Novel N-Ligand Stabilized Transition Metal Complexes of the Group IV Triad as Efficient Catalysts for Polymerization and Oligomerization

DISSERTATION

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To my parents, for their love and constant support

and

to Basti for his endless patience, encouragement and love

"Finis coronat opus."

latin quotation of medieval times based on Publius Ovidius Naso

„Und wenn es noch nicht gut ist, dann ist es noch nicht das Ende."

Anna-Maria Dietel

Abbreviations

Ap	aminopyridinate
Ar	aryl
Å	Ångström
BF_{20}	$[(C_6H_5)_3C]^+[B(C_6F_5)_4]^-$ trityl tetrakis(pentafluorophenyl)borate
Bn	benzyl
br	broad
*t*Bu	*tert*-butyl
°C	degree Celsius
calcd	calculated
CCTP	coordinative chain transfer polymerization
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
CTA	chain transfer agent
d	doublet
δ	chemical shift (ppm)
equiv	equivalent
fac	facial
FI	phenoxyimine
g	gram
GC	gas chromatography
GCMS	gas chromatography mass spectrometry
GPC	gel permeation chromatography
h	hour
Hz	Hertz
J	coupling constant (Hz)
KKTP	Koordinative Kettentransfer-Polymerisation
LAOs	linear α-olefins
m	multiplet
MAO	methylalumoxane
d-MAO	dry-methylalumoxane
Me	methyl
mer	meridional
min.	minute
mL	milliliter

mmol	millimol
MPa	megapascal
NMR	nuclear magnetic resonance
PDI	polydispersity index
PE	polyethylene
Ph	phenyl
ppm	parts per million
*i*Pr	*iso*-propyl
q	quartet
rpm	revolutions per minute
rt	room temperature
s	singlet
sept	septet
t	triplet
TEA	triethylaluminum
TIBA	triisobutylaluminum
TMA	trimethylaluminum
UHMWPE	ultra-high molecular weight polyethylene

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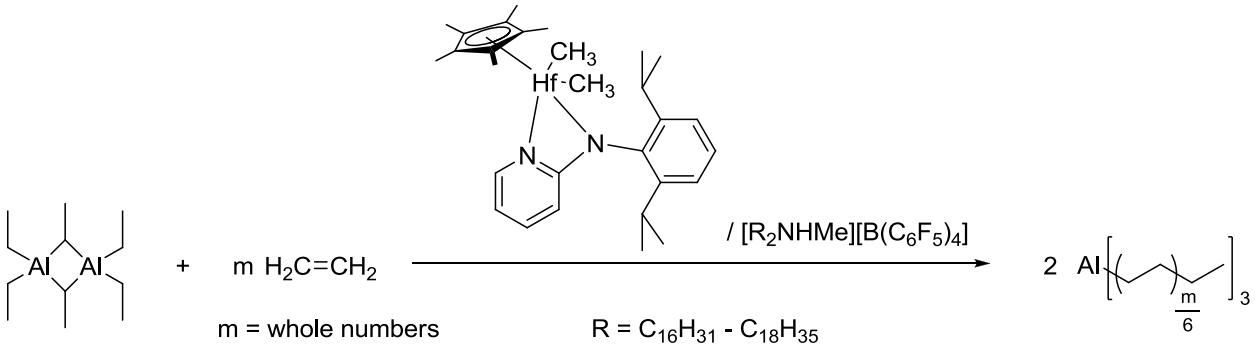
1 Summary

In the present work, novel transition metal complexes of group IV were developed for the use in polymerization or oligomerization of ethylene or 1-hexene. Besides the synthesis and the complete characterization of the ligands and complexes, mechanistic aspects concerning the individual poly-/oligomerizations and the detailed analysis of the resulting poly-/oligomeric products were covered. The new complexes were tailored for specific polymerization methods by combining two anionic ligands. Depending on the system the two directing ligands were either not or covalently connected. Fine-tuning of the reactivity was achieved by varying the substituents at the ligands.

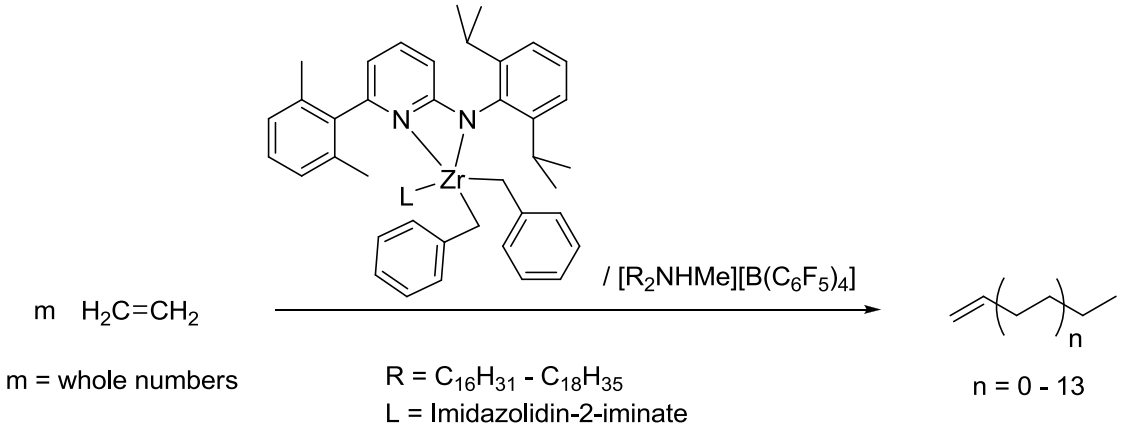
Previous works on rare earth and lanthanide systems have shown that they are suitable as highly active catalysts for the coordinative chain transfer polymerization (CCTP) of ethylene. However, these systems' applications are limited by their sensitivity towards aluminum alkyls, fast ligand transfer to aluminum and the tendency for C-H activation during the polymerization of α-olefins. To overcome these inherent difficulties of the lanthanides, in this work a mixed 1,2,3,4,5-pentamethylcyclopentadienyl (Cp*)- and aminopyridinato (Ap)-ligand-stabilized catalyst system based on hafnium was developed (Scheme 1).



Scheme 1. Synthesis of aluminum-terminated linear PE with a mixed cyclopentadienyl-/aminopyridinato-hafnium complex.

The new complexes were fully characterized by NMR spectroscopy and elemental analysis as well as in selected cases by X-ray structure analysis. Then the newly developed system was tested in the polymerization of ethylene via CCTP. Through precise adjustment of the reaction conditions such as ethylene pressure, temperature, polymerization time or the amount of transfer agent the polymerization result was optimized. In addition to very good activities (2800 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$) the system [Cp*HfApMe$_2$] also showed an extremely high tolerance towards aluminum alkyls, which led to very narrow molecular weight distributions of the resulting polymer.

