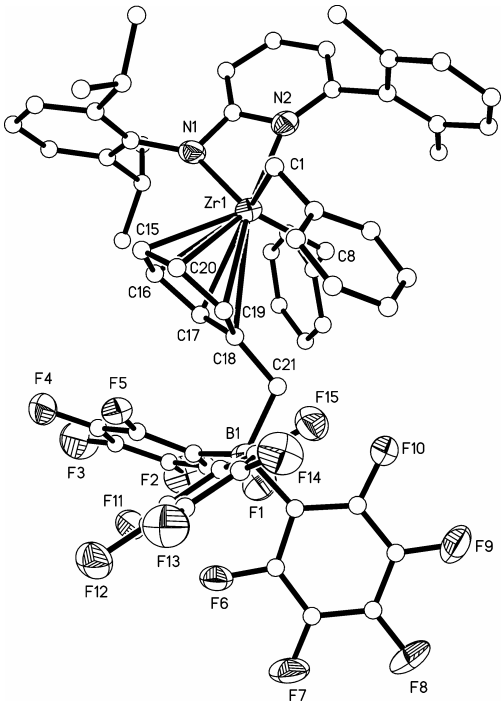


Figure 5. Molecular structure of **8a**, Hydrogen atoms and toluene molecule are omitted for clarity; selected bond lengths [Å] and angles [°]: C1-Zr1 2.258(5), C8-Zr1 2.267(5), C15-Zr1 2.616(5), C16-Zr1 2.614(5), C17-Zr1 2.705(5), C19-Zr1 2.762(5), C18-Zr1 2.844(5), C19-Zr1 2.762(5), C20-Zr1 2.668(5); C1-Zr1-C8 113.7(2), N1-Zr1-N2 59.00(14), C1-Zr1-C22 101.85(17), C8-Zr1-C22 99.24(17).

The reaction of **6a** (in toluene) or **6b** (in C_6D_6) with $B(C_6F_5)_3$ at room temperature results in the formation of **9a** or **9b**, respectively in quantative yield (Scheme 5). Complex **9a** was isolated as orange crystals when a concentrated toluene solution was layered with pentane. The molecular structure of **9a** as a toluene solvate was determined by single crystal analysis with a toluene solvate. The molecular structure consists of $[Ap^{9Me}Zr(CH_2C_6H_5)_2]^+$ cation π-coordinated to the $BCH_2C_6H_5$ moiety of the $[B(CH_2C_6H_5)(C_6F_5)_3]^-$ anion (Figure 6). The two benzyl ligands are η^1-coordinated, with Zr-CH_2 distances of [2.235(5) and 2.264(5) Å]. The phenyl ring of the anion is η^6-coordinated to the Zr centre. The distance for Zr-C_{ipso} [2.816(5) Å] is comparable to that of **8a** [2.844(5) Å]. The *m*, *p*-carbons were found closer to Zr with bond distances of [2.650(5) Å] and [2.667(5) Å], respectively, compared to *o*-carbons with an averaged distance of [2.720(5) Å].

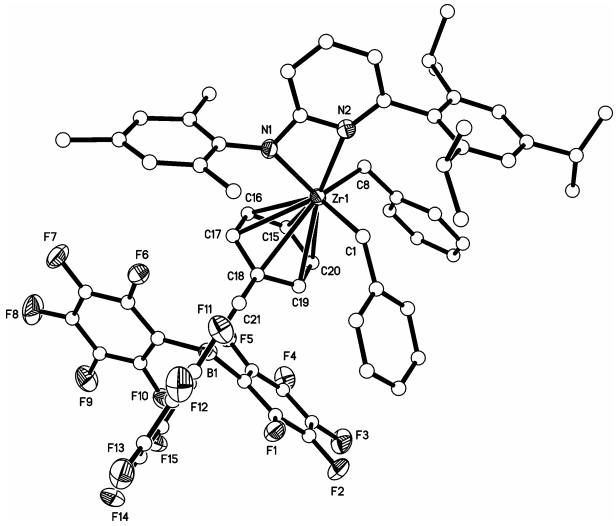


Figure 6. Molecular structure of **9a**, Hydrogen atoms and toluene molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: C1-Zr1 2.235(5), C8-Zr1 2.264(5), C15-Zr1 2.651(5), C16-Zr1 2.667(5), C17-Zr1 2.731(5), C18-Zr1 2.816(5), C19- Zr1 2.708(5), C20-Zr1 2.650(5), N1-Zr1 2.123(4), N2-Zr1 2.401(4); C1-Zr1-C8 108.70(2), N1-Zr1-N2 59.01(16), C1-Zr1-C22 97.75(18), C8-Zr1-C22 99.37(18).

Noteworthy, in the ^{1}H NMR spectra are two doublets of AB system for **9a** at 2.37 and 2.76 ppm and for **9b** at 2.01 and 2.22 ppm for the non equivalent Zr-CH_2 protons and broad singlets at 3.22 and 3.30 ppm for B-CH_2 protons of **9a** and **9b**, respectively. Moreover a doublet, triplet and triplet pattern of multiplicity for *o*-, *m*- and *p*-protons of B-bound benzyl was observed at 6.09, 5.81 and 5.71 for **9a** and at 6.22, 6.00 and 5.92 for **9b** respectively. The large values of $\Delta\delta$[(*p*-F)-(*m*-F)] of 4.0 and 3.9 ppm for **9a** and **9b** respectively, reflect the formation of these zwitterionic complexes.[18] The different Zr-N_{amido} [2.143(4)/ 2.123(4)] Å

and Zr-$N_{pyridine}$ [(2.334(4))/2.401(4)] Å for **8a/9a** respectively, indicate a localized binding mode of the aminopyridinato ligand. We also studied by NMR spectroscopy the stability and possible abstraction of the second benzyl group by reacting the zwitterionic complex **7a** with one equivalent of $B(C_6F_5)_3$. However this complex was quite stable and didn't undergo any noticeable change.

Table 2. Details of the X-ray crystal structure analyses.

Compound	**8a+C_7H_8**	**9a+2C_7H_8**
Crystal system	triclinic	monoclinic
Space group	P-1	P2(1)/n
a [Å]	10.0540(11)	12.4160(6)
b [Å]	14.7200(18)	24.1090(12)
c [Å]	22.042(3)	22.8350(12)
α [°]	77.993(10)	
β [°]	77.251(10)	99.396(4)
γ [°]	72.677(9)	
V [$Å^3$]	3001.7(6)	6743.7(6)
crystal size [mm^3]	0.26 x 0.20 x 0.18	0.25 x 0.17 x 0.09
ρ_{calcd} [g cm^{-3}]	1.467	1.413
μ [mm^{-1}] (Mo Kα)	0.276	0.252
T [K]	133(2)	133(2)
θ range [°]	1.47 to 25.74	1.69-25.79
No. of unique refl.	11035	12608
No. of obsd. refl. [$I > 2\sigma(I)$]	4883	7937
No. of parameters	814	838
wR^2 (all data)	0.1356	0.1925
R value [$I > 2\sigma(I)$]	0.0615	0.0778

Polymerization studies

The polymerization activities of the catalyst precursors **4a-6a** and **4b** were studied in the ethylene polymerization and the catalysts have been explored in terms of the cocatalyst used for the generation of the catioinic species Table 3. It was observed that activating **4a** with $B(C_6F_5)_3$ shows very low activity towards ethylene polymerization at 50°C even if H_2 was

introduced into the system to generate more active hydride species (entry 1 and 3). This might be understandable as it forms the zwitterionic complex which essentially blocks the coordination site and leads to an inactive catalyst. At higher temperature the dormant catalyst could be forced to achieve a moderate single site polymerization activity (M_w/M_n = 1.9) with the formation of high molecular weight polyethylene. To get more insight into this behaviour and to study the possible blockage of the coordination site of the catalyst we switched to ammonium borate as an activator. The abstraction of one of the benzyls of **4a** leads to a quite active polymerization system (entry 4) and the catalyst is stable even at high temperature. However the single site behaviour observed above was replaced by different active sites producing a trimodal distributed PE. Introduction of H_2 into the system did not have a pronounced effect on the catalytic activity (entry 5) but leads to a strong dropdown in average Mw of the polymer. For sterically less crowded systems **5a** and **6a** comparatively low activities were observed under identical conditions. It is also worth to note that Hf system **4b** which has the same steric demand as **4a**, yielded much longer PE chains with a broad but mono modal distribution (run 10 and 11).

Table 3. Activator dependence of the ethylene polymerization catalyzed by Zr and Hf tribenzyl complexes.[a]

pre-Cat. [µmol]		**Activator** [µmol]		**T** [°C]	$\mathbf{m_{Pol.}}$ [g]	**Activity** [$kg_{PE}mol_{cat}^{-1}h^{-}bar^{-1}$]	$\mathbf{M_w}$ [$gmol^{-1}$]	$\mathbf{M_w/M_n}$
		$B(C_6F_5)_3$	$B(C_6F_5)_4^{-}$ [c]					
4a	2	2.2		50	0.05	20	-	-
4a[b]	2	2.2		80	0.30	120	1130000	1.9
4a[d]	2	2.2		50	0.05	20	-	-
4a	2		2.2	30	0.70	280	70000	19.9
4a	2		2.2	50	2.30	920	72900	21.1
4a	2		2.2	80	2.80	1120	71800	21.6
4a[d]	2		2.2	80	2.70	1080	16100	6.4
5a	2		2.2	50	1.60	640	328000	62.3
6a	2		2.2	50	1.20	480	45200	14.2
4b	1.8		2.2	80	1.20	533	212000	5.5
4b[b]	1.8		2.2	80	2.70	1200	108000	3.1

[a]Toluene: 260 mL, pressure: 5 bar, t: 15 min, scavenger: TIBAO (50 µmol) or [b]TIBA (110 µmol); pre-catalyst and activator premixed before injection; [c]ammonium borate, $[R_2(CH_3)NH]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$); [d]80 mL H_2 added.

Since in the case of tribenzyl systems, the coordination of the abstracted benzyl seems to interfere with the polymerization process we became interested in a possible double activation of these catalysts (Table 4). The results show that these species can be converted into active catalysts especially if premixing of the zwitterionic complexes **7a-9a** is carried out with ammonium borate before injection into the autoclave. Nevertheless the broad molecular weight distribution of the produced polymers, the similar average Mw and activities compared to entries 8 and 9 (Table 3) suggest, that this is rather the result of an anion exchange than formation of a well defined dicationic catalyst.

Table 4. Ethylene polymerization catalyzed by zwitterionic Zr-complexes.[a]

pre-Cat. [µmol]		**Activator** [µmol]		$\mathbf{m_{Pol.}}$ [g]	**Activity** [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]	$\mathbf{M_w}$ [$gmol^{-1}$]	$\mathbf{M_w/M_n}$
		$B(C_6F_5)_3$	$B(C_6F_5)_4^{-}$ [b]				
4a	2	2.2		0.30	120	1130000	1.9
4a	2	2.2	2.2	1.30	520	1256000	1.9
8a	2			0.07	28	-	-
8a	2		2.2	1.70	680	455000	102.9
9a	2			0.08	32	534000	23.9
9a	2		2.2	1.50	600	13700	7.1

[a]Toluene: 260 mL, pressure: 5 bar, t: 15 min, temperature: 80°C, scavenger: TIBA (110 µmol), pre-catalyst and activator premixed before injection; [b]ammonium borate, $[R_2(CH_3)NH]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$).

Table 5. Propylene homo- and ethylene/propylene co-polymerization using **4a/b**.

pre-Cat. [µmol]		**Pressure** [bar]		$\mathbf{m_{Pol.}}$ [g]	**Activity** [$kg_{PE}mol_{cat}^{-1}h^{-1}$]	$\mathbf{M_w}$ [$gmol^{-1}$]	$\mathbf{M_w/M_n}$
		ethene	propene				
4a	2		5	0.05	100	-	-
4a	2	5	3	3.10	6200	14700	11.6
4a	2	5	4	2.50	5000	14300	8.0
4b	1.80		5	0.05	110	-	-
4b	1.80	5	3	2.20	4889	94600	2.4
4b	1.80	5	4	2.20	4889	76000	2.4

[a]Toluene: 260 mL, t: 15 min, temperature: 80°C, scavenger: TIBA (110 µmol), activator: ammonium borate, $[R_2(CH_3)NH]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$); pre-catalyst and activator premixed before injection.

The catalyst systems based on **4a/b** are not active towards propylene polymerization (Table 5 entry 1 and 4). However, presence of ethylene reactivates the catalysts and leads to copolymerization. NMR spectra of the copolymers produced by **4a/b** reveal quite different nature of the resulting copolymers. Zirconium complex **4a** gives long chain α-olefins, where one can detect the resonances for the olefinic and methyl end groups, at 14, 114 and 139 ppm (Figure 7). In contrast hafnium complex **4b** based on the same steric bulk gives a long chain copolymer with isolated/alternated propene units and with no evidence of PP sequences (Figure 8). It is noteworthy that the resulting EP-copolymer has a much smaller molecular weight distribution than the ethylene homo-polymer observed under similar conditions.

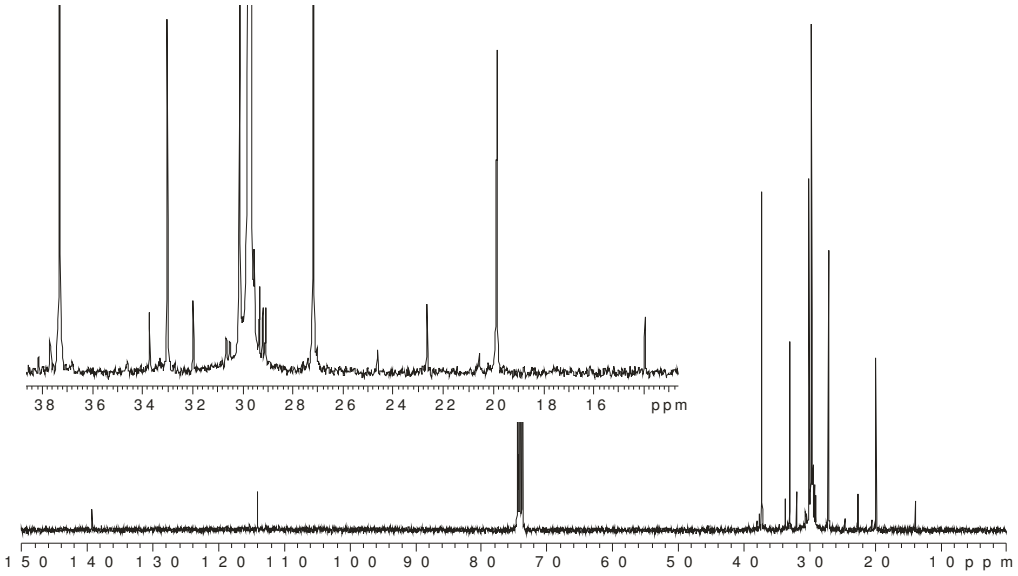


Figure 7. ^{13}C NMR spectrum ($C_2D_2Cl_4$) of poly(ethylene-co-propene) obtained with **4a**/[R_3NH][$B(C_6F_5)_4$] (Table 5, entry 2).

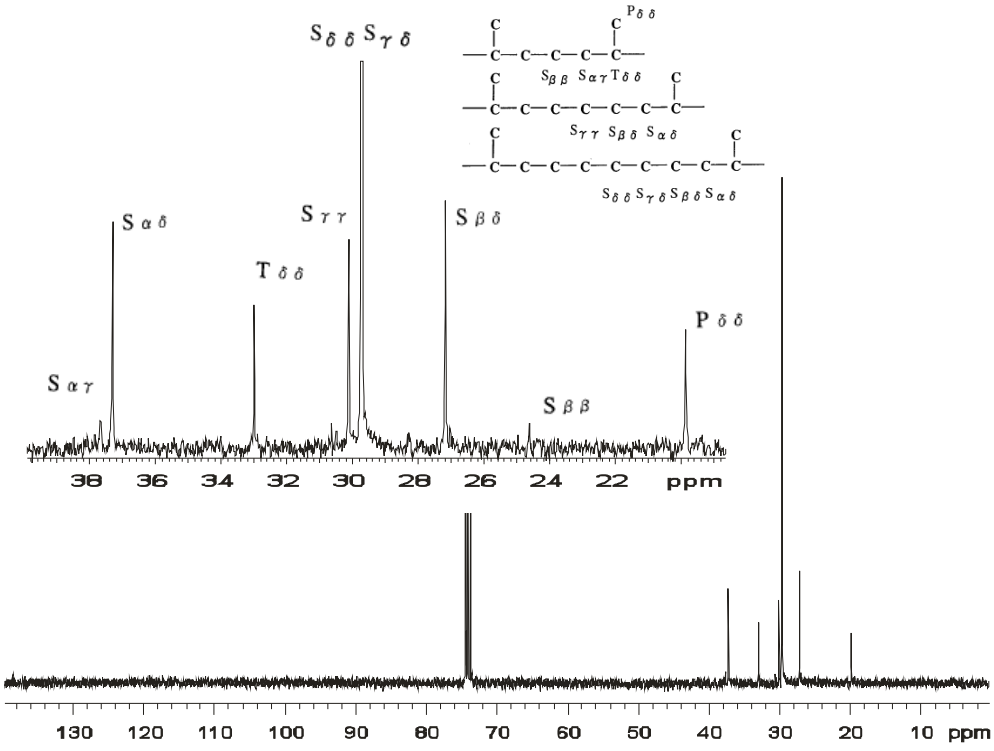


Figure 8. ^{13}C NMR spectrum ($C_2D_2Cl_4$) of poly(ethylene-co-propene) obtained with **4b**/[R_3NH][$B(C_6F_5)_4$] (Table 5, entry 5).