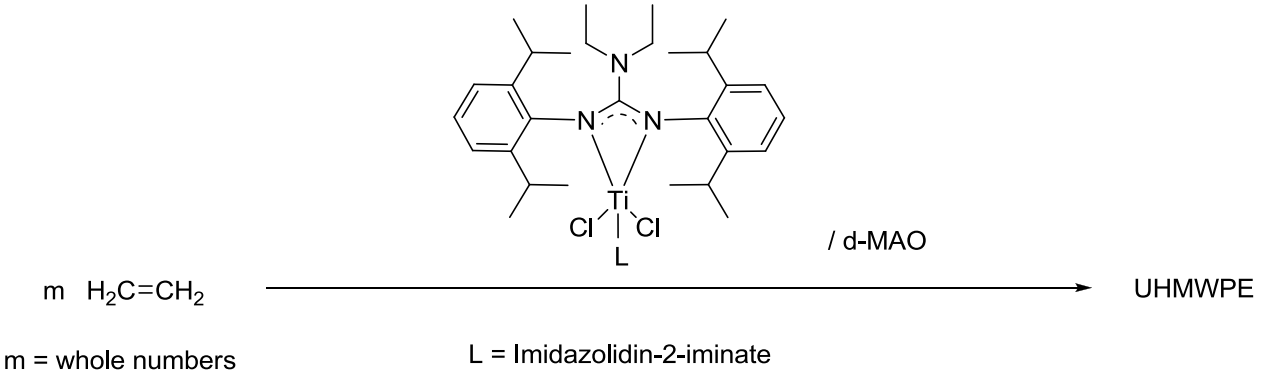
Aminopyridinato ligand-stabilized zirconium tribenzyl catalysts have been developed especially for the polymerization of ethylene and the copolymerization of ethylene and propylene. In this work, the catalytic properties of the primary tribenzyl zirconium complex could be changed significantly by introducing an additional directing ligand. Thereby caused steric and electronic changes in the catalyst system generated a change of the former polymerization properties to oligomerization (Scheme 2). All synthesized complexes were isolated and characterized by current characterization techniques and X-ray structure analysis.



Scheme 2. Mixed η^2-aminopyridinato/η^1-imidazolidiniminato zirconium dibenzyl complex for the oligomerization of 1-hexene.

The use of imidazolidin-2-iminate as additional directing ligand caused a change in the reactivity from polymerization to highly active oligomerization (activities of up to 48750 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$) whereas the introduction of an additional phenoxide ligand had no dramatic effect on the catalytic properties. The generated α-olefins could be certainly characterized by GC analysis. It was possible to adjust the product range of oligomers by fine-tuning the aminopyridinate ligands and the individual reaction parameters.

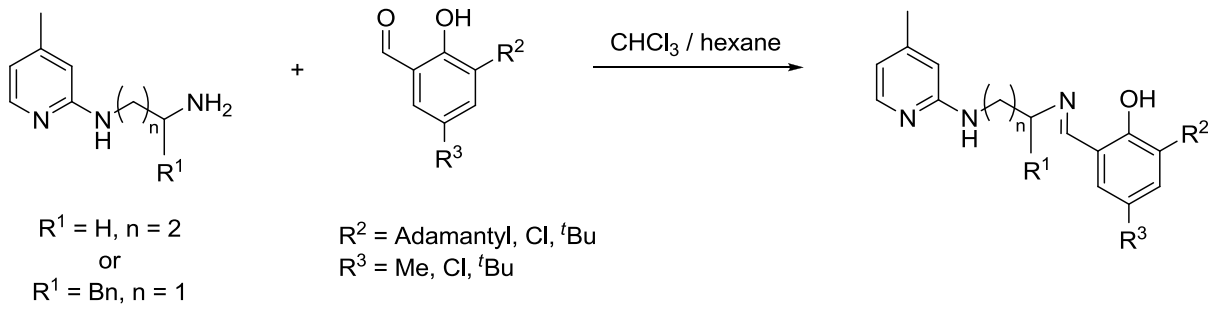
Structurally related to aminopyridinate ligands are guanidinate ligands which represent an interesting symmetric version of bidentate monoanionic *N,N*-ligands compared to aminopyridinate ligands. On the basis of a highly effective guanidinato-stabilized titanium CCTP system, additional monoanionic ligands were introduced and the resulting changes of the polymerization properties were documented. For the synthesis of the mixed complexes a second directing ligand, i. e., a guanidinate, amide or phenoxide was added to the precursor complex [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato] titanium trichloride. The new titanium-based systems are no longer active in CCTP, but show through the directing effect of the additional ligands the tendency for the formation of ultra-high molecular weight polyethylene (UHMWPE) (Scheme 3).



Scheme 3. Mixed guanidinato-/imidazolidin-2-iminato-stabilized titanium complexes for the synthesis of ultra-high molecular weight poylethylene.

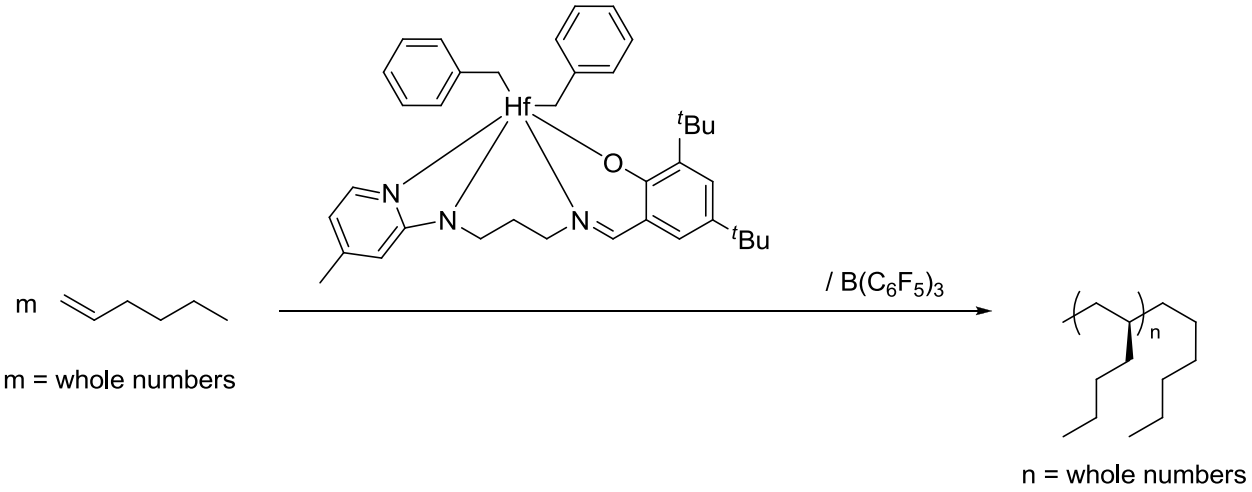
The new titanium complexes were characterized via NMR spectroscopy, elemental analysis and X-ray structure analysis. Some of the additionally introduced anionic ligands led to a dramatic increase in activity (from 1360 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$ to 5560 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$) of the catalyst system. Adjusting the catalyst concentration and changing the activator from MAO to d-MAO finally led to the formation of ultra-high molecular weight polyethylene.

In the last two chapters of this work the development of a novel class of ligands is described. This new ligands arise from covalently connected compounds which already represent well-established ligand systems in the field of homogeneous polymerization catalysts. These novel Ap-FI ligands consist of two parts which were connected covalently either by a propylene or a substituted ethylene bridge. The first part features the structural motif of aminopyridinate ligands (Ap) and the second part is deduced from phenoxyimine ligands (FI). The ligand synthesis (Scheme 4) was carried out by a one-step condensation of an aliphatic amine with one equivalent of the corresponding substituted salicylaldehyde. The used diamines derive from a selective iridium-catalyzed alkylation of aromatic amines.



Scheme 4. Synthesis of the Ap-FI ligands.