6.3. Conclusions

Mono(aminopyridinato) tribenzyl complexes of zirconium and hafnium can be prepared by toluene elimination in high yield when the tetrabenzyl metal precursor is reacted with one equivalent of the corresponding aminopyridine. In the solid state, one of the three benzyls is η^2-coordinated and rest are η1-coordinated to the electron deficient metal centres. Moreover, one of the three benzyls has been partially abstracted using $B(C_6F_5)_3$, the phenyl ring of B-bounded benzyl shows an η^6-coordination fashion. These zwitterionic complexes do not react with a second equiv. of $B(C_6F_5)_3$ to allow abstraction of a second benzyl. Polymerization studies revealed that the B-bounded benzyl is too strongly bounded to the metal to generate active catalyst systems. If activation of the tribenzyls occurs with ammonium borate instead of borane a quite high ethylene polymerization activity was observed but the multimodale distribution of the polymer suggests that the catalyst is rather ill defined. However, if one applies this system to ethylene-propylene copolymerization a high regioselectivity including alternating EP units was detected.

6.4. Experimental Section

General Procedures:

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 nitrogen filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1ppm O_2). Non-halogenated solvents were dried by distillation from sodium / benzophenone. Deteurated solvents were obtained from Cambridge Isotope Laboratories. Benzene-d_6 and toluene-d_8 were dried over sodium/potassium alloy and bromobenzene-d_5 over molecular sieves, degassed and distilled prior to use. Toluene for polymerization (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4Å). Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4Å). N,N,N-trialkylammonium (tetrapentafluorophenyl)borate ($[R_2NMeH][B(C_6F_5)_4]$, R = $C_{16}H_{33}$ – $C_{18}H_{37}$, 6.2 wt-% $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals), and tri-*iso*-butyl aluminium (TIBA, 2.0 M in toluene, Aldrich) were used as received. Tetra-*iso*-butyl aluminoxane ($[i\text{-}Bu_2Al]_2O$, TIBAO) was prepared according to published procedure.[19] Commercial $ZrCl_4$ (Strem) and $HfCl_4$ (Across Organics) were used as received. $[Zr(CH_2C_6H_5)_4]$ and $[Hf(CH_2C_6H_5)_4]$, were prepared according to the literature procedures.[20] NMR spectra were recorded on a Bruker (ARX 250 MHz) and Varian Inova (400 MHz) spectrometers. The chemical shifts are reported in ppm referenced to internal TMS for ^1H and ^{13}C. Elemental analyses (CHN) were determined using a Vario EL III instrument. X-ray Crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit and Bruker[21] SMART APEX CCD diffractometer (Platform with full three-circle goniometer). Structure solution and refinement was accomplished using SIR97,[22] SHELXL97[23] and WinGX.[24] Crystallographic details are summarized in Table 1 and Table 2. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-681000 (compound **4a**), CCDC-681001 (compound **4b**), CCDC-681005 (compound **5a**), CCDC-681002 (compound **5b**), CCDC-681003 (compound **8a**) and CCDC-681004 (compound **9a**). 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.

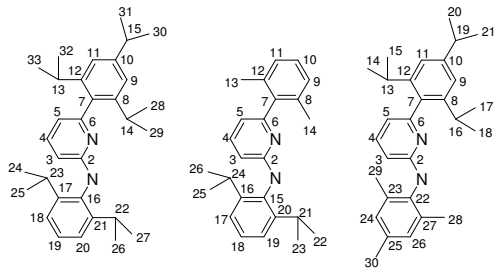
General description of ethylene polymerization experiments:

The catalytic ethylene polymerization reactions were performed in a stainless steel 1 L autoclave (Medimex) 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 co-catalyst injection systems and a sample outlet for continuous reaction monitoring. Up to 15 bar of ethylene pressure multiple injections of the catalyst with a pneumatically operated catalyst injection system were used. 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 125 °C prior to use. The reactor was then brought to desired temperature, stirred at 600 rpm and charged with 230 mL of toluene together with 1 mL of a 0.05 M solution of TIBAO (tetra-*iso*-butyl aluminoxan, Zr or Hf/Al = 1/100) or 0.1 mL of a 1.1 M solution of TIBA (tri-*iso*-butyl aluminium, Zr or Hf/Al = 1/110) in toluene as mentioned in the text. After pressurizing with ethylene to reach 5 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 together with 30 mL of toluene, to start the reaction. The catalyst mixture was prepared by successively adding 1 mL of toluene and 1 mL of a 0.002 M catalyst stock solution in toluene to 25 mg of $[R_2NMeH][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$, 6.2 wt-% $B(C_6F_5)_4^-$ in Isopar, Zr or Hf/B = 1/1.1). During the run ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing flow. After 15 min reaction time the reactor was vented and the residual aluminium alkyls were destroyed by addition of 100 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.

The polymer samples for NMR 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 Polymer Laboratories Ltd. (PL-GPC210) chromatograph, equipped with a capillary differential viscometer (Viscotek), a refractive index (RI) detector and a two-angle (15° and 90°) light scattering photometer at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% weight/volume) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (M_w = 50000 g/mole) and polystyrene (M_w =100000–500000 g/mole) standards. The reported values are the average of at least two independent determinations.

General description of ethylene/propylene co-polymerization experiments:

The general procedure and conditions as described above were followed, using successively 3 bar or 4 bar propylene and 5 bar ethylene to pressurize the reactor.



Scheme 6. NMR signals labelling of the synthesized metal complexes.

Synthesis of 4a: Toluene (20 mL) was added to **1** (0.456 g, 1 mmol) and $[Zr(CH_2(C_6H_5))_4]$ (0.456 g, 1 mmol) at room temperature. The solution mixture was stirred overnight in the absence of light at room temperature. The solution was evaporated to dryness and the product was extracted with pentane (10 mL). The filtrate was cooled to -25 °C affording yellow crystalline material of the product. Yield: 0.603 g (74%). $C_{53}H_{64}N_2Zr$ (820.31): calcd. C 77.60, H 7.86, N 3.41; found C 76.74, H 7.81, N 3.76. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.06-1.30 (m, 30H, $H^{24,25,26,27,28,29,30,31,32,33}$), 2.08 (s, 6H, $H^{CH2(benzyl)}$), 2.87 (m, 3H, $H^{13,14,15}$), 3.60 (sep, 2H, $H^{22,23}$), 5.72 (d, 1H, H^3), 6.13 (d, 1H, H^5), 6.46 (dd, 6H, $H^{CH(benzyl)}$), 6.73 (t, 1H, H^4), 6.86-7.24 (m, 14H, $H^{9,11,18,19,20,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298K): δ = 22.3 ($C^{28,29,32,33}$), 24.1 ($C^{24,25,26,27}$), 24.2 ($C^{30,31}$), 25.5 ($C^{24,25,26,27}$), 26.7 ($C^{28,29,32,33}$), 29.1 ($C^{22,23}$), 31.0 ($C^{13,14}$), 34.9 (C^{15}), 80.6 ($C^{CH2(benzyl)}$), 106.2 (C^3), 114.2 (C^5), 121.4 ($C^{9,11}$), 123.2 (C^{benzyl}), 124.7 ($C^{18,20}$), 126.7 (C^{19}), 127.8 (C^{benzyl}), 129.9 (C^{benzyl}), 134.3 (C^7), 141.0 (C^4), 143.2 (C^{benzyl}), 143.5 (C^{16}), 144.0 ($C^{17,21}$), 147.0 ($C^{8,12}$), 150.7 (C^{10}), 155.7 (C^6), 173.0 (C^2) ppm.

Synthesis of 4b: $[Hf(CH_2(C_6H_5))_4]$ (0.543 g, 1 mmol) was added to **1** (0.456 g, 1 mmol) in toluene (15 mL) at room temperature. A sudden colour change to orange yellow was observed. The reaction mixture was stirred for four hours. Volume was reduced and the product was allowed to crystallize at -25 °C. Yield: 0.56 g (78%, NMR scale 100%). $C_{53}H_{64}HfN_2$ (908.45): calcd. C 70.14, H 7.11, N 3.09; found C 69.84, H 7.42, N 3.09. ^{1}H NMR (250MHz, C_6D_6, 298K): δ = 1.06 (d, 6H, $H^{28,29,32,33}$), 1.14 (d, 6H, $H^{30,31}$), 1.17 (d, 6H, ^{24,25,26,27}), 1.22 (d, 6H, $H^{24,25,26,27}$), 1.31 (d, 6H, $H^{28,29,32,33}$), 1.85 (s, 6H, $H^{CH2(benzyl)}$), 2.89 (m, 3H, $H^{13,14,15}$), 3.47 (sep, 2H, $H^{22,23}$), 5.64 (d, 1H, H^3), 6.24 (d, 1H, H^5), 6.46 (d, 6H,

$H^{CH(benzyl)}$), 6.74 (dd, 1H, H^4), 6.86 (dd, 3H, $H^{CH(benzyl)}$), 7.04 (dd, 6H, $H^{CH(benzyl)}$), 7.18 (s, 2H, $H^{9,11}$), 7.22 (m, 3H, $H^{18,19,20)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 22.3 ($C^{28,29,32,33}$), 24.1 ($C^{24,25,26,27}$), 24.2($C^{30,31}$), 25.5 ($C^{24,25,26,27}$), 26.6 ($C^{28,29,32,33}$), 29.1 ($C^{22,23}$), 31.1 ($C^{13,14}$), 34.9 (C^{15}), 86.8 ($C^{CH2\text{-}benzyl}$), 106.2 (C^3), 115.3 (C^5), 121.5 ($C^{9,11}$), 123.1 (C^{benzyl}), 124.6 ($C^{18,20}$), 129.3 (C^{19}), 129.4 (C^{benzyl}), 134.2 (s, C^7), 141.4 (C^4), 142.6 ($C^{16/benzyl}$), 143.6 ($C^{17,21)}$), 145.1 (C^{benzyl}), 147.0 ($C^{8,12}$), 150.9 (C^{10}), 155.9 (C^6), 170.1 (C^2) ppm.

Synthesis of 5a: $[Zr(CH_2(C_6H_5))_4]$ (0.456 g, 1 mmol) was added to a solution of **2** (0.358 g, 1 mmol) in toluene (15 mL) with stirring at room temperature. A yellow coloured product quickly precipitated. The reaction mixture was further stirred for four hours and then filtered leaving behind a yellow coloured product. The filtrate was concentrated under vacuum and allowed to crystallize at low temperature to give yellow crystals suitable for X-ray analysis. Yield 0.6 g (83%, NMR scale 100%). $C_{46}H_{50}N_2Zr$ (722.13): calcd. C 76.51, H 6.98, N 3.88; found C 76.15, H 6.85, N 3.52. ^1H NMR (250 MHz, C_6D_6, 298 K): δ = 1.21 (d, 12H, $H^{22,23,25,26}$), 1.24 (d, 6H, $H^{22,23,25,26}$), 2.04 (s, 6H, $H^{CH2(benzyl)}$), 2.06 (s, 6H, $H^{13,14}$), 3.63 (sep, 2H, $H^{21,24}$), 5.64 (dd, 1H, H^3), 5.71 (dd, 1H, H^5), 6.45 (d, 6H, $H^{CH(benzyl)}$), 6.74 (t, 1H, H^4), 6.83-6.93 (m, 5H, $H^{17,19,CH(benzyl)}$), 7.01-7.24 (m, 10H, $H^{9,10,11,18,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 20.1 ($C^{13,14}$), 24.1 ($C^{22,23,25,26}$), 25.5 ($C^{22,23,25,26}$), 29.0 ($C^{21,24}$), 80.2 ($C^{CH2\text{-}benzyl}$), 105.7 (C^3), 111.9 (C^5), 123.2 (C^{benzyl}), 124.7 ($C^{17,19)}$), 126.7 (C^7), 127.8 ($C^{9,11}$), 128.2 (C^{18}), 129.1 (C^{10}), 129.9 (C^{benzyl}), 136.1 ($C^{16,20}$), 138.6 (C^4), 142.2 (C^{benzyl}), 143.0 (C^{15}), 143.2 ($C^{8,12}$), 144.8 (C^{benzyl}), 155.9 (C^6), 172.8 ppm (C^2).

Synthesis of 5b: $[Hf(CH_2(C_6H_5))_4]$ (0.543 g, 1 mmol) was added to a solution of **2** (0.358 g, 1 mmol) in toluene (15 mL) with stirring at room temperature. A yellow coloured product quickly precipitated. The reaction mixture was further stirred for four hours and then filtered leaving behind a yellow coloured product. The filtrate was reduced under vacuum and allowed to crystallize at low temperature to give yellow crystals suitable for X-ray analysis. Yield 0.78 g (96%, NMR scale 100%). $C_{46}H_{50}HfN_2$ (810.34): calcd. C 68.26, H 6.23, N 3.46; found C 67.68, H 6.50, N 3.42. ^1H NMR (250 MHz, C_6D_6, 298 K): δ = 1.15 (d, 12H, $H^{22,23,25,26}$), 1.18 (d, 6H, $H^{22,23,25,26}$), 1.83 (s, 6H, $H^{CH2(benzyl)}$), 2.05 (s, 6H, $H^{13,14}$), 3.49 (sep, 2H, $H^{21,24}$), 5.57 (dd, 1H, H^3), 5.81 (dd, 1H, H^5), 6.47 (d, 6H, $H^{CH(benzyl)}$), 6.74 (t, 1H, H^4), 6.85-6.90 (m, 5H, $H^{17,19,CH(benzyl)}$), 7.00-7.22 (m, 10H, $H^{9,10,11,18,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 20.1 ($C^{13,14}$), 24.0 ($C^{22,23,25,26}$), 25.4 ($C^{22,23,25,26}$), 29.0 ($C^{21,24}$), 87.0 ($C^{CH2(benzyl)}$), 105.6 (C^3), 112.8 (C^5), 123.1 (C^{benzyl}), 124.6 ($C^{17,19)}$), 128.2 ($C^{9,11}$), 128.5 (C^{18}),

128.9 (C^{10}), 129.3 (C^{benzyl}), 136.0 ($C^{16,20}$), 137.8 (C^{7}), 138.5 (C^{4}), 142.2 (C^{benzyl}), 142.5 (C^{15}), 143.4 ($C^{8,12}$), 145.0 (C^{benzyl}), 156.0 (C^{6}), 170.2 ppm (C^{2}).

Synthesis of 6a: Toluene (20 mL) was added to **3** (0.3 g, 0.72 mmol) and $Zr(CH_2(C_6H_5))_4$ (0.33 g, 0.72 mmol) at room temperature. The reaction mixture was stirred overnight in the absence of light. The solution was evaporated to dryness and the product was extracted with pentane (10 mL). The filtrate was cooled to -25 °C affording yellow needle like crystals of the product. Yield: 0.285 g (50%). $C_{50}H_{58}N_2Zr$ (778.3): calcd. C 77.17, H 7.51, N 3.60; found C 76.63 , H 7.69, N 3.65. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.08 (d, 6H, $H^{14,15,17,18}$), 1.22 (d, 6H, $H^{14,15,17,18}$), 1.30 (d, 6H, $H^{20,21}$), 2.10 (s, 6H, $H^{CH2(benzyl)}$), 2.19 (s, 3H, H^{30}), 2.23 (s, 6H, $H^{28,29}$), 2.90 (m, 3H, $H^{13,16,19}$), 5.67 (d, 1H, H^{3}), 6.17 (d, 1H, H^{5}), 6.45(d, 6H, $H^{CH(benzyl)}$), 6.78 (t, 1H, H^{4}), 6.85-7.26 (m, 13H, $H^{9,11,26,24,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz C_6D_6, 298K): δ = 18.7 ($C^{28,29}$), 20.7 (C^{30}), 22.1 ($C^{14,15,17,18}$), 24.0 ($C^{14,15,17,18}$), 26.5 ($C^{20,21}$), 30.8 ($C^{13,16}$), 34.6 (C^{19}), 79.5 ($C^{CH2(benzyl)}$), 103.9 (C^{3}), , 114.1 (C^{5}), 120.5 ($C^{9,11}$), 121.1 ($C^{9,11}$), 122.8 ($C^{24,26}$), 127.5 (C^{benzyl}), 129.6 (C^{benzyl}), 129.5 (C^{benzyl}), 133.5 ($C^{23,27}$), 134.4 (C^{7}), 141.1 (C^{25}), 142.8 ($C^{8,12}$), 143.0 (C^{10}), 146.5 (C^{4}), 146.8 (C^{benzyl}), 150.3 (C^{22}), 155.7 (C^{6}), 170.6 ppm (C^{2}).

Synthesis of 6b: $[Hf(CH_2(C_6H_5))_4]$ (0.543 g, 1 mmol) was added to **3** (0.441 g, 1 mmol) in toluene (15 mL) at room temperature. The resulting clear yellow solution was stirred for four hours. The volume of the solution was reduced and the reaction mixture was cooled to -25 °C affording yellow needle like crystals of the product. Yield: 0.518 g (60%, NMR scale 100 %). $C_{50}H_{58}HfN_2$ (865.50): calcd. C 69.39, H 6.75, N 3.24; found C 69.15, H 7.42, N 3.02 . ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.07 (d, 6H, $H^{14,15,17,18}$), 1.23 (d, 6H, $H^{14,15,17,18}$), 1.33 (d, 6H, $H^{20,21}$), 1.88 (s, 6H, $H^{CH2(benzyl)}$), 2.15 (s, 6H, $H^{28,29}$), 2.20 (s, 3H, H^{30}), 2.90 (m, 3H, $H^{13,16,19}$), 5.63 (dd, 1H, H^{3}), 6.27 (dd, 1H, H^{5}), 6.47 (d, 6H, $H^{CH(benzyl)}$), 6.78 (t, 1H, H^{4}), 6.83-6.90 (m, 5H, $H^{24,26,CH(benzyl)}$), 7.04 (dd, 6H, $H^{CH(benzyl)}$), 7.19 (s, 2H, $H^{9,11}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298K): δ = 18.7 ($C^{28,29}$), 20.9 (C^{30}), 22.4 ($C^{14,15,17,18}$), 24.3 ($C^{14,15,17,18}$), 26.8 ($C^{20,21}$), 31.1 ($C^{13,16}$), 34.9 (C^{19}), 86.7 ($C^{CH2(benzyl)}$), 104.2 (C^{3}), 115.2 (C^{5}), 121.4 ($C^{9,11}$), 123.0 ($C^{(benzyl)}$), 129.3 ($C^{CH(benzyl)}$), 129.7 ($C^{24,26}$), 134.1 ($C^{23,27}$), 134.2 (C^{7}), 135.1 (C^{25}), 141.8 (C^{10}), 142.4 (C^{4}), 143.5 ($C^{CH(benzyl)}$), 147.0 ($C^{8,12}$), 150.8 (C^{22}), 156.0 (C^{6}), 168.4 ppm (C^{2}).