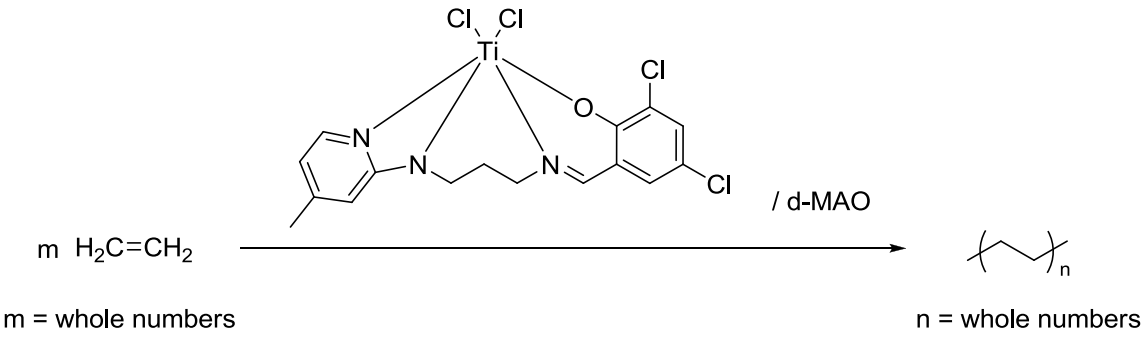
Subsequent complex syntheses were carried out using either alkane, alcohol or amine elimination from the respective transition metal precursors. All obtained compounds were certainly characterized using NMR spectroscopy, elemental analysis and to some extent X-ray structure analyses. The coordination mode of the new Ap-FI ligands has been discussed in detail by means of the data on bond lengths and angles of the X-ray structure analyses. It appeared that depending on the leaving group and the central metal differences concerning the coordination mode could be observed. Accordingly clear differences in the polymerization properties of the precursors were highlighted. While the zirconium complexes were not suitable for use in polymerization, the synthesized hafnium complexes represent active catalysts for the highly selective poylmerization of 1-hexene after activation with boranes or borates (activities of 150 $g \cdot mmol^{-1} \cdot h^{-1}$) (Scheme 5).



Scheme 5. Ap-FI ligand-stabilized hafnium dibenzyl catalysts for the synthesis of highly isoselective poly(1-hexene).

Extremely narrow molecular weight distributions (PDI of 1.02) point out the living character of this polymerization. Furthermore, the resulting poly(1-hexene) possesses up to 92% isotactic [*mmmm*] pentades. A possible deactivation of the hafnium system by alkylation of the imine function which is a special feature of the new ligand class was depicted and discussed by X-ray structure analysis of the deactivation product.

While the novel Ap-FI titanium complexes were inactive in polymerization of α-olefins they showed moderate activity in the polymerization of ethylene (Scheme 6).



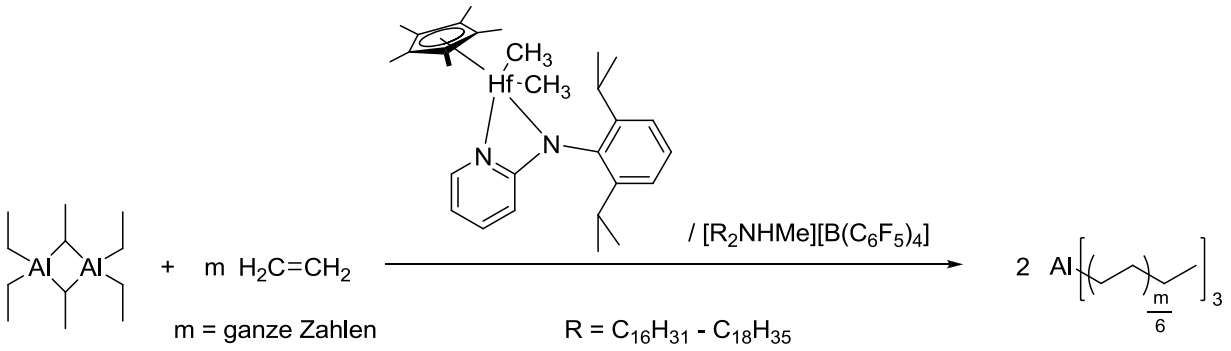
Scheme 6. Ap-FI ligand-stabilized titanium dichloride catalyst system for the synthesis of polyethylene.

With the use of MAO as activator, the adamantyl-substituted titanium catalyst precursor gave polydispersities consistent with a single-site catalyst. However, with the chloro-substituted titanium catalystprecursor exclusively bimodal polydispersities were achieved. The bimodal molecular weight distributions indicate a structural change of the catalyst during the polymerization process; they are in accordance with the observations about the deactivation product of the Ap-FI stabilized hafnium catalysts. Through the switchover of the activator from MAO to d-MAO these structural changes of the catalyst during the polymerization process were avoided and an increase in activity (from 5800 $g \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$ to 6600 $g \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$) was achieved, accompanied by a monomodal molecular weight distribution as well as high molecular weight (1,751,000 g/mol) of the polymeric product.

Zusammenfassung

Im Rahmen der vorliegenden Arbeit wurden neuartige Übergangsmetallkomplexe der Gruppe IV für den Einsatz in der Polymerisation oder Oligomerisation von Ethylen oder 1-Hexen entwickelt. Neben der Synthese der Liganden und Komplexe sowie deren vollständiger Charakterisierung waren mechanistische Fragen bezüglich der einzelnen Poly-/Oligomerisationen und die detaillierte Analyse der resultierenden poly-/oligomeren Produkte weitere wichtige Aspekte dieser Arbeit. Durch die Kombination zweier anionischer Steuerliganden, je nach System nicht oder kovalent miteinander verbunden, konnten die neuen Komplexverbindungen für spezielle Polymerisationsmethoden maßgeschneidert werden. Die Feinabstimmung der Reaktivität wurde über die Variation der Substituenten an den Liganden realisiert.

Frühere Arbeiten zu Seltenerd- und Lanthanoid-Systemen haben gezeigt, dass sich diese als hochaktive Katalysatoren für die Koordinative Kettentransfer-Polymerisation (KKTP) von Ethylen eignen. Allerdings sind diese Systeme durch ihre hohe Empfindlichkeit gegenüber Aluminiumalkylen, schnellen Ligandentransfer zum Aluminium und die Tendenz zur CH-Aktivierung bei der Polymerisation von α-Olefinen in ihren Anwendungsmöglichkeiten sehr limitiert. Um diese in der Natur der Lanthanoide liegende Problematik zu lösen wurde in dieser Arbeit ein gemischtes, durch 1,2,3,4,5-Pentamethylcyclopentadienyl (Cp*)- und Aminopyridinato (Ap)-Liganden stabilisiertes Katalysatorsystem auf Basis von Hafnium entwickelt (Schema 1).

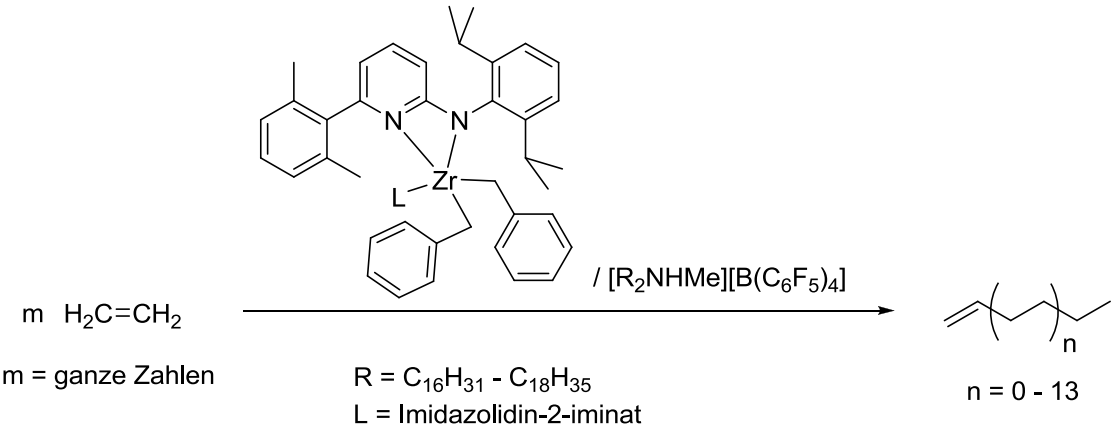


Schema 1. Synthese von Aluminium-terminiertem linearem PE mit einem gemischten Cyclopentadienyl-/Aminopyridinato-Hafniumkomplex.