Synthesis of 7a: $B(C_6F_5)_3$ (0.064 g, 0.125 mmol) was added to **4a** (0.1 g, 0.125 mmol) in toluene (2 mL). A colour change from yellow to red was observed. The reaction mixture was stirred briefly, resulting in clear oily solution which was layered with pentane and was cooled

to -25 °C affording orange crystals over two weeks. Yield: 0.099 g (60%). $C_{71}H_{64}BF_{15}N_2Zr.C_{3.5}H_4$ (1378.36): calcd. C 64.92, H 4.97, N 2.03; found C 64.92, H 5.22 , N 2.36. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.89 (d, 6H, $H^{28,29,32,33}$), 0.94 (d, 6H, $H^{30,31}$), 1.04 (d, 12H, ^{24,25,26,27}), 1.12 (d, 6H, $H^{28,29,32,33}$), 2.42 (d, 2H, H^{CH2}), 2.68 (m, 5H, $H^{13,14,15,22,23}$), 2.80 (d, 2H, H^{CH2}), 3.15 (br s, 2H, H^{CH2}), 5.33 (d, 1H, H^3), 5.77 (br, 1H, $H^{CH(benzyl}$), 5.89 (br t, 2H, $H^{CH(benzyl}$), 6.22 (br d, 2H, $H^{CH(benzyl}$), 6.36 (d, 1H, H^5), 6.46 (d, 4H, $H^{CH(benzyl)}$), 6.66 (t, 1H, H^4), 6.88 (t, 2H, $H^{CH(benzyl)}$), 7.00-7.20 (m, 9H, $H^{9,11,18,19,20,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 21.8 ($C^{28,29,32,33}$), 23.0 ($C^{24,25,26,27}$), 24.1 ($C^{30,31}$), 26.0 ($C^{24,25,26,27}$), 27.1 ($C^{28,29,32,33}$), 28.4 ($C^{22,23}$), 31.8 ($C^{13,14}$), 34.7 (C^{15}), 76.6 ($C^{CH2(benzyl)}$), 106.5 (C^3), 118.8 (C^5), 121.6 ($C^{9,11}$), 124.6 ($C^{18,20}$), 125.5 (C^{benzyl}), 125.7 (C^{19}), 128.6 (C^{benzyl}), 129.3 (C^7), 129.8 (C^{benzyl}), 135.4 (br, C^{BC6F5}), 141.8 (C^4), 142.7 (C^{benzyl}), 143.0 (C^{16}), 143.5 ($C^{17,21}$), 146.8 (br, C^{BC6F5}), 147.2 ($C^{8,12}$), 150.7 (br, C^{BC6F5}), 151.8 (C^{10}), 156.2 (C^6), 168.2 (C^2) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = -164.97 (t, *m*-F), -160.70 (t, *p*-F), -131.51 (d, *o*-F) ppm.

Synthesis of 7b: An NMR tube was charged with **1** (23 mg) and [Hf($CH_2(C_6H_5)$)$_4$] (27 mg) in C_6D_6 (0.5 mL). B(C_6F_5)$_3$ (26 mg) was added to this solution. Afterwards the tube was shaken for 5 min to form a clear solution before measurement. $C_{71}H_{64}BF_{15}HfN_2$ (1419.56): calcd. C 60.07, H 4.54, N 1.97; found C 60.01, H 5.26 , N 2.21. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.89-1.03 (m, 12H, $H^{28,29,32,33}$), 1.12 (d, 12H, ^{24,25,26,27}), 1.12 (d, 6H, $H^{30,31}$), 2.12 (d, 2H, H^{CH2}), 2.24 (d, 2H, H^{CH2}), 2.69 (m, 5H, $H^{13,14,15,22,23}$), 3.31 (br d, 2H, H^{CH2}), 5.28 (d, 1H, H^3), 5.85 (br t, 1H, $H^{CH(benzyl}$), 6.14 (br t, 2H, $H^{CH(benzyl}$), 6.21 (d, 1H, H^5), 6.42 (d, 2H, $H^{CH(benzyl}$), 6.51 (d, 4H, $H^{CH(benzyl)}$), 6.70 (t, 1H, H^4), 6.85-7.23 (m, 11H, $H^{9,11,18,19,20,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 22.7 ($C^{28,29,32,33}$), 23.0 ($C^{24,25,26,27}$), 24.0 ($C^{30,31}$), 25.9 ($C^{24,25,26,27}$), 27.0 ($C^{28,29,32,33}$), 28.6 ($C^{22,23}$), 31.9 ($C^{13,14}$), 34.7 (C^{15}), 83.9 ($C^{CH2(benzyl)}$), 106.3 (C^3), 119.1 (C^5), 121.5 ($C^{9,11}$), 124.4 ($C^{18,20}$), 126.3 (C^{benzyl}), 129.0 (C^{19}), 129.0 (C^{benzyl}), 133.4 (s, C^7), 135.4 (br, C^{BC6F5}), 139.4 (br, C^{BC6F5}), 142.2 (C^4), 143.9 (C^{benzyl}), 144.3 ($C^{17,21)}$), 146.8 (C^{16}), 147.1 (C^{benzyl}), 150.5 (br, C^{BC6F5}), 151.8 (C^{10}), 156.1 ($C^{8,12}$), 162.2 (C^6), 166.6 (C^2) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = -165.30 (t, *m*-F), -161.37 (t, *p*-F), -130.17 (d, *o*-F) ppm. ^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = -11.35 (s, $B^{C6H5CH2B(C6F5)3}$) ppm.

Synthesis of 8a: [Zr($CH_2(C_6H_5)$)$_4$] (0.255 g, 0.56 mmol) and **2** (0.2 g, 0.56 mmol) were stirred together in toluene (5 mL) as **5a** soon precipitated as yellow material. B(C_6F_5)$_3$ (0.286 g, 0.56 mmol) was added to this suspension. A colour change from yellow to dark red was

observed. It was stirred briefly, resulting in clear oily solution which was layered with pentane and cooled to -25 °C affording orange crystals overnight. Yield: 0.56 g (81%). $C_{64}H_{50}BF_{15}N_2Zr$ (1234.11): calcd. C 62.29, H 4.08, N 2.27; found C 62.27 , H 3.76 , N 1.93. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.88 (d, 6H, $H^{22,23,25,26}$), 0.98 (d, 6H, $H^{22,23,25,26}$), 1.93 (s, 6H, $H^{13,14}$), 2.44 (br d, 2H, $H^{CH2(benzyl)}$), 2.63 (sep, 2H, $H^{21,24}$), 2.76 (d, 2H, H^{CH2}), 3.21 (br s, 6H, $H^{B\text{-}CH2}$), 5.21 (d, 1H, H^3), 5.71 (br s, 1H, $H^{CH(benzyl)}$), 5.81 (d, 1H, H^5), 5.95 (br s, 2H, $H^{CH(benzyl)}$), 6.24 (br s, 2H, $H^{CH(benzyl)}$), 6.52 (d, 4H, $H^{CH(benzyl)}$), 6.60 (t, 1H, H^4), 6.74 (d, 2H, $H^{17,19}$), 6.87-7.18 (m, 11H, $H^{9,10,11,18,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 21.4 ($C^{13,14}$), 23.0 ($C^{22,23,25,26}$), 25.9 ($C^{22,23,25,26}$), 28.4 ($C^{21,24}$), 77.8 (br, $C^{CH2(benzyl)}$), 106.0 (C^3), 116.7 (C^5), 124.6 (C^{18}), 125.4 ($C^{17,19}$), 125.6 (C^{benzyl}), 127.8 ($C^{9,11}$), 129.3 (C^{benzyl}), 129.7 (C^{benzyl}), 129.8 (C^{10}), 133.2 (br, C^{BC6F5}), 136.1 ($C^{16,20}$), 136.2 (C^7), 137.8 (C^4), 142.7 (C^{benzyl}), 143.2 (C^{15}), 142.9 ($C^{8,12}$), 143.5 (C^{benzyl}), 145.2 (C^6), 146.8 (br, C^{BC6F5}), 150.7 (br, C^{BC6F5}), 156.3 (C^2) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = -165.30 (t, *m*-F), -161.2 (br, *p*-F), -130.30 (br, *o*-F) ppm. ^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = -11.44 (s, $B^{C6H5CH2B(C6F5)3}$) ppm.

Synthesis of 8b: An NMR tube was charged with **2** (16 mg) and [$Hf(CH_2(C_6H_5))_4$] (25 mg) in C_6D_6 (0.5 mL). $B(C_6F_5)_3$ (24 mg) was added to this deuterated solution. Afterwards the tube was shaken for 5 min to form a clear solution before recording NMR spectra. $C_{64}H_{50}BF_{15}HfN_2$ (1321.37): calcd. C 58.17, H 3.81, N 2.12; found C 57.98, H 4.28 , N 2.34. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.90 (d, 6H, $H^{22,23,25,26}$), 0.97 (d, 6H, $H^{22,23,25,26}$), 1.9 (s, 6H, $H^{13,14}$), 2.10 (br s, 2H, $H^{CH2(benzyl)}$), 2.24 (br s, 2H, $H^{CH2(benzyl)}$), 2.65 (br s, 2H, $H^{21,24}$), 3.38 (br s, 2H, $H^{B\text{-}CH2}$), 5.19 (br d, 1H, H^3), 5.84 (d, 1H, H^5), 6.13 (br t, 2H, $H^{CH(benzyl)}$), 6.42 (br d, 2H, $H^{CH(benzyl)}$), 6.54 (d, 4H, $H^{CH(benzyl)}$), 6.63 (t, 1H, H^4), 6.74 (br d, 2H, $H^{CH(benzyl)}$), 6.88 (t, 2H, $H^{CH(benzyl)}$), 7.00-7.20 (m, 10H, $H^{9,10,11,17,18,19,CH(benzyl)}$) ppm. ^{1}H NMR (400 MHz, C_7D_8, 296 K): δ = 0.92 (d, 6H, $H^{22,23,25,26}$), 1.00 (d, 6H, $H^{22,23,25,26}$), 1.99 (s, 6H, $H^{13,14}$), 2.10 (br s, 2H, $H^{CH2(benzyl)}$), 2.22 (br s, 2H, $H^{CH2(benzyl)}$), 2.66 (br s, 2H, $H^{21,24}$), 3.30 (br s, 2H, $H^{B\text{-}CH2}$), 5.20 (br s, 1H, H^3), 5.92 (br d, 1H, H^5), 6.14 (br t, 2H, $H^{CH(benzyl)}$), 6.38 (br d, 2H, $H^{CH(benzyl)}$), 6.54 (d, 4H, $H^{CH(benzyl)}$), 6.75 (t, 1H, H^4), 6.88 (t, 2H, $H^{CH(benzyl)}$), 6.97-7.17 (m, 10H, $H^{9,10,11,17,18,19,CH(benzyl)}$) ppm. ^{1}H NMR (400 MHz, C_7D_8, 253 K): δ = 0.89 (d, 6H, $H^{22,23,25,26}$), 0.94 (d, 6H, $H^{22,23,25,26}$), 1.95 (s, 6H, $H^{13,14}$), 2.11 (d, 2H, $H^{CH2(benzyl)}$), 2.26 (d, 2H, $H^{CH2(benzyl)}$), 2.57 (sep, 2H, $H^{21,24}$), 3.38 (br s, 2H, $H^{B\text{-}CH2}$), 5.13 (d, 1H, H^3), 5.70 (t, 1H, $H^{CH(benzyl)}$), 5.80 (d, 1H, H^5), 6.07 (t, 2H, $H^{CH(benzyl)}$), 6.36 (d, 2H, $H^{CH(benzyl)}$), 6.54 (d, 4H, $H^{CH(benzyl)}$), 6.60 (t, 1H, H^4), 6.70 (d, 2H, $H^{CH(benzyl)}$), 6.88-7.20 (m, 10H, $H^{9,10,11,17,18,19,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 20.3 ($C^{13,14}$), 24.6

($C^{22,23,25,26}$), 25.8 ($C^{22,23,25,26}$), 28.6 ($C^{21,24}$), 85.9 (br, $C^{CH2(benzyl)}$), 106.0 (C^{3}), 117.0 (C^{5}), 124.5 ($C^{17,19)}$), 125.4 ($C^{9,11}$), 125.6 (C^{18}), 126.5 ($C^{(benzyl)}$), 128.6 (C^{benzyl}), 129.1 (C^{benzyl}), 129.3 ($C^{16,20}$), 129.9 (C^{10}), 133.6 (C^{7}), 136.1 (C^{benzyl}), 137.8 (C^{4}), 139.3 (br, C^{BC6F5})143.5 (C^{15}), 144.0 ($C^{8,12}$), 144.4 (br, C^{benzyl}), 146.8 (br, C^{BC6F5}),150.5 (br, C^{BC6F5}), 156.1 (C^{6}), 162.2 ppm (C^{2}). ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = -165.3 (*m*-F), -161.3 (*p*-F), -130.25 (*o*-F) ppm.^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = -11.32 (s, $B^{C6H5CH2B(C6F5)3}$)

Synthesis of 9a: $[Zr(CH_2(C_6H_5))_4]$ (0.248 g, 0.54 mmol) and **3** (0.225 g, 0.54 mmol) were stirred together in toluene (5 mL). Then $B(C_6F_5)_3$ (0.279 g, 0.54 mmol) was added to the clear yellow solution. A colour change to dark red was observed. The mixture was stirred briefly, resulting in clear oily solution which was layered with pentane and kept at low temperature -25 °C to afford orange crystals overnight. Yield 0.624 g (84%). $C_{68}H_{58}BF_{15}N_2Zr.C_7H_8$ (1382.35): calcd. C 65.16, H 4.81, N 2.03; found C 65.12 , H 4.45, N 1.84. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.96 (d, 6H, $H^{14,15,17,18}$), 1.00 (d, 6H, $H^{14,15,17,18}$), 1.15 (d, 6H, $H^{20,21}$), 1.87 (s, 6H, $H^{28,29}$), 2.31 (s, 3H, H^{30}), 2.37 (d, 2H, H^{CH2}), 2.67 (sep, 3H, $H^{13,16,19}$), 2.76 (d, 2H, $H^{CH2(benzyl)}$), 3.22 (br s, 2H, H^{CH2}), 5.32 (d, 1H, H^{3}), 5.71 (br t, 2H, $H^{CH(benzyl)}$), 5.81 (br t, 1H, $H^{CH(benzyl)}$), 6.09 (br d, 2H, $H^{CH(benzyl)}$), 6.41 (d, 1H, H^{5}), 6.45 (d, 4H, $H^{CH(benzyl)}$), 6.72-6.90 (m, 5H, $H^{4,24,26,CH(benzyl)}$), 7.01-7.07 (m, 6H, $H^{9,11,CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 18.4 ($C^{28,29}$), 20.7 (C^{30}), 21.7 ($C^{14,15,17,18}$), 24.0 $C^{14,15,17,18}$), 27.3 ($C^{20,21}$), 31.9 ($C^{13,16}$), 34.7 (C^{19}), 78.5 ($C^{CH2(benzyl)}$), 103.6 (C^{3}), 118.7 (C^{5}), 121.5 ($C^{9,11}$), 124.3 ($C^{24,26}$), 125.6 (C^{benzyl}), 129.6 (C^{benzyl}), 132.6 (C^{benzyl}), 137.6 ($C^{23,27}$), 137.8 (C^{7}), 135.3 (br, C^{BC6F5}), 139.2 (br, C^{BC6F5}), 142.5 (C^{25}), 143.0 (C^{10}), 144.2 ($C^{8,12}$), 146.8 (br, C^{BC6F5}), 147.3 (C^{benzyl}), 150.3 (br, C^{BC6F5}), 151.5 (C^{4}), 156.1 (C^{22}), 160.2 (C^{6}), 166.5(C^{2}) ppm. ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = -165.35 (t, *m*-F), -161.32 (t, *p*-F), -130.70 (br, *o*-F) ppm.^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = -11.53 (s, $B^{C6H5CH2B(C6F5)3}$).

Synthesis of 9b: An NMR tube was charged with **3** (83 mg) and $[Hf(CH_2(C_6H_5))_4]$ (109 mg) in C_6D_6 (0.5 mL). Then $B(C_6F_5)_3$ (102 mg, mmol) was added to this solution. Afterwards the tube was shaken for 5 min to form a clear solution before measurement. $C_{68}H_{58}BF_{15}HfN_2$ (1377.48): calcd. C 59.29, H 4.24, N 2.03; found C 58.43, H 4.46 , N 2.15. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.95 (d, 6H, $H^{14,15,17,18}$), 1.00 (d, 6H, $H^{14,15,17,18}$), 1.14 (d, 6H, $H^{20,21}$), 1.92 (s, 6H, $H^{28,29}$), 2.01 (d, 2H, $H^{CH2benzyl}$), 2.22 (d, 2H, $H^{CH2(benzyl)}$), 2.34 (s, 3H, H^{30}), 2.68 (sep, 3H, $H^{13,16,19}$), 3.30 (br s, 2H, H^{CH2-B}), 5.30 (d, 1H, H^{3}), 5.92 (br t, 2H, $H^{CH(benzyl)}$), 6.00 (br t, 1H, $H^{CH(benzyl)}$), 6.22 (br d, 2H, $H^{CH(benzyl}$), 6.45 (m, 5H, $H^{5,CH(benzyl)}$), 6.83 (t, 3H,

$H^{4,CH(benzyl)}$), 6.92 (s, 2H, $H^{,24,26}$), 7.03 (s, $2H^{9,11}$), 7.12 (t, 4H, $H^{CH(benzyl)}$) ppm. ^{13}C NMR (63 MHz, C_6D_6, 298 K): δ = 18.3 ($C^{28,29}$), 20.7 (C^{30}), 21.7 ($C^{14,15,17,18}$), 24.1 $C^{14,15,17,18}$), 27.3 ($C^{20,21}$), 32.2 ($C^{13,16}$), 35.8 (C^{19}), 87.1 ($C^{CH2(benzyl)}$), 103.7 (C^3), 119.1 (C^5), 121.5 ($C^{9,11}$), 124.3 ($C^{24,26}$), 125.1 (C^{benzyl}), 129.1 (C^{benzyl}), 133.0 (C^{benzyl}), 134.0 ($C^{23,27}$), 135.4 (br, C^{BC6F5}), 137.7 (C^7), 139.2 (br, C^{BC6F5}), 142.4 (C^{25}), 143.0 (C^{10}), 145.6 ($C^{8,12}$), 146.8 (br, C^{BC6F5}), 147.3 (C^{benzyl}), 150.8 (br, C^{BC6F5}), 151.6 (C^4), 156.0 (C^{22}), 160.7 (C^6), 165.0 (C^2) ppm ^{19}F NMR (376 MHz, C_6D_6, 298 K): δ = -165.34 (t, *m*-F), -161.41 (t, *p*-F), -130.57 (br, *o*-F) ppm.^{11}B NMR (80 MHz, C_6D_6, 298 K): δ = -11.46 (s, $B^{C6H5CH2B(C6F5)3}$).

Attempted Abstraction of the second benzyl: In an NMR tube one equiv. of $B(C_6F_5)_3$ was added to the zwitterionic complex **7a** and the reaction was studied by NMR spectroscopy. No conversion was observed.

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7. Acetylenetitanium Complex Stabilized by Aminopyridinato Ligands

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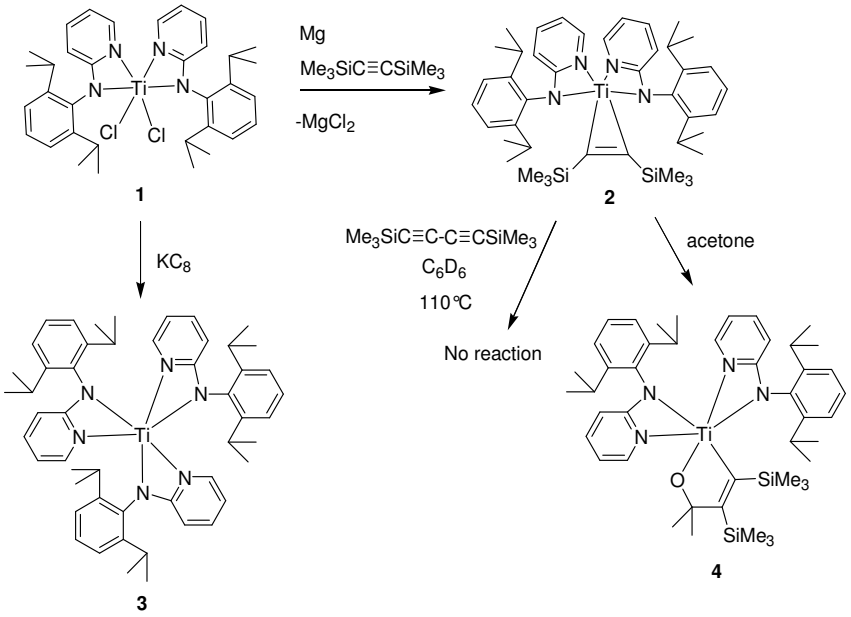
Abstract: The first acetylenetitanium complex stabilized by aminopyridinato ligands has been prepared by the reaction of [Ap_2TiCl_2] [Ap-H = (2, 6-diisopropyl-phenyl)(pyridin-2-yl)-amine], (**1**) with equimolar amount of bis(trimethylsilyl)acetylene in the presence of Mg. The complex was characterized by spectroscopic methods as well as by X-ray single crystal structure analysis. Reduction of **1** with KC_8 under N_2 in the absence of any other stabilizing ligand leads to the ligand rearrangement product [Ap_3Ti]. In the reaction of the acetylenetitanium complex with acetone the titanaoxacyclopentene was formed.

7.1. Introduction

The stabilization of highly reactive low-valent early transition metal complexes is the key to rich and selective small molecule activation chemistry of these compounds. A challenge is to generate these complexes as stable and easy to handle but nevertheless highly reactive compounds. One strategy is the protection of the reactive sites by an easly replaceable ligand. This strategy has been successfully applied to titanocenes and zirconocenes by using alkynes as a protecting ligand.[1] The chemistry of these complexes, and particularly their bonding situation, their spectroscopic properties, their reactivity and mechanistic behavior etc., has been described in several reviews.[1,2] Such complexes have been studied either using Cp (Cp = cyclopentadienyl) or variations of Cp ligands. However, using possible alternatives to Cp ligands to stabilize reduced group 4-metal centres have been investigated to a lesser extent.[3] In order to investigate such alternatives, we decided to employ aminopyridinato ligands. We have explored aminopyridinato ligands for many years[4] and only recently started to work with bulky versions of these ligands.[5] Herein we report on the synthesis and structure of a Cp-free acetylenetitanium complex and some preliminary reactivity studies of this compound.

7.2. Results and Discussion

The starting complex **1** (Scheme 1) was prepared in excellent yields by reacting two equivalents of (2,6-diisopropyl-phenyl)-pyridin-2-yl-amine)[6] with $[(CH_3)_2NTiCl_3]$[7]. Crystals of **1** containing two toluene molecules per titanium atom were grown from concentrated toluene solution. The titanium centre has a distorted octahedral coordination (Figure 1). The Cl1–Ti–Cl2 angle [93.76(10)°] is close to the ideal value of 90° and smaller than in similar (aminopyridinato)chlorotitanium [97.03(5)°[8] and 100.54(3)°][9]. The first acetylene complex of titanocene without additional ligands was prepared by the reduction of $[Cp_2TiCl_2]$ with equimolar amounts of magnesium in the presence of tolane in THF.[10,11] We have found that this procedure can be used successfully to synthesize Aminopyridinato-stabilized titanium complexes as well. The reaction of **1** with magnesium proceeds smoothly in the presence of bis(trimethylsilyl)acetylene at room temperature, affording the corresponding acetylene complex **2** in moderate yields (Scheme 1).



Scheme 1. Synthesis of **2**, **3**, and **4**.

Complex **2** was isolated as dark blue crystals and characterized by NMR spectroscopy. The structure was confirmed by X-ray diffraction studies.[12] The molecular structure of **2** is shown in Figure 2. The small N-Ti-N angle [64.22(18)°] expresses the strained binding situation of the aminopyridinato ligands and the shorter N_{amido}-Ti [2.058(5) Å] distance compared to $N_{pyridine}$-Ti [2.152(5) Å] indicates the localization of the anionic function at the amido N-atom.[13]

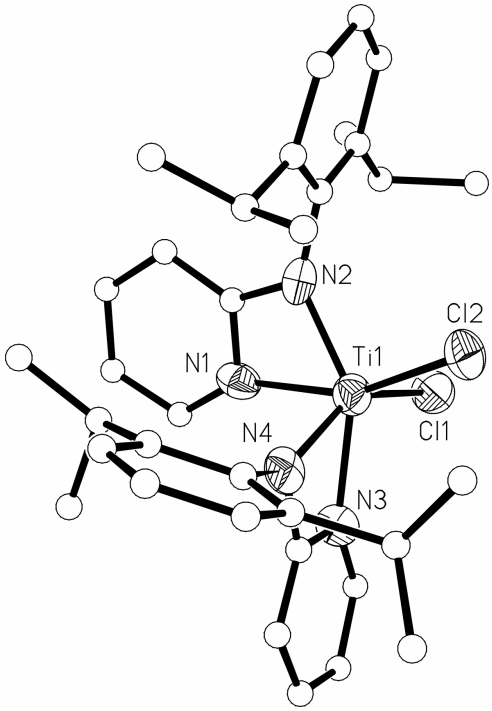


Figure 1. Molecular structure of **1** (ellipsoids correspond to the 50% probability level). Hydrogen atoms and two toluene molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: N1-Ti1 2.179(8), N2-Ti1 1.954(6), N3-Ti1 2.124(7), N4-Ti1 2.036(7), Cl1-Ti1 2.310(3), Cl2-Ti1 2.247(3); N4-Ti1-N3 63.2(3), N2-Ti1-N1 63.8(3), Cl2-Ti1-Cl1 93.76(10).

The carbon atoms of the acetylene, together with the silicon atoms bonded to them, form almost a planar system. The torsion angle SiC≡CSi is 2.0(2)°. The coordinated C≡C bond of the acetylene ligand [1.338(13) Å] is much longer than the normal C≡C bond (1.181 Å), its length being close to the value of 1.331 Å, typical for the C=C bond.[14] Furthermore, this value is significantly higher than that observed for [$Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$] [1.283(6) Å].[2c] The distances between the titanium atom and the carbon atoms of the coordinated alkyne are 2.090(7) Å which are slightly shorter than the values found for [$Cp_2Ti(Me_3SiC{\equiv}CsiMe_3)$] [2.136(5) and 2.139(4) Å]. The CCSi angles of 138.9(2) ° differ from 180° to approach a value of 120°, typical of sp^2-hybridized carbon atoms and are smaller than what was found for the Cp stabilized complex [145.7(4) and 147.8(4)°]. In the solid state **2** is stable under argon at room temperature but rapidly decomposes in the presence of air and moisture.

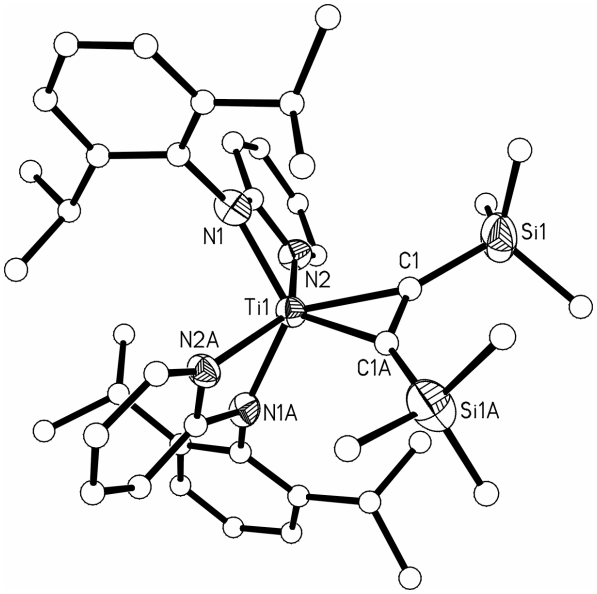


Figure 2. Molecular structure of **2** (ellipsoids correspond to the 50% probability level). Selected bond lengths [Å] and angles [°]: C1-C1A 1.338(13), C1-Ti1 2.090(7), Ti1-N1 2.058(5), Ti1-N2 2.152(5); C1-C1A-Si1 138.9(2), C1-C1A-Ti1 71.33(18), N1-Ti1-N1A 121.4(3), C1-Ti1-C1A 37.3(4), N1-Ti1-N2 64.22(18).

Noteworthy, in the ^{1}H NMR spectrum of **2** is a singlet corresponding to $SiMe_3$ at δ = 0.16 ppm, four doublets for the four diastereotropic methyl groups and two separate septets for CH protons of the aminopyridinato ligand at δ = 2.86 and 3.42 ppm. The ^{13}C NMR spectrum shows, in addition to other signals, the characteristic signal for carbon atoms of acetylene coordinated to Ti (δ = 209.7 ppm) which is comparatively upfield than what has been observed for other titanium-stabilized alkyne complexes indicating a weakly bound acetylene ligand.[2c,15] Reduction of **1** with KC_8 under N_2 atmosphere in the absence of any supporting ligand leads to a homoleptic tris(aminopyridinato)titanium complex **3** the only product that could be isolated (Scheme 1) owing most probably due to ligand rearrangement. Since the paramagnetic nature of **3** prevents structural characterization by NMR spectroscopy, X-ray analysis was performed Figure 3.[12] Only very weakly diffracting crystals of **3** could be obtained resulting in a low-quality structure, therefore detailed discussion of bond lengths and angles is waived. However, the connectivity was established.

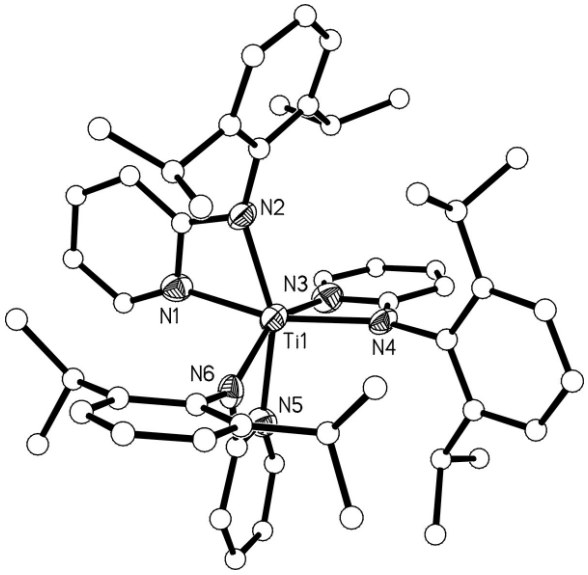


Figure 3. Molecular structure of **3** (ellipsoids correspond to the 50% probability level).

NMR-tube experiments indicate that **2** did not react with 1,4-bis(trimethylsilyl)-1,3-butadiyne even when harsh conditions were applied (a C_6D_6 sample of the mixture was heated at 110 °C for 48 hours). This experiment also indicates that **2** itself is rather stable in solution at high temperature since no decomposition was observed. Complex **2** is capable of insertion reactions as it reacts with one equivalent of acetone in hexane and gives **4** in quantitative yield. Complex **4** has been isolated as red crystals and X-ray analysis[12] reveals two independent molecules per asymmetric unit along with one hexane solvate molecule. The molecular structure of **4** is shown in Figure 4. The ^{1}H NMR spectrum of **4** shows two sets of signals for the non-equivalent $SiMe_3$ groups at δ = 0.26 and 0.42 ppm and two sets of signals for the aminopyridinato ligands. The C(1)-C(2) distance of 1.370(4) Å and the C3-O1 distance [1.432 (3) Å] are in the expected ranges for C-X (X = C, O) bonds.[14]

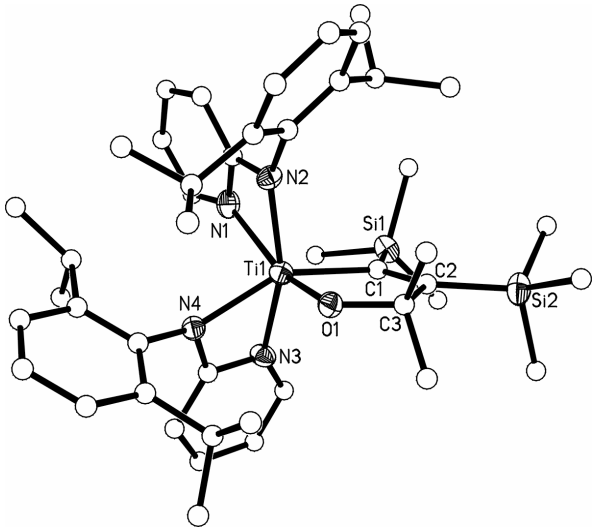


Figure 4. Molecular structure of **4** (ellipsoids correspond to the 50% probability level). Selected bond lengths [Å] and angles [°]: C1-C2 1.370(4), C1-Ti1 2.178(3), C3-O1 1.432(3), Ti1-N1 2.263(3), Ti1-N2 2.008(3), O1-Ti1 1.776(2); O1-Ti1-C1 79.83(11), N2-Ti1-N1 61.99(10).

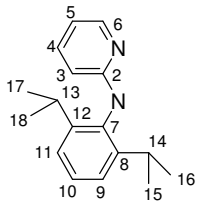
7.3. Conclusions

Complex **2** can be prepared from [Ap_2TiCl_2] via reduction with magnesium in the presence of bis(trimethylsilyl)acetylene. The spectroscopic data of **2** justifies it having a weakly bound acetylene complex. Compound **2** is not only quite stable at room temperature but also at high temperature under argon atmosphere. The reduction of [Ap_2TiCl_2] using KC_8 in the absence of any protecting ligand leads to a homoleptic tris(aminopyridinato)titanium complex. Complex **2** is capable of insertion reactions as it reacts with one equivalent of acetone. In future attempts we are interested in exploring the reactivity of **2** and related titanium as well as zirconium aminopyridinates.

7.4. Experimental Section

General Procedures: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in N_2 filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded with Brucker (250 MHz), Varian Inova (300 MHz) or Varian Inova

(400 MHz) spectrometers at ambient temperature. Atom labelling is shown in Scheme 2. The chemical shifts are referenced to internal TMS for ^{1}H and ^{13}C.



Scheme 2. Atom numbering in Ap ligand of Ap complexes.