Die neuen Komplexverbindungen wurden über NMR-Spektroskopie und Elementaranalyse sowie in ausgewählten Fällen durch Einkristallröntgenstrukturanalyse vollständig charakterisiert. Anschließend wurde das neu entwickelte System in der Polymerisation von Ethylen im Rahmen der KKTP getestet. Durch exaktes Einstellen der Reaktionsbedingungen wie z.B. Ethylendruck, Temperatur,

Polymerisationszeit oder Menge an Transferreagenz konnte das Polymerisationsergebnis optimiert werden. Neben sehr guten Aktivitäten (2800 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$) zeigte das [Cp*HfApMe$_2$]-System auch eine enorm hohe Toleranz gegenüber Aluminiumalkylen, was zu einer sehr engen Molmassenverteilung des resultierenden Polymers führte.

Mono(aminopyridinato)-stabiliserte Zirkoniumtribenzyl-Katalysatoren wurden speziell für die Polymerisation von Ethylen und die Copolymerisation von Ethylen und Propen entwickelt. In dieser Arbeit konnten die ursprünglichen Katalyseeigenschaften der Zirkoniumtribenzyle durch das Einbringen eines zusätzlichen Steuerliganden maßgeblich verändert werden. Die dadurch bewirkten sterischen und elektronischen Veränderungen des Katalysatorsystems verursachen einen Wandel der Polymerisationseigenschaften hin zur Oligomerisation (Schema 2). Alle synthetisierten Komplexverbindungen wurden isoliert und durch die gängigen Charakterisierungsmethoden sowie Einkristallröntgenstrukturanalyse beschrieben.

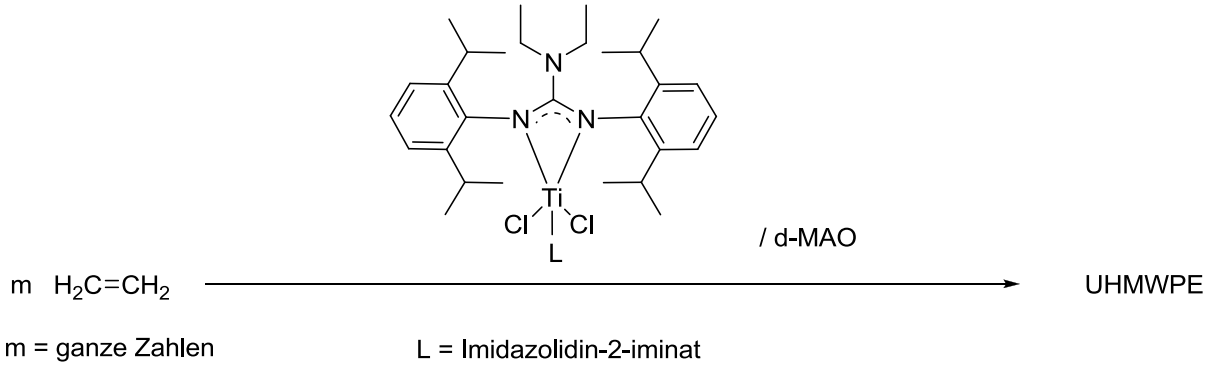


Schema 2. Gemischter η^2-Aminopyridinato-/η^1-Imidazolidiniminato-Zirkoniumdibenzylkomplex für die Oligomerisation von 1-Hexen.

Die Verwendung von Imidazolidin-2-iminaten als zusätzliche Steuerliganden bewirkte einen Wechsel der Reaktivität von Polymerisation zu hochaktiver Oligomerisation (Aktivitäten von bis zu 48750 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$), wohingegen das Einbringen eines zusätzlichen Phenoxid-Liganden keine drastische Wirkung auf die Katalyseeigenschaften mit sich brachte. Die bei der Oligomerisation entstandenen α-Olefine konnten mittels GC-Analysen eindeutig charakterisiert werden. Über das Finetuning des Aminopyridinat-Liganden und der einzelnen Reaktionsparameter war es möglich das Produktspektrum der Oligomere genau einzustellen.

Stukturverwandt zu den Aminopyridinat-Liganden sind die Guanidinat-Liganden. Sie stellen eine interessante symmetrische Version von bidentat monoanionischen *N,N*-Liganden im Vergleich zu den Ap-Liganden dar. Auf der Basis eines hocheffektiven, Guanidinato-stabilisierten Titan-KKTP-Systems

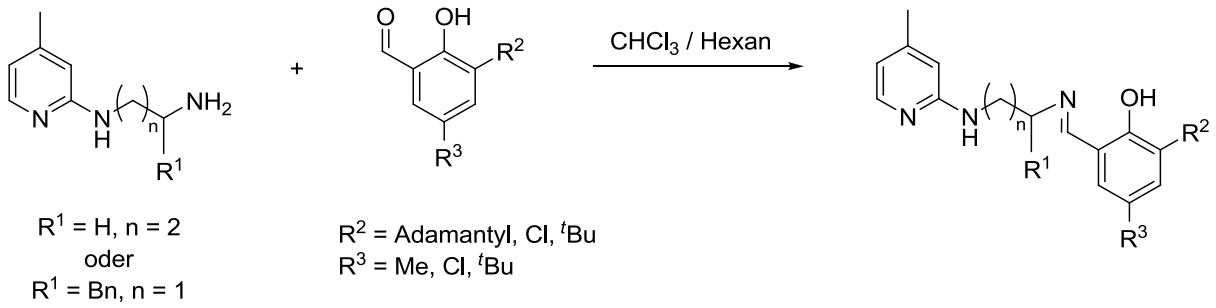
wurden zusätzliche monoanionische Steuerliganden eingebracht und die daraus resultierenden Veränderungen der Polymerisationseigenschaften dokumentiert. Für die Mischkomplexe wurde ausgehend von [1,2-Bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato]-titantrichlorid jeweils ein neuer Steuerligand aus den Verbindungsklassen der Guanidinate, Amide oder Phenoxide hinzugefügt. Die neuen Titan-basierten Systeme sind nicht mehr aktiv in der KKTP, sondern zeigen durch den dirigierenden Effekt der zusätzlichen Liganden die Tendenz zur Bildung von ultrahochmolekularem Polyethylen (UHMWPE) (Schema 3).



Schema 3. Gemischter Guanidinato-/Imidazolidin-2-iminato-stabilisierter Titankomplex für die Synthese von ultrahochmolekularem Polyethylen.

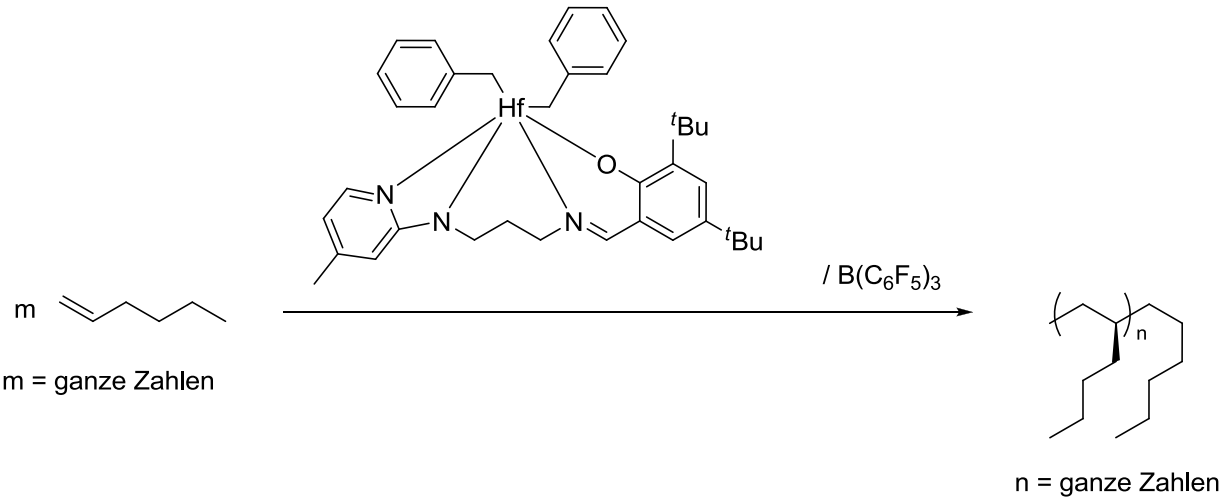
Die neuen Titankomplexe wurden mittels NMR-Spektroskopie, Elementaranalyse und Einkristallröntgenstrukturanalyse charakterisiert. Einige der zusätzlich eingebrachten anionischen Liganden führen zu einer drastischen Aktivitätssteigerung des Katalysatorsystems (von 1360 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$ zu 5560 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$). Das Anpassen der Katalysatorkonzentration und der Wechsel des Aktivators zu d-MAO führten schließlich zur Bildung von ultrahochmolekularem Polyethylen.

In den letzten beiden Kapiteln dieser Arbeit wird die Entwicklung einer völlig neuartigen Ligandenklasse beschrieben, die aus der kovalenten Verbindung zweier in der Forschung für homogene Polymerisationskatalysatoren bereits etablierter Systeme hervorgeht. Diese neuartigen Ap-FI-Liganden bestehen aus zwei Teilen, die kovalent über eine Propylkette oder eine substituierte Ethylkette miteinander verbunden sind. Der erste Teil trägt das Strukturmotiv der Aminopyridinat-Liganden (Ap) und der zweite Teil wird durch das Strukturmotiv der Phenoxyimin-Liganden (FI) bestimmt. Die Ligandensynthese (Schema 4) erfolgte über eine einfache Kondensationsreaktion eines aliphatischen Diamins mit dem entsprechenden substituierten Salicylaldehyd. Die verwendeten Diamine wurden zuvor durch selektive Iridium-katalysierte Aminalkylierung hergestellt.



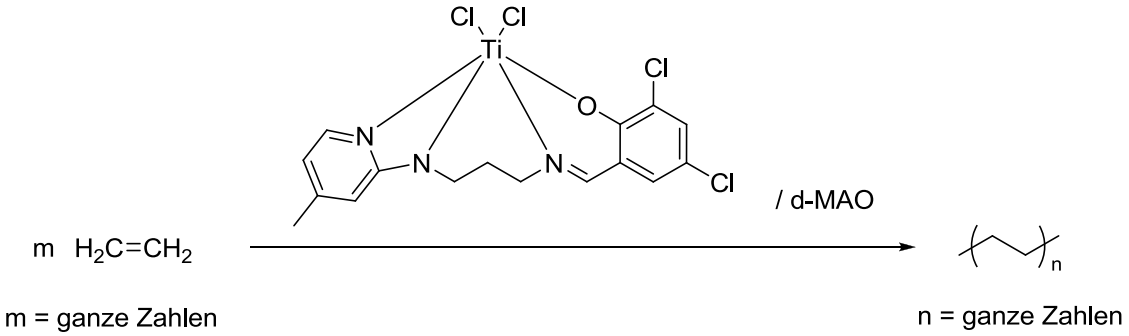
Schema 4. Synthese der Ap-FI-Liganden.

Die anschließenden Komplexsynthesen erfolgten wahlweise über Alkan-, Alkohol- oder Amineliminierung ausgehend von den jeweiligen Übergangsmetallvorstufen. Alle erhaltenen Komplexverbindungen wurden über NMR-Spektroskopie, Elementaranalysen und zum Teil auch durch Einkristallröntgenstrukturanalyse eindeutig charakterisiert. Der Koordinationsmodus der neuen Ap-FI-Liganden wurde anhand der Daten zu den Bindungslängen und –winkeln aus der Einkristallröntgenstrukturanalyse ausführlich diskutiert. Dabei zeigten sich je nach Abgangsgruppe bei der Komplexsynthese und Zentralmetall sehr deutliche Unterschiede bezüglich der Koordination des Liganden am Metallzentrum. Dementsprechend konnten auch deutliche Unterschiede in den Polymerisationseigenschaften der einzelnen Precursoren herausgearbeitet werden. Während die Zirkoniumkomplexe keine geeigneten Komplexe für den Einsatz in der Polymerisation darstellen, sind die synthetisierten Hafniumkomplexe nach der Aktivierung mit Boranen oder Boraten geeignete Katalysatoren (Aktivitäten von 150 $g \cdot mmol^{-1} \cdot h^{-1}$) für die hochselektive Polymerisation von 1-Hexen (Schema 5).



Schema 5. Ap-FI-Ligandstabilisiertes Hafniumdibenzyl-Katalysatorsystem für die Synthese von hoch isotaktischem Poly(1-hexen).

Dabei deuten die extrem engen Molekulargewichtsverteilungen (PDI von 1,02) auf den lebenden Charakter der Polymerisation hin und das resultierende Poly(1-hexen) weist zudem noch bis zu 92% isotaktische [*mmmm*]-Pentaden auf. Eine mögliche Deaktivierung des Hafnium-Systems durch die Alkylierung der Iminfunktion, eine Besonderheit der neuen Ligandenklasse, konnte mit Hilfe einer Einkristallröntgenstrukturanalyse des Deaktiverungsprodukts charakterisiert und diskutiert werden.
Die neuen Ap-FI-Titankomplexe hingegen sind in der Polymerisation von α-Olefinen inaktiv, zeigen jedoch moderate Aktivitäten bei der Polymerisation von Ethylen (Schema 6).



Schema 6. Ap-FI-Ligandstabilisiertes Titandichlorid-Katalysatorsystem für die Synthese von Polyethylen.

Bei der Verwendung von MAO als Aktivator zeigte der adamantyl-substituierte Komplex Polydispersitäten ähnlich zu „single-site" Katalysatoren, wohingegen mit dem chloro-substituierten Titankomplex ausschließlich bimodale Molekulargewichtsverteilungen erhalten werden konnten. Die bimodalen Verteilungen deuten auf eine strukturelle Veränderung des Katalysators während der Polymerisation hin und stehen im Einklang mit den Beobachtungen zum Deaktivierungsprodukt der Ap-FI-stabilisierten Hafniumkatalysatoren. Durch den Wechsel des Aktivators von MAO zu d-MAO konnten die strukturellen Veränderungen des Katalysators während der Polymerisation verhindert werden und eine Aktivitätssteigerung (von 5800 $g \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$ auf 6600 $g \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$), eine monomodale Molekulargewichtsverteilung sowie hochmolekulares Polyethylen (1,751,000 g/mol) als Produkt erreicht werden.

2 Introduction

The global plastic consumption stood at 230 million tons in the year 2012.[1] Due to their versatility and their excellent technical properties plastics have conquered numerous fields of application.[2] Traditional materials such as glass or metal are increasingly being substituted by plastics to meet the sophisticated material requirements in rapidly growing markets such as medical technology, photovoltaics or consumer electronics.[3] State of the art and performance of the polymer industry are closely linked to the progress in catalysis.[4] Thus, the development of new catalyst systems and new polymerization mechanisms is essential in order to satisfy the needs of our modern society.