Synthesis of 1: Ether (15 mL) was added to (2,6-diisopropyl-phenyl)-pyridin-2-yl-amine) (0.508 g, 2 mmol) and $[(CH_3)_2NTiCl_3]$ (0.198 g, 1 mmol) at ambient temperature. The resulting purple solution was stirred overnight and then filtered in order to separate a dark product. The filtrate was kept at low temperature to afford crystalline material. Yield: (0.598 g, 95.67%). $C_{34}H_{42}Cl_2N_4Ti.C_7H_8$ (717.64): calcd. C 68.62, H 7.02, N 7.81; found C 68.50, H 7.12, N 7.68. ^{1}H NMR (250 MHz, C_6D_6): δ = 0.92 (d, J = 6.8 Hz , 12H, $H^{15,16,17,18}$), 1.21 (d, J = 6.8 Hz, 12H, $H^{15,16,17,18}$), 3.28 (br s, 2H, $H^{13,14}$), 5.52 (d, J = 8.4 Hz, 1H, H^{3}), 5.96 (m , 2H, H^{5}), 6.70 (m, 2H, H^{4}), 7.10-7.18 (m, 6H, $H^{9,10,11}$), 7.78 (d, J = 5.1 Hz, 2H, H^{6}) ppm. ^{13}C NMR (63 MHz, C_6D_6): δ = 24.5 ($C^{15,16,17,18}$), 25.7 ($C^{15,16,17,18}$), 28.3 ($C^{13,14}$), 105.2 (C^{3}), 113.9 (C^{5}), 124.7 ($C^{9,11}$), 137.8 (C^{4}), 141.8 (C^{4}), 142.2 ($C^{8,12}$), 143.9 (C^{7}), 145.2 (C^{6}), 169.6 (C^{2}) ppm.

Synthesis of 2: Bis(timethylsilyl)acetylene (0.44 mL, 1.92 mmol) was added to **1** (1.2 g, 1.92 mmol) and Mg (0.066 g, 2.72 mmol) in THF (20 mL). The solution was stirred overnight at room temperature during which time the colour changed from purple to blue. Solvent was evaporated in vacuum and product was extracted with hexane (2 x 20 mL). The filtrate was kept at low temperature to afford dark blue crystals of **2**. Yield 0.632 g (45.4%). $C_{42}H_{60}N_4Si_2Ti$ (724.99). Calcd. C 59.58, H 8.34, N 7.73; found C 58.97, H 8.21, N 7.76. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.16 (s, 18H, -$SiMe_3$), 0.84 (d, J = 6.9 Hz , 6H, $H^{15,16,17,18}$), 1.04 (d, J = 6.9 Hz , 6H, $H^{15,16,17,18}$), 1.17 (d, J = 6.9 Hz , 6H, $H^{15,16,/7,18}$), 1.20 (d, J = 6.9 Hz , 6H, $H^{15,16,/7,18}$), 2.86 (sep, J = 6.9 Hz, 2H, $H^{13,14}$), 3.42 (sep, J = 6.9 Hz, 2H, $H^{13,14}$), 5.48 (d, J = 8.4 Hz, 2H, H^{3}), 5.86 (t, J = 6.1 Hz, 2H, H^{5}), 6.63 (t, J = 7.2 Hz , 2H, H^{4}), 7.21 (m, 6H, $H^{9,10,11}$), 7.68 (d, J = 5.1 Hz, 2H, H^{6}) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 1.5 ($C_2(Si\mathit{Me}_3)_2$), 24.3 ($C^{15,16,17,18}$), 25.2 ($C^{15,16,17,18}$), 25.7 ($C^{15,16,17,18}$), 27.8 ($C^{13,14}$), 28.5 ($C^{13,14}$), 105.0 (C^{3}), 111.2 (C^{5}), 124.5 (d, $C^{9,11}$), 126.5 ($C^{9,11}$), 140.2 ($C^{8,12}$), 141.3 (C^{10}), 144.8 (C^{4}), 145.7 (C^{7}), 150.4 (C^{6}), 160.3 (C^{2}), 209.7 ($\mathit{C}_2(SiMe_3)_2$) ppm.

Synthesis of 3: THF (30 mL) was added to **1** (1.251 g, 2.00 mmol) and KC_8 (1.083 g, 8.00 mmol) at ambient temperature. Warming up was observed and suddenly the colour changed to black. The reaction mixture was stirred under N_2 for 24 hours. The solvent was evaporated in vacuum and the product extracted with hexane. The dark filtrate was kept at room temperature to afford red crystals of the product. Yield 0.205 g (12.7%). $C_{51}H_{63}N_6Ti$ (807.95). Calcd. C 75.81, H 7.86, N 10.40; found C 74.94, H 7.86, N 10.86. ^{1}H NMR (400 MHz, C_6D_6): δ = -11.79 (s), -8.33 (s), 0.38 (s), 0.86-1.23 (br m), 1.40 (d), 1.62 (s), 2.98 (s), 3.57 (s), 4.05 (br s), 5.78 (d), 6.11 (br s), 6.94 (d), 7.02 (d), 7.96 (s), 8.38 (br s), 9.82 (s) ppm.

Synthesis of 4: Acetone (0.02 mL, 0.28 mmol) was added to **2** (0.2 g, 0.28 mmol) in hexane (5 mL) at room temperature; the colour of the mixture changed from blue to dark red. The solution was stirred for five minutes and then kept at low temperature to afford red crystals of **4**. Yield 0.186 g (80.4%). $C_{45}H_{66}N_4Osi_2Ti$ + 0.5 hexane (826.16). Calcd. C 69.78, H 8.91, N 6.78; found C 70.19, H 8.87, N 6.95. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.26 (s, 9H, -Si*Me*$_3$), 0.42 (s, 9H, -Si*Me*$_3$), 0.72 (d, *J* = 6.6 Hz, 6H, $H^{15,16,17,18}$), 0.87 (d, *J* = 6.6 Hz, 3H, $H^{15,16,17,18}$), 1.12 (s, 3H, CH_3), 1.18 (d, *J* = 6.6 Hz, 3H, $H^{15,16,17,18}$), 1.20 (d, *J* = 6.6 Hz, 3H, $H^{15,16,17,18}$), 1.28 (s, 3H, H^{CH3}), 1.33 (d, *J* = 6.9 Hz, 3H, $H^{15/16/17/18}$), 1.50 (d, *J* = 6.9 Hz, 3H, $H^{15/16/17/18}$), 2.22 (sep, *J* = 6.6 Hz, 1H, $H^{13/14}$), 2.35 (sep, *J* = 6.6 Hz, 1H, $H^{13/14}$), 3.87 (sep, *J* = 6.9 Hz, 1H, $H^{13/14}$), 4.06 (sep, *J* = 6.9 Hz, 1H, $H^{13/14}$), 5.60 (d, *J* = 8.5 Hz, 1H, H^3), 5.73 (d, *J* = 8.7 Hz, 1H, H^3), 5.90 (t, *J* = 6.4 Hz, 1H, H^5), 6. 06 (t, *J* = 6.0 Hz, 1H, H^5), 6.72 (m , 1H, H^4), 6.87 (m, 1H, H^4), 7.04-7.31 (m, 6H, $H^{9,10,11}$), 7.69 (dd, 1H, H^6), 8.20 (dd, 1H, H^6) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 4.5 (-$SiMe_3$), 6.0 (- $SiMe_3$), 25.0 ($C^{15,16,17,18}$), 25.2 ($C^{15,16,17,18}$), 25.7 ($C^{15,16,17,18}$), 26.3 ($C^{15,16,17,18}$), 27.3 ($C^{15,16/17,18}$), 27.6 ($C^{15,16/17,18}$), 28.2 ($C^{13/14}$), 28.4 ($C^{13/14}$), 28.6 ($C^{13/14}$), 28.7 ($C^{13/14}$), 29.2 (C^{CH3}), 31.9 (C^{CH3}), 92.8 (CO), 106.0 (C^3), 107.3 (C^3), 108.7 (C^5), 111.4 (C^5), 123.2 ($C^{9/11}$), 124.0 ($C^{9/11}$), 124.6 ($C^{9/11}$), 125.4 ($C^{9/11}$), 125.7 ($C^{9/11}$), 126.6 ($C^{9/11}$), 139.9 ($C^{8,12}$), 140.8 ($C^{8,12}$), 143.7 (C^4), 143.9 (C^4), 144.6 (C^{10}), 144.7 (C^7), 145.1 (C^7), 145.4 (C^6), 145.7 (C^6), 170.2 (C^2), 173.0 (Ti-C=C*), 186.9 (Ti-C*=C) ppm.

Acknowledgments

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[12] Selected details of the X-ray crystal structure analyses for **1** x 2 C_7H_8: space group: P2(1)2(1)2(1), a = 32.213(3) Å, b = 9.2810(10) Å, c = 14.6820(18) Å; V = 4389.5(8) Å^3, z = 4, reflections collected/unique/observed = 38832/7336/3110, parameters = 498, R (obs.) = 0.0787, wR_2 (all data) = 0.1991, wR_2 (obs.) = 0.1711; **2**: space group: P3(2)21, a = 19.4919(14) Å, b = 19.4919(15) Å, c = 9.4918(7) Å; V = 3123.1(4) Å^3, z = 3, reflections collected/unique/observed = 29109/2736/2231, parameters = 229, R (obs.) = 0.0741, wR_2 (all data) = 0.1522, wR_2 (obs.) = 0.1444; **3**: space group: P 2(1)/c, a = 13.3860 (11) Å, b = 13.3220 (11) Å, c = 25.739 (2) Å; β = 99.441(7)°, V = 4527.8 (7) Å^3, z = 4, reflections collected/unique/observed = 8598/8598/3463, parameters = 523, R (obs.) = 0.1059, wR_2 (all data) = 0.2251, wR_2 (obs.) = 0.1781; **4**: space group: P-1, a = 10.4280(8) Å, b = 13.532(11) Å, c = 18.1300(15) Å; α = 95.933(6), β = 106.305(6), γ = 101.491(6)°, V = 2371.5(3) Å^3, z = 2, reflections collected/unique/observed = 8950/8950/3513, parameters = 511, R (obs.) = 0.0425, wR^2 (all data) = 0.0805, wR^2 (obs.)

= 0.0692; X-ray crystal structure analysis was carried out with a STOE IPDS II diffractometer equipped with an Oxford Cryostream low-temperature unit. CCDC-676560 (**1**), CCDC-676561 (**2**), CCDC-676562 (**3**) and CCDC-676563 (**4**) 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.

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8. Synthesis and Structure of Low Valent Chromium Complexes Stabilized by η^2-Coordinated Aminopyridinato Ligands

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Keywords: Amidopyridine ligands / Aminopyridinato ligands / Chromium / N ligands / η^2-coordination

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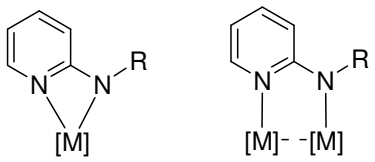
Abstract: Reacting one equivalent of the deprotonated sterically demanding aminopyridines **1** {**1** = (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine}, and **2** {**2** = (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amine} with $[CrCl_3(thf)_3]$ or $CrCl_2$ leads to η^2-coordinated monomeric $[ApCrCl_2(thf)_2]$ or dimeric $[ApCr(\mu\text{-}Cl)(thf)_n]_2$ complexes, respectively (Ap = Aminopyridinato and n = 0-1). However the reaction of comparatively less steric version of such ligands, **3** {**3** = (2,4,6- trimethyl-phenyl)- [6-(2,4,6-trimethyl-phenyl)–pyridin-2-yl]-amine} with $[CrCl_3(thf)_3]$ or $CrCl_2$, leads to the bis(aminopyridinates) $[Ap_2CrCl(thf)]$ and $[Ap_2Cr]$, respectively. All these complexes are paramagnetic, and four of them have been characterized by X-ray analyses in addition to other analytical techniques. The complexes described in this paper are the first examples of η^2-coordinated Cr^{II} aminopyridinates.

8.1. Introduction

M^{III} amido complexes of the early transition metals were first described by Bürger and Wannagat[1] and simultaneously explored by Bradley et al..[2] They were investigated with regard to structural aspects and the nature of the amido metal bond.[3] The first Cr^{II} amido complex was published by Cotton et al.[4] We are investigating the coordination chemistry of aminopyridinato ligands[5] and have reported the first η^2-coordinated homoleptic Cr^{III} aminopyridinate in 1998.[6] The dominating binding mode of aminopyridinato ligands in early transition metals and lanthanide chemistry[7] is the strained η^2-coordination (Scheme 1, left).



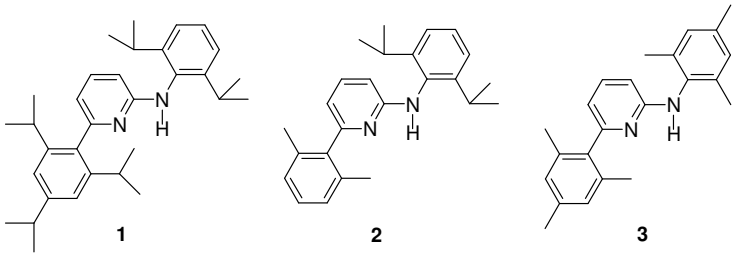
Scheme 1. Important binding modes of deprotonated 2-aminopyridines ([M] = transition metal; R = aryl, silyl, or alkyl substituent).

All Cr^{II} complexes stabilized by deprotonated aminopyridines so far did show the bridging binding mode (Scheme 1, right).[4,8] It should be possible to avoid the classic paddlewheel arrangement which was observed for these compounds by introducing steric bulk. We started recently to investigate the coordination chemistry of bulky aminopyridinates [9] and were able to observe unique catalytic chemistry resulting from this bulkiness.[9c,e,f,h] Here we report on the syntheses and structures of mono- and bis(aminopyridinato) Cr^{II} and Cr^{III} complexes stabilized by η^2-coordinated aminopyridinato ligands.

8.2. Results and Discussion

Syntheses and Structures of Complexes

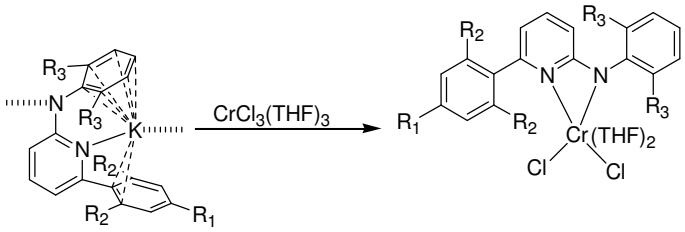
The aminopyridines **1**, **2**, and **3** (Scheme 2) were synthesized according to the published procedures.[9a,c,10]



Scheme 2**.** Applied aminopyridines.

Reacting one equivalent of **4** (potassium salt of deprotonated **1**) or **5** (potassium salt of deprotonated **2**)[9a] in THF with $[CrCl_3(thf)_3]$ and crystallization from hexane leads to the formation of monomeric Cr^{III} complexes **6** and **7**, respectively, (Scheme 3). Crystals of **6** suitable for X-ray analysis were grown from concentrated hexane solution as a hexane solvate at room temperature. Details of the X-ray structure analysis are given in Table 1. The coordination can be best described as pseudo octahedral with two THF ligands in *cis* positions and two chlorides in *trans* positions (Figure 1). The main reason for the distortion is the

narrow N1-Cr-N2 angle [65.95 (8)°] in the four membered chelate ring. Other *cis* angles vary between 87.72(7) and 108.91(7)°. The Cr-$N2_{(pyridine)}$ distance [2.050(2) Å] is slightly longer than Cr-$N1_{(amide)}$ distance [2.006(19) Å] suggesting the localization of the anionic function of the ligand at the amido N-atom[11] which is in contrast to the literature values of the chromium complexes with less bulky version of such ligands (silylaminopyridinato ligands) [Cr-$N_{(pyridine)}$ 2.04 Å and Cr-$N_{(amide)}$ 2.06 Å] where delocalization was observed for.[6] However, siloxane-bridged bis(aminopyridinato) ligands coordinate in the amidopyridine form [Cr-$N_{(pyridine)}$ 2.102(7) Å and Cr-$N_{(amide)}$ 1.999(5) Å].[12]



4, 5 **6, 7**

Scheme 3: Synthesis of **6** and **7** (**4**, **6**: $R_1 = R_2 = R_3$ = i-Pr), (**5**, **7**: R_1 = H, R_2 = Me, R_3 = i-Pr).

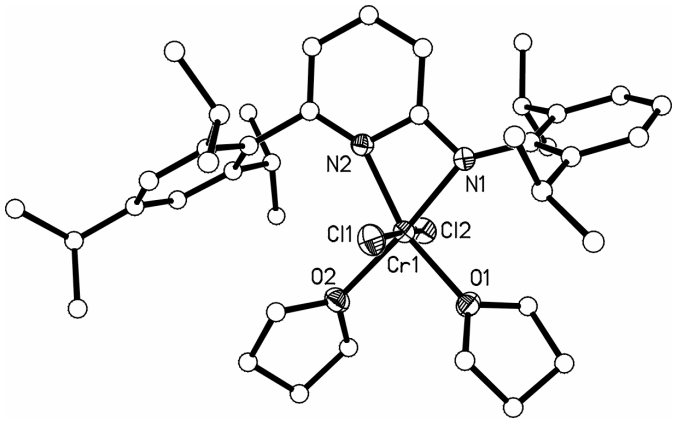


Figure 1. Molecular structure of **6** (ellipsoids coreesponds to 50% probability); Hydrogen atoms and one hexane molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Cr1 2.0056(19), N2-Cr1 2.050(2), O1-Cr1 2.0461(17), O2-Cr1 2.0927(16), Cl1-Cr1 2.3028(9), Cl2-Cr1 2.3217(9); N1-Cr1-O1 97.49(7), N1-Cr1-N2 65.95(8), O1-Cr1-O2 87.71(7), N2-Cr1-O2 108.91(7), Cl1-Cr1-Cl2 173.42(3).

Dark green crystals of **7** suitable for X-ray analysis were grown from THF : hexane (1:10) mixture at room temperature. The octahedral geometry around the Cr centre is similarly distorted as in **6** (Figure 2). However, noteworthy are the equal bond distances N1-Cr1 2.023(3) and N2-Cr1 2.022(3) Å for the amido and pyridine N-atoms. Thus, a delocalised

binding mode with equivalent nitrogen to metal bonds such as known for benzamidinate[13] complexes is proposed for **7**, which is in contrast to the binding situation in complex **6**.

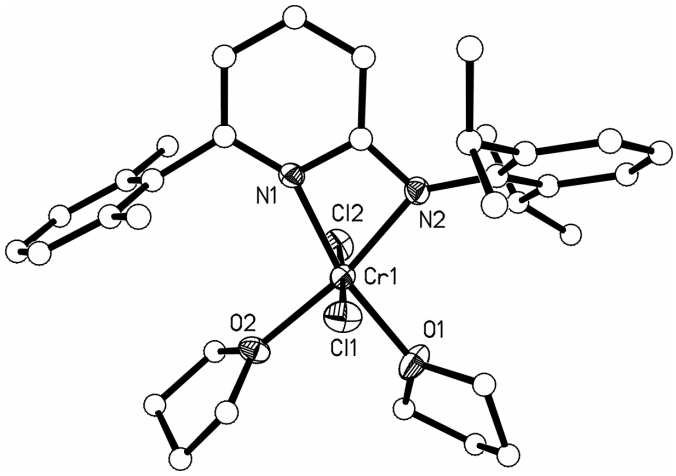
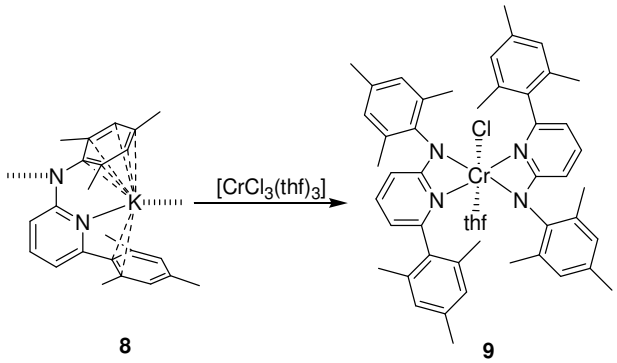


Figure 2. Molecular structure of **7** (ellipsoids corresponds to 50% probability); Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Cr1 2.023(3), N2-Cr1 2.022(3), O1-Cr1 2.037(3), O2-Cr1 2.070(3), Cl1-Cr1 2.3071(12), Cl2-Cr1 2.33183(12); N2-Cr1-N1 65.75(12), N2-Cr1-O1 101.53(12), O1-Cr1-O2 88.16(11), N1-Cr1-O2 104.57(11), Cl1-Cr1-Cl2 177.94(5).

However, when one or two equivalents of less bulky **8**[9j] (potassium salt of **3**) are reacted with $[CrCl_3(thf)_3]$ a bis(aminopyridinato) Cr complex **9** is formed (Scheme 4). The effective magnetic moments of μ_{eff} = 3.38, 3.37 and 3.01 μ_B for **6, 7** and **9**, respectively, indicate the presence of three unpaired electrons as expected for octahedral Cr^{III} complexes.

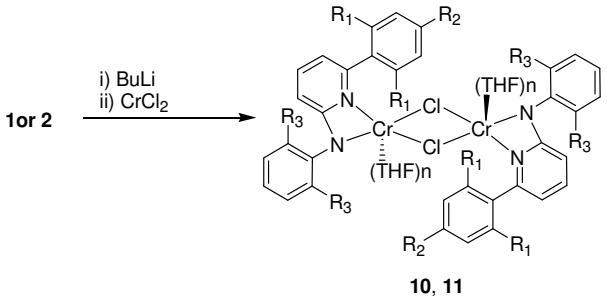


8 **9**

Scheme 4. Synthesis of **9**.

In analogous way to Cr^{III} complexes, Cr^{II} complexes were prepared but using solutions of lithium salts instead of potassium salts of the corresponding ligands. Thus, when one equivalent of lithiated ligands **1** or **2** was reacted with $CrCl_2$ in THF very moisture and air

sensitive mono(aminopyridinato) chromium complexes **10** and **11**, respectively, were formed (Scheme 5).



Scheme 5. Synthesis of **10** and **11** (**10**: $R_1 = R_2 = R_3 = CH(CH_3)_2$, n = 0, **11**: $R_1 = CH_3$, $R_2 = H$, $R_3 = CH(CH_3)_2$, n = 1).

Complex **10** was extracted from reaction mixture with hexane and X-ray quality crystals were grown from concentrated hexane solution at room temperature. The compound crystallizes with one hexane solvate molecule. X-ray single crystal analysis reveals it to be a dimeric compound. The geometry around the metal centre can best be described as distorted square planar with the two nitrogen atoms of the ligand and the two bridging chlorine atoms completing the coordination sphere (Figure 3). The smaller N_{amido}-Cr-$N_{pyridine}$ angle of 65.71(7)° leads to wider $N_{pyridine}$-Cr-Cl and N_{amido}-Cr-Cl angles of 102.71(5)° and 100.36(6)°, respectively. However, the Cl-Cr-Cl angle [91.24(2)°] is close to the ideal angle. The coordination of THF to chromium is prevented by the steric bulk of the ligand. The distance of 3.304 Å argues against any close contact between the two chromium atoms. The bridging Cl atoms have comparable bond distances to Cr of 2.358(7) and 2.366(6) Å.

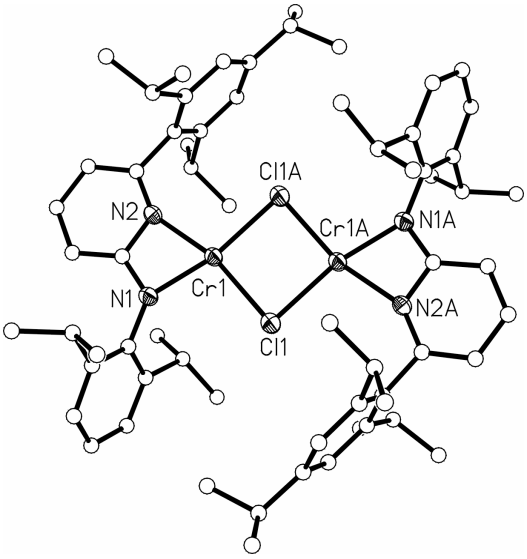
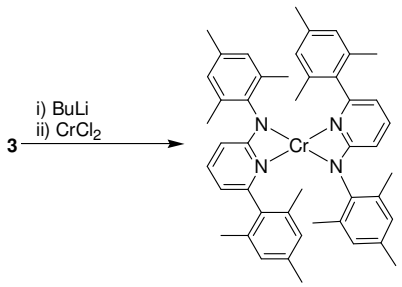


Figure 3. Molecular structure of **10** (ellipsoids corresponds to 50% probability); Hydrogen atoms and one hexane molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Cr1 2.0201(18), N2-Cr1 2.0634(19), Cl1-Cr1 2.3582(7), Cl1-Cr1 2.3662(6); N1-Cr1-N2 65.71(7), N1-Cr1-Cl1 100.36(6), N2-Cr1-Cl1A 102.71(5), Cl1A-Cr1-Cl1 91.24(2).

To the best of our knowledge these are the first η^2-coordinated aminopyridinato Cr^{II} complexes. The effective magnetic moments of 4.77 and 5.61 μ_B for **10** and **11**, respectively, indicate that each of these complexes has four unpaired electrons.



Scheme 6. Synthesis of **12**.

However, one equivalent of lithiated less bulky ligand, **3** reacts with $CrCl_2$ to afford η^2-coordinated homoleptic bis(aminopyridinato) chromium complex **12** (Scheme 6). Red crystals of **12** of X-ray quality were grown from toluene solution. The structure elucidation reveals it to be a monomeric chromium complex without any coordinated THF molecules (Figure 4). The geometry can best be described as distorted square planar. The reason for the distortion is again the narrow N2-Cr1-N1 bond angle [66.36(8)°]. The two coordinated aminopyridinato

ligands adopt *trans* arrangement with respect to each other with the pyridine rings lying in the coordination plane of chromium.

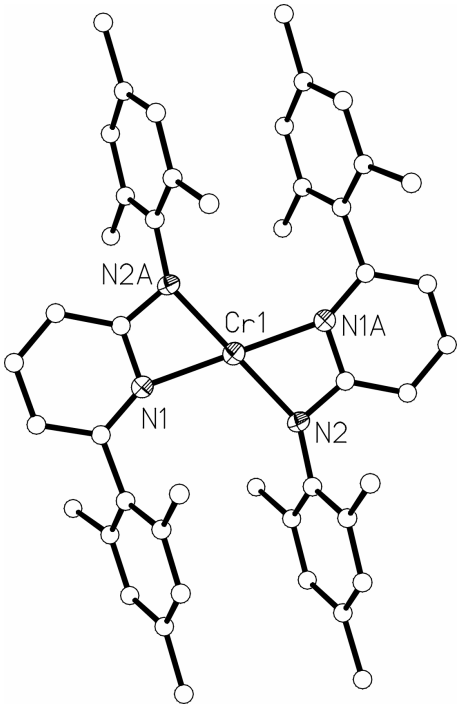


Figure 4. Molecular structure of **12** (ellipsoids corresponds to 50% probability); Hydrogen atoms and one toluene molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Cr1 2.076(2), N2-Cr1 2.021(2); N1-Cr1-N1 180.00(13), N2-Cr1-N1 66.36(8), N2-Cr1-N1 113.64(9).

The effective magnetic moment of 4.08 μ_B reveals it to have four unpaired electrons. Due to the paramagnetic nature all these complexes show only broad signals in ^{1}H NMR spectra.

8.3. Conclusions

The chemistry of low valent chromium stabilized by sterically demanding aminopyridinato ligands has been explored. η^2-coordinated monomeric and dimeric mono(aminopyridinato) chromium complexes can be synthesized in good yields by reacting sterically bulky deprotonated ligands with $CrCl_3$ or $CrCl_2$ respectively. However less bulky version of such ligands selectively gave rise bis(aminopyridinato) chromium complexes.

Table 1. Details of the X-ray structure analyses.

Compound	**6** x C_6H_{14}	**7**	**10** x C_6H_{14}	**12** x C_7H_8
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	P-1	P2(1)/c	P2(1)/n	P-1
a [Å]	10.5940(10)	13.2360(8)	14.9700(7)	11.2430(12)
b [Å]	14.8900(10)	11.4430(7)	14.9590(8)	11.3130(12)
c [Å]	15.4030(10)	21.3800(13)	16.4569(8)	12.0010(14)
α [°]	63.156(5)			102.200(9)
β [°]	86.600(5)	90.678(5)	117.018(4)	109.077(8)
γ [°]	78.347(5)			113.482(8)
V [$Å^3$]	2121.8(3)	3238.0(3)	3282.9(3)	1216.1(2)
crystal size [mm^3]	0.4 x 0.3 x 0.1	0.7 x 0.6 x 0.3	0.7 x 0.4 x 0.4	0.7 x 0.7 x 0.4
ρ_{calcd} [g cm^{-3}]	1.199	1.281	1.186	1.222
T [K]	190(2)	133(2)	133(2)	133(2)
θ range [°]	1.48 to 25.80	1.54 to 25.71	1.53 to 25.63	1.95 to 25.68
No. of unique refl.	8002	6115	5995	4580
No. of obsd. Refl. [I > 2σ(I)]	5425	4520	5249	3742
No. of parameters	451	363	352	295
wR_2 (all data)	0.1005	0.1685	0.1334	0.1801
R value [I > 2σ(I)]	0.0443	0.0611	0.0490	0.0594

8.4. Experimental Section

General Procedures: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in N_2 filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. Commercial [$CrCl_3(thf)_3$] (Aldrich) $CrCl_2$ (Alfa Aesor) were used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded on a Bruker ARX (250 MHz), Varian (300 MHz) and Varian (400 MHz) spectrometers at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS for ^1H and ^{13}C. Elemental analyses (CHN) were determined using a Vario EL III instrument. The effective magnetic moments were determined using Sherwood Scientific Magentic

Susceptibility Balance. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97, [14] SHELXL97 [15] and WinGX.[16] Crystallographic details are summarized in Table 3.

Synthesis of 6: THF (20 mL) was added to $[CrCl_3(thf)_3]$ (0.375 g, 1.0 mmol) and **4** (0.495 g, 1.0 mmol) at 0 °C. The resulting brown solution was allowed to warm up to room temperature and was stirred overnight. THF was removed under vacuum and the product was extracted with hexane (20 mL). The filtrate was reduced and allowed to stay at room temperature affording brownish green crystals. Yield: 0.446 g (62%). $C_{40}H_{59}Cl_2CrN_2O_2$ (722.81): Calcd. C 66.47 H 8.23 N 3.88; found C 66.99 H 8.68 N 3.80. ^{1}H NMR (250 MHz, C_6D_6): δ = 0.86 (br s), 1.15 (br s), 2.85 (br d), 3.31 (br s), 5.87 (br s), 6.59 (br s) ppm.

Synthesis of 7: THF (20 mL) was added to $[CrCl_3(thf)_3]$ (0.375 g, 1.0 mmol) and **5** (0.397 g, 1.0 mmol). The resulting brown solution was allowed to warm up to room temperature and was stirred overnight. THF was removed in vacuum and the product was extracted with hexane (20 mL). The filtrate was reduced and allowed to afford brownish green crystals at room temperature. Yield: 0.422 g (68%). $C_{33}H_{45}Cl_2CrN_2O_2$ (624.62): Calcd. C 63.45 H 7.26 N 4.48; found C 63.31 H 7.63 N 4.52. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.00 (v br t), 2.17 (s), 3.67 (v br s), 6.74 (br s), 8.59 (br s), 23.06 (v br s) ppm.

Synthesis of 9: THF (20 mL) was added to $[CrCl_3(thf)_3]$ (0.209 g, 0.55 mmol) and **8** (0.410 g, 1.11 mmol) at 0 °C. The resulting brown solution was allowed to warm up to room temperature and was stirred overnight. THF was removed under vacuum and the product was extracted with hexane (20 mL). The filtrate was reduced till crystallization started and allowed to stand at room temperature to afford green crystalline material. Yield: 0.181 g (29%) [0.523 g (85%) when reacted with two equivalents of the ligand]. $C_{50}H_{58}ClCrN_4O$ (818.47): Calcd. C 73.37 H 7.14 N 6.85; found C 72.83 H 7.46 N 6.41. ^{1}H NMR (400 MHz, C_6D_6): δ = -8.35 (v br s), 0.85 (m), 1.36 (v br m), 2.09-2.24 (m), 2.35-2.49 (br m), 3.64 (v br s), 5.61 (s), 5.86 (s), 6.00 (s), 6.25 (d), 6.43 (s), 6.80 (d), 6.96 (s), 7.35 (s), 7.67 (br s), 9.29 (br s), 12.54 (br s) ppm.

Synthesis of 10: BuLi (1.31 mL, 2.09 mmol) was added to **1** (0.958 g, 2.09 mmol) in THF (20 mL) at 0 °C and was stirred for two hours at room temperature. The lithiated solution was

then added to $CrCl_2$ (0.257 g, 2.09 mmol) in THF (5 mL) at 0 °C. The resulting brownish green solution was warmed to room temperature and was stirred overnight. THF was removed under vacuum and the product was extracted with hexane (10 mL). The filtrate was allowed to stand overnight to afford green crystalline material. Yield: 0.874 g (68%). $C_{36}H_{51}ClCrN_2O$ (615.25): Calcd. C 70.76, H 7.98 N 5.16; found C 70.08 H 7.62 N 5.30. ^{1}H NMR (400 MHz, C_6D_6): δ = -0.13 (br s), 0.89 (br m), 2.88 (br m), 3.34 (br s), 4.66 (v br s), 5. 65 (v br s), 5.89 (br s), 6.59 (d, J = 4.7 Hz), 6.72 (s), 6.95 (s), 7.24 (s), 7.95 (v br s) ppm.

Synthesis of 11: BuLi (2.5 mL, 4.00 mmol) was added to **2** (1.434 g, 4.00 mmol) in THF (20 mL) at 0 °C and was stirred for two hours at room temperature. The lithiated solution was then added to $CrCl_2$ (0.492 g, 4.00 mmol) in THF (5 mL) at 0 °C. The resulting brownish green solution was allowed to warm to room temperature and was stirred overnight. THF was removed under vacuum and the product was extracted with pentane (20 mL). The filtrate was allowed to stand overnight at -25 °C to afford green crystalline material. Yield: 0.89 g (43%). $C_{29}H_{37}ClCrN_2O$ (517.7): Calcd. C 67.36 H 7.21 N 5.42; found C 66.69 H 6.86 N 5.38. ^{1}H NMR (250 MHz, C_6D_6): δ = 0.87 (br s), 1.09 (br s), 1.23 (br s), 2.22 (s), 3.31 (br s), 3.98 (v br s), 5.87 (br s), 6.39 (br s) ppm.

Synthesis of 12: BuLi (1.92 mL, 3.07 mmol) was added to **3** (1.014 g, 3.07 mmol) in THF (20 mL) at 0 °C and was stirred for two hours at room temperature. The lithiated solution was then added to $CrCl_2$ (0.378 g, 3.07 mmol) in THF (5 mL) at 0 °C. The resulting brownish green solution was allowed to warm to room temperature and was stirred overnight. THF was removed under vacuum and the product was extracted with toluene (20 mL). The filtrate was allowed to stand overnight at -25 °C to afford red crystals of **12**. Yield: 0.37 g (33%). $C_{46}H_{50}CrN_4$ (710.91): Calcd. C 77.72 H 7.09 N 7.88; found C 76.73 H 7.45 N 7.72. ^{1}H NMR (300 MHz, C_6D_6): δ = -5.05 (v br s), 0.28 (br s), 0.86 (br s), 1.22 (br s), 2.07 (s), 2.20 (d), 3.04 (v br s), 5.16 (v br s), 5.83 (s), 6.41 (s), 6.74 (s), 8.24 (v br s) ppm.