In 1933, Fawcett and coworkers cleared the way for polymer industry with the invention of the ICI high-pressure process.[5] But it was only after the discovery of heterogeneous Ziegler-Natta catalysts[6] in the late 1950s that catalysis found its way into polymer research. With this milestone the rapid development of polymer research and the connected polymer industry began. Concerning homogeneous catalysis enormous effort has been put into research and development of metallocenes[7] (**A**, Figure 1) after Kaminsky and coworkers[8] presented their zirconium and hafnium metallocene/MAO systems in 1980. Subsequently the era of post-metallocene catalysts began. Pioneering work on the next generation of homogeneous polymerization catalysts (**B**, Figure 1) was done by Bercaw and coworkers in 1994.[9] These so-called constrained geometry catalysts gave access to a more open geometry at the active metal center and made a dramatic impact on polyolefin industry.[10]

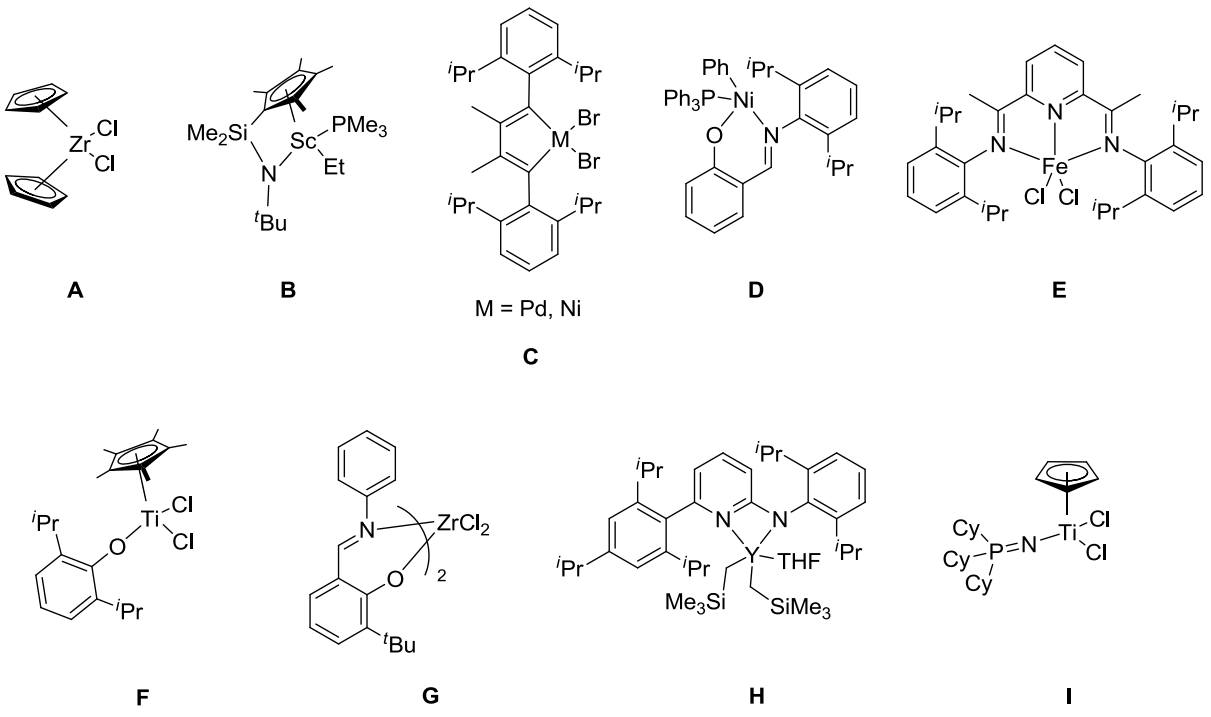


Figure 1. Selected examples of successful olefin polymerization catalysts.

In the following years completely new ligand families received much attention as constrained-geometry successors. Different ligand systems have been developed within very short time intervals in order to realize more complex polymer architectures. Brookhart and coworkers for instance have developed diimine Ni(II)- and Pd(II)-based systems (**C**, Figure 1) which polymerize ethylene and α-olefins to branched polymers with high strength and processing properties.[11] The work on nickel catalysts was extended by Grubbs and coworkers with the development of neutral Ni(II) salicylaldiminato complexes (**D**, Figure 1) which are highly active for the polymerization of ethylene at moderate conditions.[12] In 1998, Brookhart[13] as well as Gibson and coworkers[14] independently discovered a new series of iron complexes possessing 2,6-bis(imino)pyridine ligands (**E**, Figure 1). These complexes displayed very high ethylene polymerization activity comparable to that of metallocenes.[15] At the same time the first half-titanocene polymerization precursor containing an aryloxo ligand (**F**, Figure 1) was presented by Nomura *et al.*[16] The distinctive feature of all these half-titanocene complexes containing an ancillary anionic donor ligand is their ability to copolymerize ethylene with various other comonomers[17], for instance with sterically encumbered α-olefins, styrene or cyclic olefins.[18] Based on "ligand-oriented catalyst design", Fujita and coworkers[15] developed group 4 transition metal complexes bearing two phenoxyimine ligands, so called "FI Catalysts" (**G**, Figure 1). This new family of catalyst precursors is able to produce ultra-high molecular weight polyethylene (UHMWPE) of about $5 \cdot 10^6$ g/mol.[19] At that time research on polymerization catalysts was also looking for substitutes for the formerly ubiquitous cyclopentadienyl ligand. The work of Kempe and coworkers[20] about aminopyridinato ligands (**H**, Figure 1) and the work of Stephan *et al.*[21] about phosphinimide ligands (**I**, Figure 1) as steric or isolobal equivalents to the cyclopentadienyl ligand are two examples amongst numerous others.

The discovery of entirely new polymerization mechanisms is one of the recent advances in polymer research. Next to cationic,[22] anionic[23] and radical[24] polymerization mechanisms, coordinative chain transfer polymerization (CCTP) and its enhanced concepts such as "chain shutteling"[25] and "ternary CCTP"[26] attracted a lot of attention. Since Eisenberg and Samsel[27] as well as Mortreux and coworkers[28] cleared the way for CCTP in the early 1990s, a few very interesting ethylene/propylene CCTP systems that apply rare earth metals and transition metals with different chain transfer agents (CTAs), such as Mg, Zn, and Al alkyls, have been discovered.[29]

Parallel to the revolutionary developments in ethylene polymerization and after the initial discovery of Ziegler's „Aufbaureaktion"[30] a rapid development concerning the oligomerization of ethylene took place. The industrial application of Ziegler's "Aufbaureaktion" is called Alfen process. It produces linear α-olefins through a high pressure growth reaction on triethylaluminum followed by low pressure displacement.[31] At that time, a second commercial process for the production of linear α-olefins with four to 20 carbon atoms was the dehydration of natural alcohols.[31b] However this process is limited by the availability of such natural alcohols.[31b] In 1972 Keim *et al.*[32] developed homogeneous Ni(II)-based

catalysts with bidentate monoanionic P,O-ligands (**J**, Figure 2) which led to the well-known Shell Higher Olefin Process (SHOP). The advantage of the SHOP process compared to formerly known processes is the immense improvement in linearity and α-olefin content of the resulting product olefins.[4]

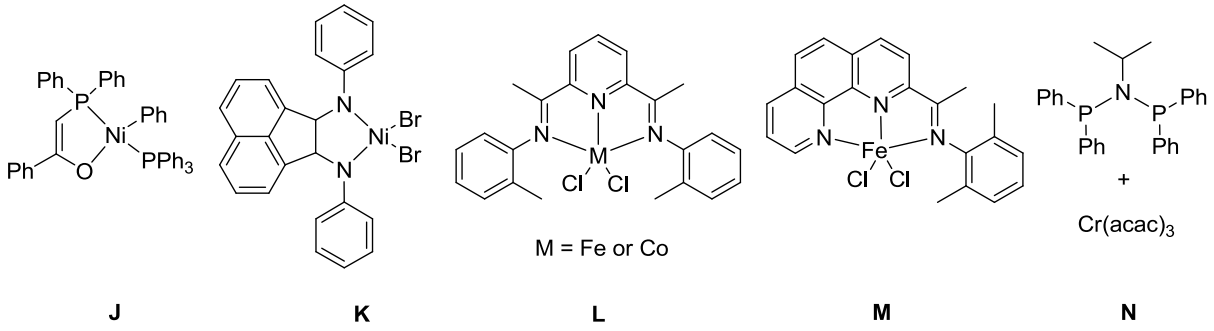


Figure 2. Selected examples of successful olefin oligomerization catalysts.