Acknowledgments

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9. Metal-Metal Distances at the Limit: A Coordination Compound with an Ultra Short Cr-Cr-Bond**

In memoriam Franz Hein

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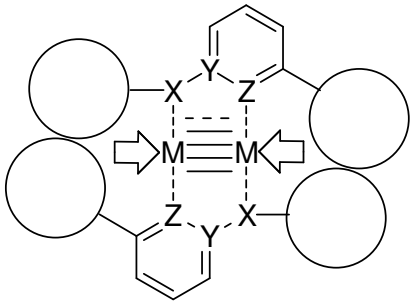
9.1. Main Text

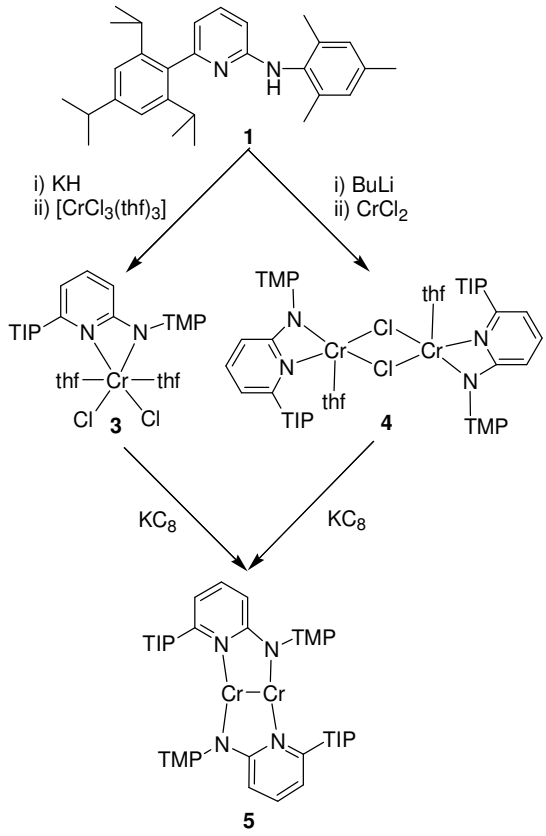
The nature of the chemical bond is of fundamental importance and has always fascinated scientists.[1] Metal-metal bonds are hereby of special interest since unique multibond systems are known[2,3] as well as assumed.[4] The quest for the shortest metal-metal bond is tightly connected to the element chromium[2,5] and has only very recently been reinitiated after the first observation of a bonding order greater than four for this metal.[3] Hence, shortly after the shortest metal-metal bond with a Cr-Cr distance of 1.80 Å was observed in a dimeric Cr complex with such a high bonding order.[6] In parallel performed detailed studies on ArCrCrAr complexes (Ar = Aryl) support the findings that such small values can be obtained for this class of compounds.[7] Some years ago, we started to develop the chemistry of aminopyridinato complexes of chromium[8] and herein report on the synthesis and the (electronic) structure of a bimetallic Cr^{I}-complex with a drastically shortened metal-metal distance in comparison to known bond distances observed up to now. The extremely short metal-metal distance of only 1.75 Å results from a combination of Power`s concept for the stabilization of bonding orders higher than four,[3,7] Hein-Cotton`s principles on the

realization of extremely short metal-metal distances via bridging anionic ligands of type XYZ[2,9] as well as a minimization of additional metal ligand interactions by optimized steric shielding (Scheme 1).



Scheme 1. Shortening of the metal-metal distance through high bonding order, bridging coordination of anionic ligands of type X-Y-Z and minimization of additional metal-ligand interactions by steric shielding.

The deprotonation of aminopyridine **1** with KH leads to a potassiated [6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-(2,4,6-trimethyl-phenyl)-amine (**2**), that easily reacts with $[CrCl_3(thf)_3]$ affording complex **3** (Scheme 2). Compound **3** can be isolated as a green crystalline material in good yield. In the ^{1}H-NMR spectrum only broad signals can be observed and magnetic susceptibility experiments show a magnetic moment of μ_{eff}(300K) = 3.2 μ_B. When **1** is deprotonated with BuLi and reacted with $CrCl_2$ in THF, the dimeric Cr^{II} complex **4** is obtained in good yield as a green crystalline material after removal of the solvent and subsequent extraction with toluene. The molecular structure of **4** is shown in Figure 1.[10] Compound **4** is the first Cr^{II} complex in which the deprotonated aminopyridine shows a strained bidentate coordination mode and does not act as a bridging ligand.[11] The chromium-nitrogen bond lengths clearly distinguish this compound as an amidopyridine i.e., the anionic function of the ligand is localized on the N_{amido}-atom (N2).[12] Reduction of **4** with potassium graphite in THF affords **5** as a red crystalline material after the removal of the solvent and extraction with toluene (Scheme 2). The reduction of **3** with KC_8 also leads to **5**. In the ^{1}H NMR spectrum of **5** (diamagnetic) only one set of signals is observed.



Scheme 2. Synthesis of **3**, **4** and **5** (TIP = 2,4,6-Triisopropylphenyl, TMP = 2,4,6-Trimethylphenyl).

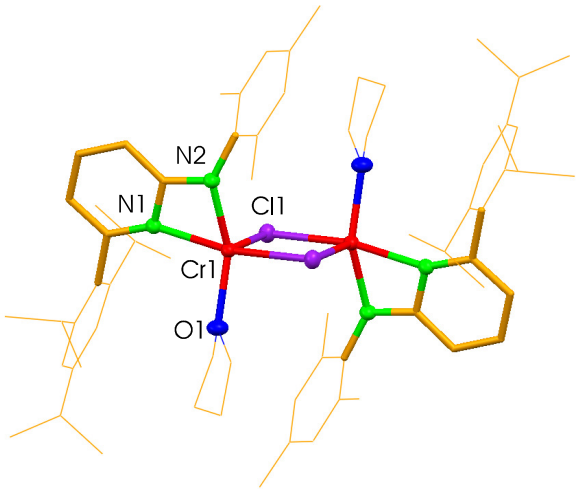


Figure 1. Molecular structure of **4** [ORTEP-Drawing (on the 50% probability level) for all non carbon atoms] Hydrogen atoms and two toluene molecules (per complex) have been omitted for clarity. Selected bond lengths and angles [Å, °]: N1-Cr1 2.1041(15), N2-Cr1 2.0411(14), Cl1-Cr1 2.3773(5), Cl1'-Cr1 2.6219(5), Cr1-O1 2.0869(13); N2-Cr1-N1 64.77(6), O1-Cr1-N1 98.74(5).

The X-ray crystal structure analysis of **5** distinguishes it as a bridgingly-coordinated bimetallic complex, with an exceptionally short metal-metal distance of 1.7488(18) Å (Figure 2).[13] The hitherto shortest metal-metal bond known [1.8028(9) Å] belongs to a dimeric Cr complex stabilized by a N-ligand as well, whose electronic structure was interpreted to show "some degree of quintuple bonding".[6] For nearly 30 years, an aryl-Cr^{II} compound structurally characterized by Cotton and coworkers,[14] which was first prepared by F. Hein and coworkers more than 40 years ago,[9a] claimed to have the shortest experimentally obtained metal-metal distance of 1.830(4) Å. Low-temperature laser-evaporated Cr_2 in the gas phase has a distance of 1.68 Å.[15]

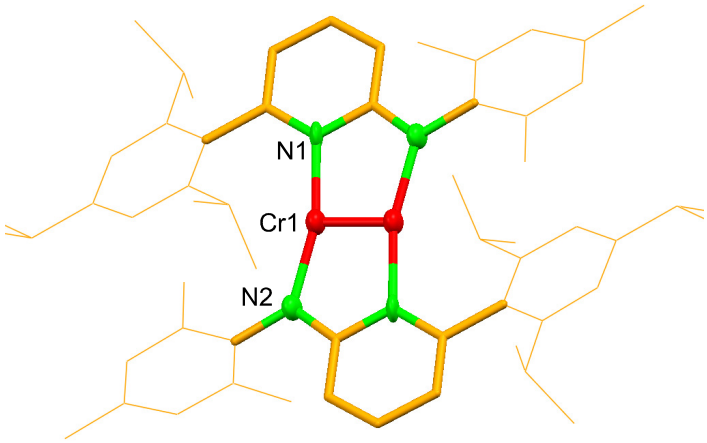


Figure 2. Molecular structure of **5** [ORTEP-Drawing (on the 50% probability level) for all non carbon atoms] Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles [Å, °]: Cr1-Cr1' 1.7488 (18), Cr1-N2 1.998 (4), Cr1-N1 2.028 (4); Cr1'-Cr1-N2 98.55 (13), Cr1'-Cr1-N1 96.78 (13), N2-Cr1-N1 164.64 (16).

In complex **5** chromium-N_{amido} bond lengths are exceptionally shorter [1.998(4) Å] and clearly lie under the average value for this bond [2.050 Å (dimeric chromium complexes with deprotonated aminopyridines as bridging ligands)[11]] and are shorter than the shortest reported bond of this kind [2.019 Å[11a]]. Similar feature is observed for the chromium-$N_{pyridine}$ bond lenghts [2.028(4) Å for **5**, average: 2.062 Å,[11] minimum: 2.023 Å [11e]]. Thus, the exceptionally short metal-metal distance in **5** cannot be explained by a weak coordination of deprotonated **1**, due to the steric demand of the ligand, and hence resulting in a nearly "naked" Cr^{2+}_2-dumbbell.

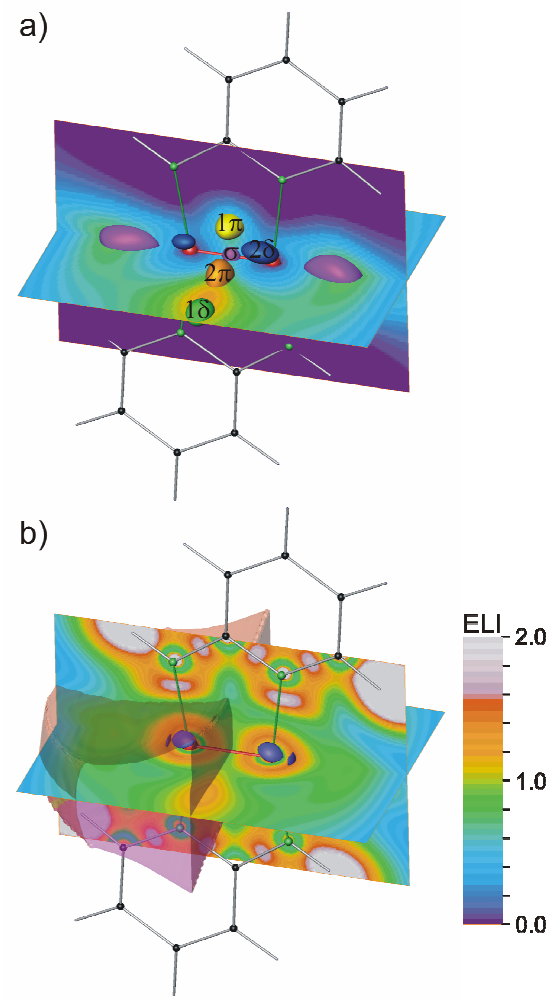


Figure 3. a) Isosurface diagram of the pELI-D contributions of dσ (purple), dπ (yellow and orange) and dδ orbitals (green und dark blue); The section planes show the sum of the five pELI-D contributions; b) Section plane shows (total-)ELI-D; the dark blue isosurface of ELI-D (value: 1.44) shows the structuring of the 3rd Cr shell; semitransparent surface shows QTAIM-basin of one of the Cr-atoms.

The electronic structure of **5** was studied in position space by means of the topological analysis of the calculated DFT-electron density[16] and the electron localizability indicator (ELI-D),[17] as well as by calculation of the delocalization index.[18] The calculations were performed on different structural models[19] of **5**. Below we will explicitly discuss only the results for model **5a**.

In analogy to the model calculations for the two already reported binuclear Cr_2-complexes with a formal quintuple bond,[3,6] we also find here for all models a $(\sigma_g)^2(\pi_u)^4(\delta_g)^4$-configuration of the chromium based MOs. The above named MOs can be found in all models within the seven highest occupied orbitals. The two δ_g-MOs always occupy HOMO and

HOMO-1, the two π_u-MOs HOMO-5 and HOMO-6, respectively. Energetically in-between these two groups the σ_g-MO and the two ligand-centered MOs with a strong N_{amido} contribution can be found. The HOMO-LUMO gap lies between 1.5 eV and 1.7 eV depending on the corresponding model. For further analysis the electron density and ELI-D were calculated in position space.[20] It was recently shown that ELI-D can be split in a physically transparent way into additive positive orbital contributions (pELI-D contributions).[17e] Here, the corresponding orbital density is simply multiplied with a position-dependent weighting function (the so called "pair volume function"). An illustration of the pELI-D contributions for the five Cr-centered MOs is shown in Fig 3. The isosurfaces show the areas where the corresponding MOs have the highest localizability contributions (pELI-D contributions) to the total ELI-D distribution. It is visible that the σ_g, the two π_u-MOs and the one δ_g-MO exhibit pELI-D maxima in the region between the two Cr atoms. The remaining δ_g-MO (HOMO; 2δ in Fig. 3) shows a pELI-D topology with four maxima at each atom (according to the shape of the δd-orbital), however, not in the interatomic region, which as a whole corresponds to a situation with two separated Cr atoms. Interestingly, this behaviour is observed for one of the two δ_g-MOs. The other one shows a strong mixing of Cr(4s) contributions, that to a large extent annihilate the δd-contributions in the direction of the ligand and reinforces the perpendicular ones. This results in the formation of a pELI-D maximum perpendicular to the molecular plane and relatively far from the bond axis. The sum of the five above named pELI-D contributions yields the ELI-D distribution shown in Fig. 3a. It already exhibits the topological points for the Cr-Cr bonding situation displayed by total (all electron) ELI-D (Fig. 3b). These are the two ELI-D maxima which are perpendicular to the molecular plane resulting from the sum of a π_u and δ_g-pELI-D orbital contribution (so called "Banana-bonds"), as well as two axially situated maxima on the bond-opposed side of the Cr atoms. Furthermore, a significant structuring of the 3rd Cr-shell signals the participation of the d-orbitals to the bond formation. The electronic population of the two bonding basins in the valence region amounts to 1.8 e^- (banana-bond) in total and for the two bond-opposed basins only 0.3 e^-.[19b] With a total of 11.8 e^- the electronic population of the Cr 3rd shell exceeds by 3.8 e^- the value corresponding to a $3s^2p^6$ configuration. Therefore, the electrons for the Cr-Cr bonding interaction are not only localized in the valence region but can also largely be found in the spatial region of the 3rd shell of the Cr atoms, where they contribute to mentioned structuring of ELI-D. The former statement can be verified by calculation of the delocalization index[18] δ(A, B) between the 3rd shells of both Cr atoms. A relatively high value for the delocalization index δ(A, B) = 2.4 is found[21] which was directly used in the

calculation of the bond order in position space according to Ángyán, Loos and Mayer.[22] According to them, the bond order in the case of a symmetrical Cr-Cr bond corresponds to the delocalization index $\delta(\Omega_{Cr1}, \Omega_{Cr2})$ between the touching density basins (QTAIM-method)[23] Ω_{Cr1} und Ω_{Cr2} of the Cr-atoms. The density basin of one Cr atom is depicted in Fig. 3b. It includes the complete 3rd shell and cuts the two ELI-D bonding basins in the middle between the two Cr atoms. In the case of **5a** a value of $\delta(\Omega_{Cr1}, \Omega_{Cr2}) = 4.2$ is found, which significantly differs from the formal bond order of 5.0. However, this finding is consistent with the above discussed weakly bonding δd-orbitals. Interestingly, a very similar bond order of 4.3 was obtained for a similar compound using "natural resonance theory analysis" in Hilbert space.[6] Since the δ-bonds in the Cr_2 model fairly contribute to the bond formation and the 4s-4s bond is energetically repulsive at the equilibrium distance,[4b] the most important effect of these electrons for the short bond distance in Cr_2 (1.68 Å)[15] could be the avoidance of a positive charge at the metal centres. This would then be the decisive factor which has to be overcomed in order to realize similar short distances with formally fivefold bonded metal atoms.

In future investigations we are interested to minimize the metal-metal bond through variation of the ligand environment as well as to explore the reactivity of the herein presented metal-metal bond and to describe in details the bonding situation in **5** in position space at explicitly correlated level of theory.

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[10] Raumgruppe: *P-1* mit a = 12.3740(7), b = 12.9060(8), c = 15.1170(10) Å; α = 71.269(5), β = 75.700(5), γ = 68.868(5)° und R_1 = 0.0375 ($I > 2\sigma(I)$) bzw. wR^2 (alle Daten) = 0.0900

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9.2. Supporting Information for the paper

Metal-Metal Distances at the Limit: A Coordination Compound with an Ultra Short Cr-Cr-Bond

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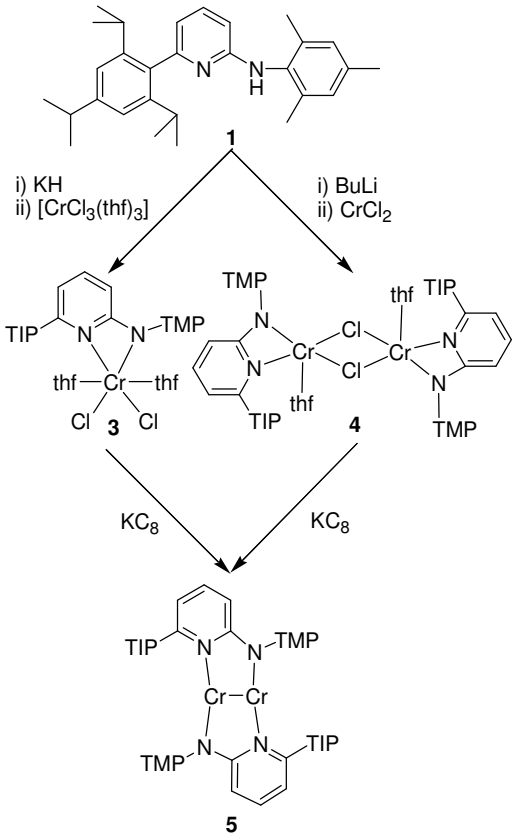
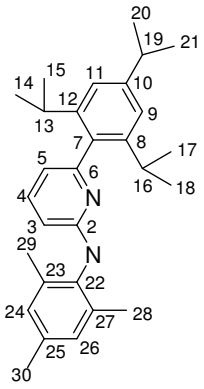
Synthesis of the metal complexes

General: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in N_2 filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1ppm O_2). Solvents were dried by distillation from sodium wire/benzophenone. Commercial $[CrCl_3(thf)_3]$ (Aldrich) and $CrCl_2$ (Alfa Aesor) were used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. NMR spectra were recorded on a Bruker ARX (250 MHz), Varian (300 MHz) and Varian (400 MHz) spectrometers at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS. Elemental analyses (CHN) were determined using a Vario EL III instrument. The effective magnetic moments were determined using Sherwood Scientific Magnetic Susceptibility Balance. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97,[1] SHELXL97[2] and WinGX.[3] CCDC-677808 (**4**) and CCDC-677809 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). The following version of Gaussian was used: Gaussian 03, Revision C.02.[4]



Scheme 1. Synthesis of **3**, **4** and **5** (TIP = 2,4,6-triisopropylphenyl, TMP = 2,4,6-trimethylphenyl).



Scheme 2. Atom labelling in the NMR spectra.

Synthesis of 2: Ether (40 mL) was added to **1** (1.0 g, 2.41 mmol) and KH (0.097 g, 2.41 mmol) at 0 °C. The reaction mixture was then allowed to warm up to room temperature and was further stirred overnight. The solution was filtered and the solvent was evaporated. The resulting off-white product was washed with cold hexane (5 mL) since excess will dissolve even the product. Yield: 0.783 g (71.77%). $C_{29}H_{37}KN_2$ (452.72): Calcd. C 76.94, H 8.24 N

6.19; found C 76.41 H 7.79 N 6.53. ^{1}H NMR (250 MHz, C_6D_6): δ = 1.13 (d, J = 6.9 Hz, 6H, $H^{14,15,17,18}$), 1.23 (m, 12H, $H^{14,15,17,18,20,21}$), 1.94 (s, 6H, $H^{28,29}$), 2.29 (s, 3H, H^{30}), 2.91 (sep, J = 7.4 Hz, 1H, H^{19}), 3.06 (sep, J = 6.8 Hz, 2H, $H^{13,16,}$), 5.76 (d, J = 8.5 Hz, 1H, H^{3}), 6.03 (d, J = 6.6 Hz, 1H, H^{5}), 6.90 (s, 2H, $H^{24,26}$), 6.97 (m, 1H, H^{4}), 7.16 (s, 2H, $H^{9,11}$) ppm. ^{13}C NMR (63 MHz, C_6D_6): δ = 19.3 ($C^{28,29}$), 20.9 (C^{30}), 24.4 ($C^{14,15,17,18}$), 24.5 ($C^{14,15,17,18}$), 25.1 ($C^{20,21}$), 30.5 ($C^{13,16}$), 34.9 (C^{19}), 105.9 (C^{3}), 106.9 (C^{5}), 120.7 ($C^{9,11}$), 129.7 ($C^{24,26}$), 132.0 (C^{7}), 136.4 ($C^{23,27}$), 139.6 (C^{25}), 146.3 ($C^{8,12}$), 146.8 (C^{10}), 148.0 (C^{4}), 149.0 (C^{22}), 158.3 (C^{6}), 164.6 (C^{2}) ppm.

Synthesis of 3: THF (20 mL) was added to $[CrCl_3(thf)_3]$ (0.375 g, 1.0 mmol) and **2** (0.453 g, 1 mmol) at 0 °C. The resulting brown solution was allowed to warm up to room temperature and was stirred overnight. THF was removed in vacuum and the product was extracted with hexane (20 mL). The filtrate was reduced and allowed to afford green crystalline material overnight at room temperature. Yield: 0.359 g (67.43%). $C_{37}H_{53}Cl_2CrN_2O_2$ (680.73): Calcd. C 65.28 H 7.85 N 4.12; found C 65.17 H 7.50 N 3.93. μ_{eff} = 3.16 μ_B. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.86 (br pent), 1.27 (br dd), 2.09 (s) 2.12 (s), 2.58 (v br s), 2.87 (br s), 3.00 (br s), 5.64 (br s), 5.88 (br s) 6.54 (s), 6.59 (s), 7.22 (s), 8.70 (v br s) ppm.

Synthesis of 4: BuLi (1.88 mL, 3.00 mmol) was added to **1** (1.324 g, 3.00 mmol) in THF (20 mL) at 0 °C and the resulting dark red solution was stirred for four hours at room temperature. The solution so obtained was then added to $CrCl_2$ (0.369 g, 3.00 mmol) in THF (5 mL) at 0 °C. The resulting brownish green solution was allowed to warm up to room temperature and was stirred overnight. THF was removed in vacuum and the product was extracted with toluene (20 mL). The filtrate was allowed to stand overnight at -25 °C to afford green crystals of **4**. Yield: 1.048 g (59.20 %). $C_{33}H_{45}ClCrN_2O$ (573.17): Calcd. C 69.15 H 7.91 N 4.89; found C 69.42, H 7.58, N 4.96. μ_{eff} = 4.95 μ_B. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.27 (br m), 2.55 (br s), 2.94 (br d), 5.63 (s), 5.87 (br s), 6.60 (s), 6.76 (s), 8.39 (v br, s), 15.47 (br, s) ppm.

Synthesis of 5: A solution of **4** (1.40 g, 2.44 mmol) in THF (10 mL) was added to freshly prepared suspension of KC_8 (0.406 g, 3.00 mmol) in THF (20 mL) at -30 °C and the resulting dark solution was stirred for 24 hours at room temperature. THF was removed and purple brown solution was then extracted with toluene (20 mL). The filtrate was reduced and allowed to stand overnight at room temperature to afford red crystals. Yield: 0.233 g (21%). $C_{59}H_{74}Cr_2N_2$ (943.24): Calcd. C 75.13 H 7.91 N 5.94; found C 74.56, H 8.15, N 5.90. ^{1}H

NMR (400 MHz, C_6D_6): δ = 0.94 (d, J = 7.6 Hz, 24H, $H^{14,15,17,18,20,21}$), (d, J = 7.2 Hz, 12H, $H^{20,21}$), 2.17 (s, 6H, H^{30}), 2.31 (sep, J = 7.6 Hz, 2H, H^{19}) , 2.34 (s, 12H, $H^{28,29}$), 2.97 (sep, J = 7.2 Hz, 4H, $H^{13,16}$), 6.15 (s, 4H, $H^{24,26}$), 6.21 (d, J = 6.8 Hz, 2H, H^3), 6.65 (s, 4H, $H^{9,11}$), 6.85 (d, J = 8.8 Hz, 2H, H^5), 7.31 (dd, ^3J(H, H) = 8.8 Hz, ^3J(H, H) = 6.8 Hz, 2H, H^4), ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 19.5 ($C^{14,15,17,18}$), 20.9 (C^{30}), 23.5 ($C^{28,29}$), 24.2 ($C^{20,21}$), 25.1 ($C^{13,16}$), 30.2 ($C^{14,15,17,18}$), 33.1 (C^{19}), 108.3 (C^3), 108.9 (C^5), 120.0 ($C^{9,11}$), 129.1 ($C^{24,26}$), 132.3 (C^7), 133.3 ($C^{23,27}$), 133.8 (C^{25}), 135.8 (C^{10}), 144.2 (C^4), 144.7 ($C^{8,12}$), 148.0 (C^{22}), 156.2 (C^6), 171.3 (C^2) ppm.

Single Crystal X-Ray Diffraction Analyses

Compound **4** x 2 C_7H_8: $C_{47}H_{61}ClCrN_2O$, M = 757.43, green crystal (1.14 x 0.97 x 0.59 mm^3); triclinic, space group *P-1*; a = 12.3740(7), b = 12.9060(8), c = 15.1170(10) Å; α = 71.269(5), β = 75.700(5), γ = 68.868(5) °; V = 2108.9(2) Å^3; Z = 2; μ = 0.37 mm^{-1}; ρ*ber*. = 1.193 g cm^{-3}; 27771 measured reflections, 6045 no. of reflections obs. [I > 2σ (I)], 7956 unique (*R*int = 0.090); 474 parameters; largest max./min. in the final difference Fourier synthesis 0.39 eÅ^{-3}/–0.29 eÅ^{-3}; R_1 = 0.0375 ($I > 2\sigma(I)$), wR^2 (all data) = 0.0900.

Compound **5**: $C_{29}H_{37}CrN_2$, M = 465.61, red-brown (0.18 × 0.17 × 0.14 mm^3); triclinic, space group *P-1*; a = 9.2100 (12), b = 12.2290 (14), c = 12.6890 (15) Å; α = 94.314 (9), β = 105.714 (10), γ = 108.185 (10) °; V = 1286.9 (3) Å^3; Z = 2; μ = 0.46 mm^{-1}; ρ*ber*. = 1.202 g cm^{-3}; 4391 measured reflections, 1673 no. of reflections obs. [I > 2σ (I)], 4391 unique (*R*int = 0.000); 289 parameters; largest max./min. in the final difference Fourier synthesis 0.42 eÅ^{-3}/–0.24 eÅ^{-3}; R_1 = 0.0570 ($I > 2\sigma(I)$), wR^2 (all data) = 0.1226.

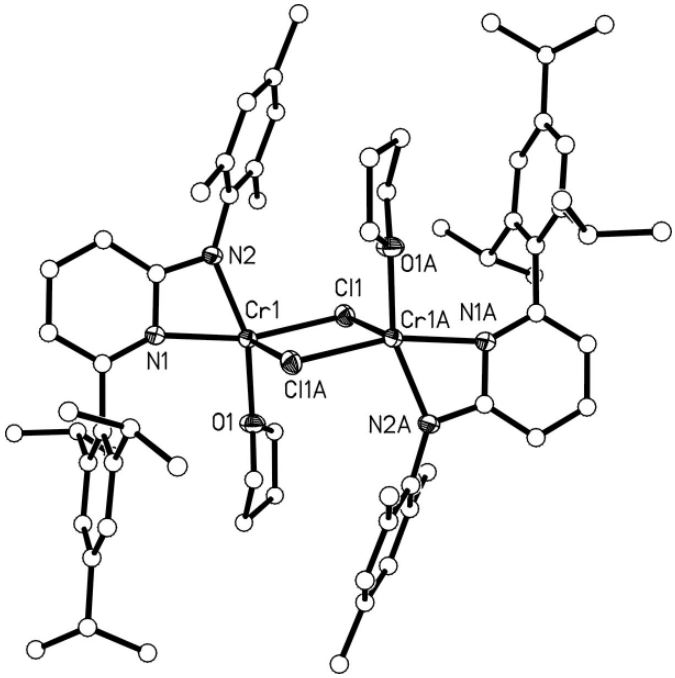


Figure 1. Molecular structure of **4** [ORTEP representation (on the 50% probability level) for all non carbon atoms); Hydrogen atoms and two toluene molecules (per complex) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Cr1 2.1041(15), N2-Cr1 2.0411(14), Cl1-Cr1 2.3773(5), Cl1-Cr1 2.6219(5), Cr1-O1 2.0869(13); N2-Cr1-O1 153.59(6), N2-Cr1-N1 64.77(6), O1-Cr1-N1 98.74(5), N2-Cr1-Cl1 99.99(4), O1-Cr1-Cl1 93.48(4), N1-Cr1-Cl1 163.95(4).

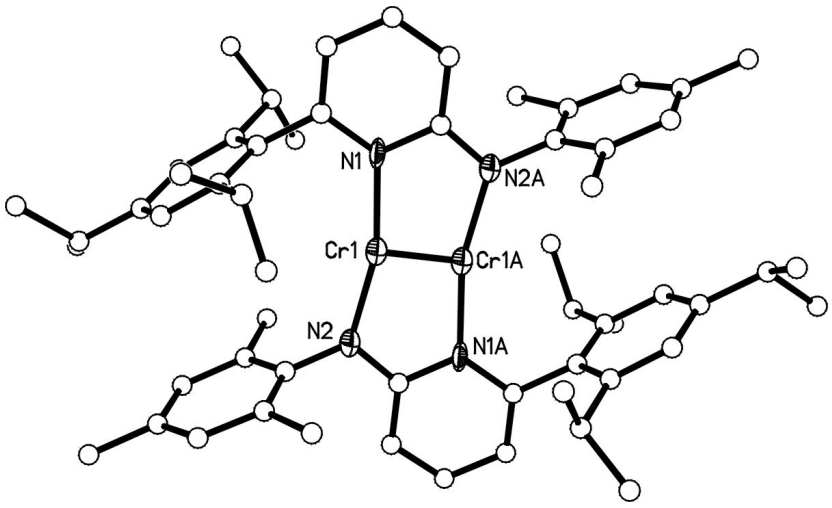


Figure 2. Molecular structure of **5** [ORTEP representation (on the 50% probability level) for all non carbon atoms); Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1-Cr1A 1.7488 (18), Cr1-N2 1.998 (4), Cr1-N1 2.028 (4); Cr1-Cr1A-N2 98.55 (13), Cr1-Cr1A-N1 96.78 (13), N2-Cr1-N1 164.64 (16).

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10. List of publications:

The following papers have been published/submitted/to be submitted during the work on this thesis:

1. Awal Noor, Winfried Kretschmer, Rhett Kempe, *Eur. J. Inorg. Chem*., **2006**, 2683-2689. "Synthesis and Structure of Trialkyltantalum Complexes Stabilized by Aminopyridinato Ligands".

2. Awal Noor, Torsten Irrgang, Rhett Kempe, *Z. Kristallogr. NCS.* **2006**, *221(3)*, 283-284. "Crystal structure of (2,6-diisopropylphenyl)[N-tris(pentafluorophenyl)boronylpyridin-2-yl]amine, $(C_6F_5)_3B(C_5H_4N)(C_{12}H_{18}N)$".

3. Awal Noor, Torsten Irrgang, Rhett Kempe, *Z. Kristallogr. NCS.* **2006**, *221(3)*, 415-418. "Crystal structure of tetrakis[(4-methylpyridin-2-yl)trimethylsilanylamido]zirconium(IV), $Zr(C_9H_{15}N_2Si)_4$".

4. Winfried P. Kretschmer, Bart Hessen, Awal Noor, Natalie M. Scott, Rhett Kempe, *J. Organomet. Chem*., **2007**, *692,* 4569-4579. "Highly Active/Selective and Adjustable Zirconium Polymerization Catalysts Stabilized by Aminopyridinato Ligands".

5. Awal Noor, Torsten Irrgang, Germund Glatz, Rhett Kempe, *Z. Kristallogr. NCS.* **2007**, *222(3)*, 263-264. "Crystal structure of (2,6-diisopropylphenyl)-pyridin-2yl-amine toluene hemisolvate, $C_{17}H_{22}N_2.0.5C_7H_8$".

6. Andrea Espiga Ayuso, Awal Noor, Torsten Irrgang, Germund Glatz, Rhett Kempe, *Z. Kristallogr. NCS.* **2007**, *222(3)*, 281-283. "Crystal structure of (2,6-diisopropylphenyl)-[6-(2,6-dimethyl-phenyl)-pyridin-2-yl]-amine-(2,6-diisopropylphenyl)-[6-(2,6-dimethyl-phenyl)-pyridin-2-yl]-amido-lithium, $Li(C_{25}H_{29}N_2)(C_{25}H_{30}N_2)$".

7. Grigorii G. Skvortsov, Georgii K. Fukin, Alexander A. Trifonov, Awal Noor, Christian Döring, and Rhett Kempe, *Organometallics* **2007**, *26,* 5770-5773. "Intramolecular (sp^3-hybridized) C-H Activation: Yttrium Alkyls versus Transient Yttrium Hydrides".

8. Awal Noor, Germund Glatz, Torsten Irrgang, Rhett Kempe, *Z. Kristallogr. NCS.* **2008**, *223(1)*, (in press). "Crystal structure of (2,6-diisopropyl-phenyl)-pyridin-2-ylamine, $C_{18}H_{24}N_2$".

9. Awal Noor, Winfried P. Kretschmer, Germund Glatz, Auke Meetsma, Rhett Kempe, *Eur. J. Inorg. Chem.* (to be submitted) "Synthesis and Structure of Zirconium and Hafnium Complexes Stabilized by very Bulky Aminopyridinato Ligands".

10. Awal Noor, Rhett Kempe, *Eur. J. Inorg. Chem*. **2008** "Acetylenetitanium Complex Stabilized by Aminopyridinato Ligands" (accepted).

11. Awal Noor, Germund Glatz, Rhett Kempe, "Synthesis and Structure of Low Valent Chromium Complexes Stabilized by η^2-Coordinated Aminopyridinato Ligands" (to be submitted).

12. Awal Noor, Frank. R. Wagner, Rhett Kempe, *Angew. Chem.* (submitted) "Metal-Metal Distances at the Limit: A Coordination Compound with an Ultra Short Cr-Cr-Bond".

13. Awal Noor; Christian Döring, Rhett Kempe, *Z. Kristallogr. NCS. (*submitted) "Crystal Structure of bis-(2,4,6-trimethyl-phenyl)-[6-(2,4,6-trimethyl-phenyl)-pyridin-2-yl]-amido- (μ-oxo)- hexachloro-ditantalum(V) $[(C_{46}H_{50}N_4)TaCl_6O]$".

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Declaration/Erklärung

Hereby I declare that this work has so for 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 doctorate.
Furthermore, I declare that I have written this work by myself and that I have not used any other sources, other than mentioned earlier in this work.

Hiermit erkläre ich, dass diese Arbeit bisher von mir weder an der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht wurde. Ferner erkläre ich, dass ich diese Arbeit selbständig verfasst und keine anderen als die darin angegebenen Hilfsmittel benutzt habe.

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Awal Noor