After this outstanding innovation notable research effort has been put into the development of late transition metal catalysts for the oligomerization of ethylene. Brookhart and coworkers[33] reported in 1996 Ni(II) dibromide complexes containing para- and unsubstituted aryl α-diimine ligands (**K**, Figure 2) to be highly active and selective catalysts for the production of linear α-olefins. Catalyst systems with exceptionally high activities and selectivities for oligomerization of ethylene to linear α-olefins based on iron(II),(III) and cobalt(II) complexes that incorporate tridentate 2,6-bis(imino)pyridine ligands (**L**, Figure 2) were independently described by Brookhart[34] and Gibson[14b] two years later. By fine-tuning the steric and electronic properties of the ligand systems, these late transition metal based oligomerization systems were further improved regarding activity and selectivity for instance by Fröhlich and coworkers[35] in 2006 (**M**, Figure 2).

Besides the abovementioned full-range processes of ethylene oligomerization which generate a range of C_4/C_6 up to C_{20+} α-olefins, the deliberate di-,[36] tri-[37] and tetramerization[38] of ethylene describes a more selective route to linear α-olefins. The most remarkable tetramerization system was developed by Bollmann *et al.*[39] in 2004. A variety of diphosphinoamine and related diphosphine ligands in combination with Cr(III) compounds (**N**, Figure 2) activated by aluminoxanes was found to be very active and efficient catalysts for tetramerization reactions yielding 1-octene in selectivities up to 70%.

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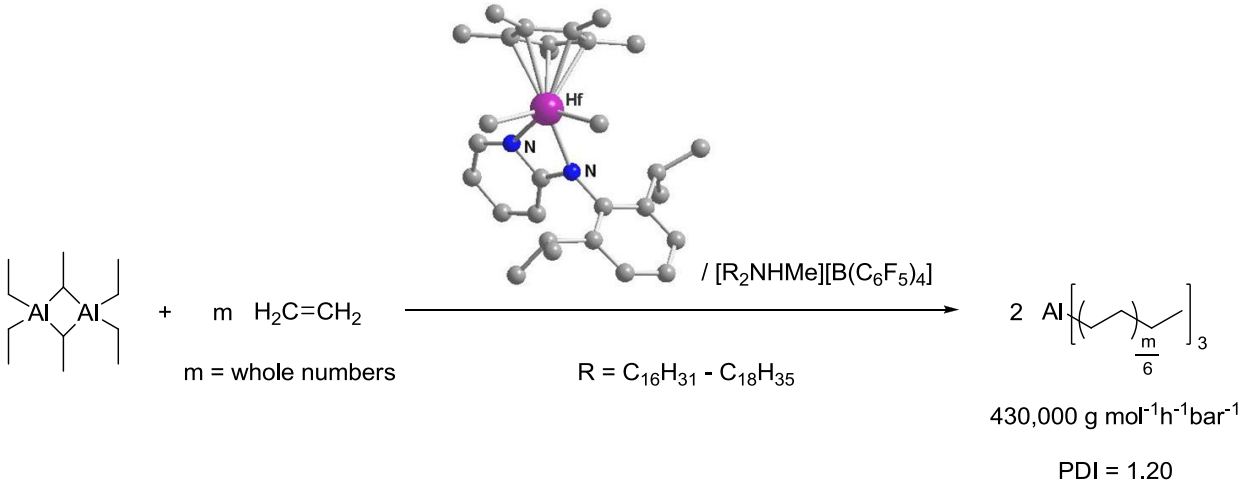
3 Overview of Thesis Results

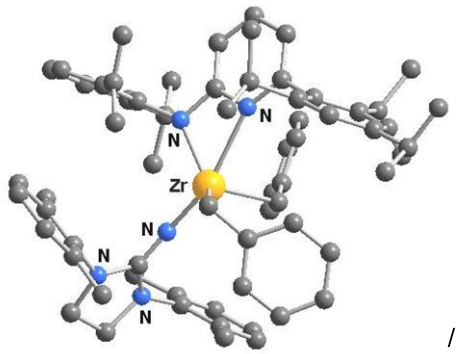
This thesis comprises five publications and one patent which are presented in chapters 4-8.

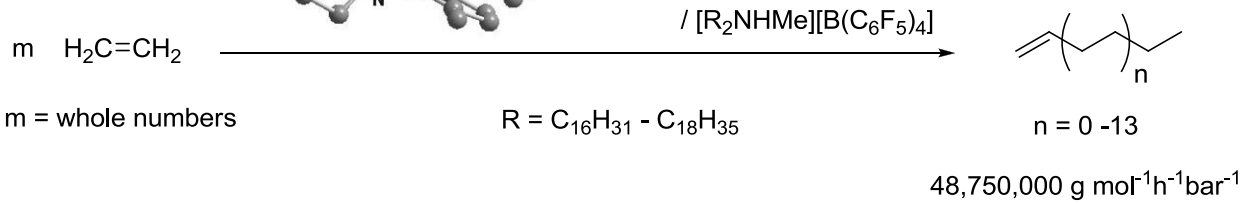
3.1 Synthesis of Aluminum-Terminated Linear PE with a Hafnium Aminopyridinate Catalyst



Coordinative chain transfer polymerization (CCTP) describes the fast and reversible polyolefin-chain transfer between a maingroup metal or zinc alkyl and a transition metal or lanthanoid complex. The "living" chain-growing process takes place exclusively on the latter. With the knowledge of previous works on an aminopyridinato (Ap)-ligand-stabilized yttrium CCTP system a new and more resistant cyclopentadienyl-/aminopyridinato ligand-stabilized hafnium catalyst system was developed. Selected small Ap-ligands reacted with [Cp*$HfMe_3$] through methane elimination to yield the corresponding catalyst precursors. A catalyst library consisting of five mixed cyclopentadienyl and aminopyridinato ligand-stabilized hafnium complexes was synthesized. After activation of the precursors with a common borate cocatalyst they were tested in CCTP with triethylaluminum as transfer agent and ethylene as monomer. This new hafnium system showed high tolerance against aluminum alkyls of up to 10,000 equiv of triethylaluminum. Furthermore, the influence of the polymerization parameters such as polymerization time, temperature, pressure and the amount of transfer agent was carved out and discussed.

3.2 Flipping the Switch from Polymerization to Oligomerization with a Monoanionic η^1-Imidazolidin-2-iminate as Ancillary π-Donor Ligand

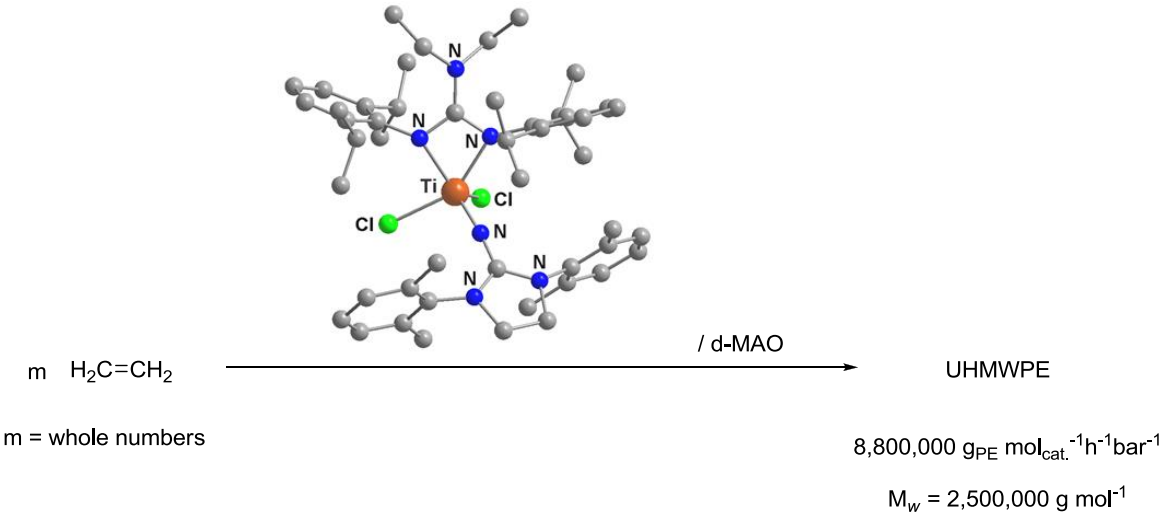




Our next goal was the improvement of the polymerization properties of a previously developed mono(aminopyridinato) stabilized zirconium tribenzyl catalyst system, which was used for the polymerization of ethylene and the copolymerization of ethylene and propylene. Inspired by a recent report of Nomura *et al.*, who reported half-titanocenes additionally stabilized by 1,3-disubstituted imidazolidin-2-iminates to be very active catalyst for the syndiospecific styrene polymerization, we attempted to adopt this mixed ligand structure to our mono(aminopyridinato) stabilized zirconium tribenzyl catalyst system. Therefore we introduced ancillary donor ligands, i.e., imidazolidin-2-iminate or 2,6-diphenylphenol, via alkane elimination to the metal center. Full characterization of the new complex species was achieved by common techniques and the complex geometry was analyzed through X-ray structure analyses. Interestingly, the catalytic performance of the primary zirconium tribenzyl was changed significantly by the introduced monoanionic imidazolidin-2-iminate. The newly developed mixed aminopyridinato and imidazolidin-2-iminato zirconium dibenzyl catalyst system did not show any polymerization activity but oligomerized ethylene to the corresponding even-numbered α-olefins. To influence the range of the product spectrum, the steric pressure at the amiopyridinate ligand, the polymerization temperature and the polymerization pressure as well as the cocatalyst were varied. The use of 2,6-diphenylphenol as additional donor ligand did not lead to oligomerization.

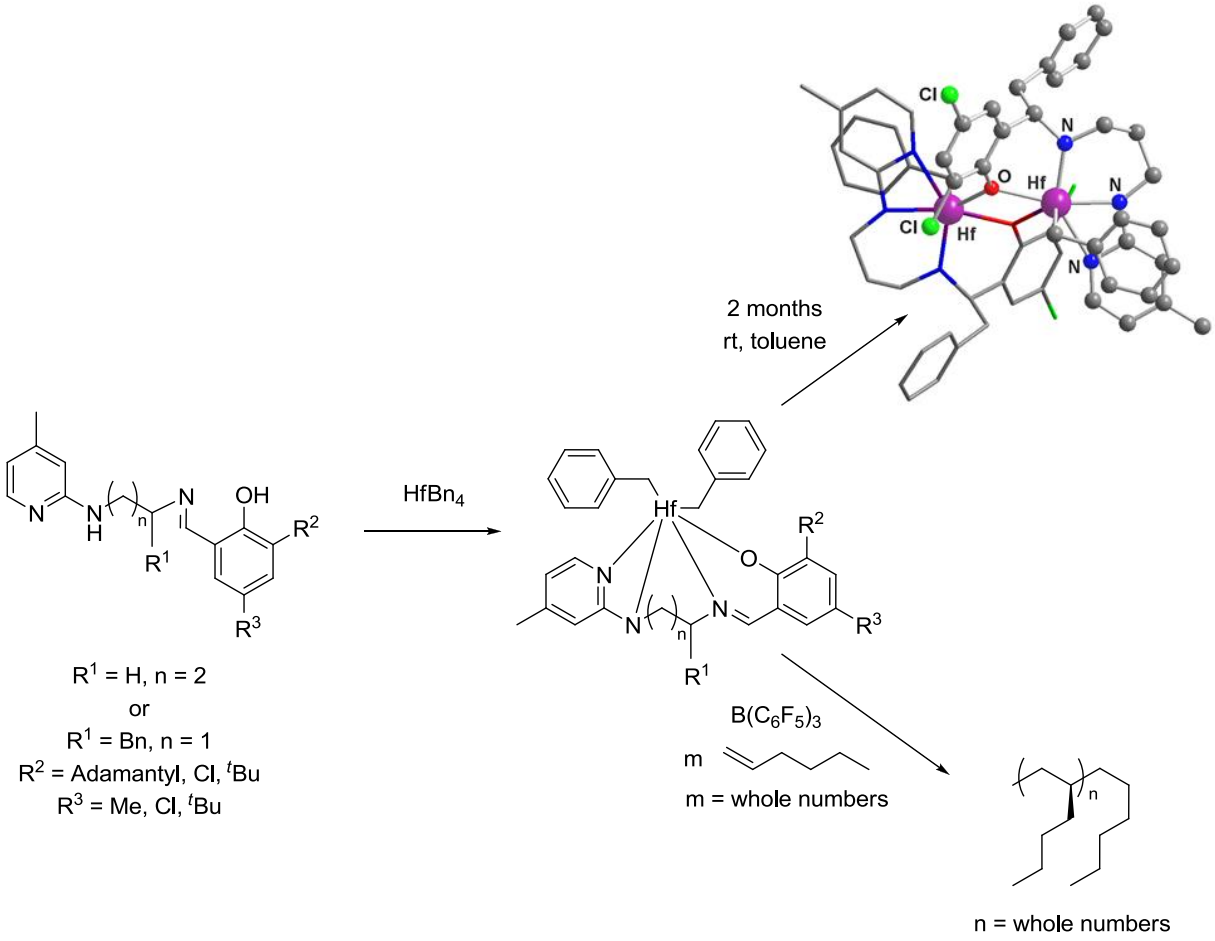
These findings were also filed in as a patent application: *EP* 13158550 'Complexes for the Catalytic Oligomerization of Olefins'

3.3 A Highly Efficient Titanium Catalyst for the Synthesis of Ultra-High Molecular Weight Polyethylene (UHMWPE)



In the course of our investigations concerning the influence of monoanionic ancillary ligands on the polymerization performance of already active catalyst systems we prepared guanidinato titanium dichloride complexes. These complexes were prepared by salt elimination reactions from [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato] titaniumtrichloride and the lithium salts of the ligand precursors 2,6-diphenylphenol, dicyclohexylamine, 1,1,3,3-bis(pentamethylene)guanidine and 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imine. The new complex species were fully characterized and their ligand environment was discussed in detail with the help of X-ray structure analyses. In contrast to the original titanium trichloride complex the new titanium dichloride complexes were not active in CCTP. They were even sensible toward aluminum alkyls and showed ligand transfer to aluminum when activated with MAO as cocatalyst. However, after activation with d-MAO, from which free trimethylaluminum was removed, a drastic increase in activity (from 1360 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$ to 5560 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$) was observed for some of the systems as compared to their trichloride parent compound. Furthermore, ultra-high molecular weight polyethylene was obtained.

3.4 Aminopyridinate-FI Hybrids, their Hafnium and Titanium Complexes and Living 1-Hexene Polymerization

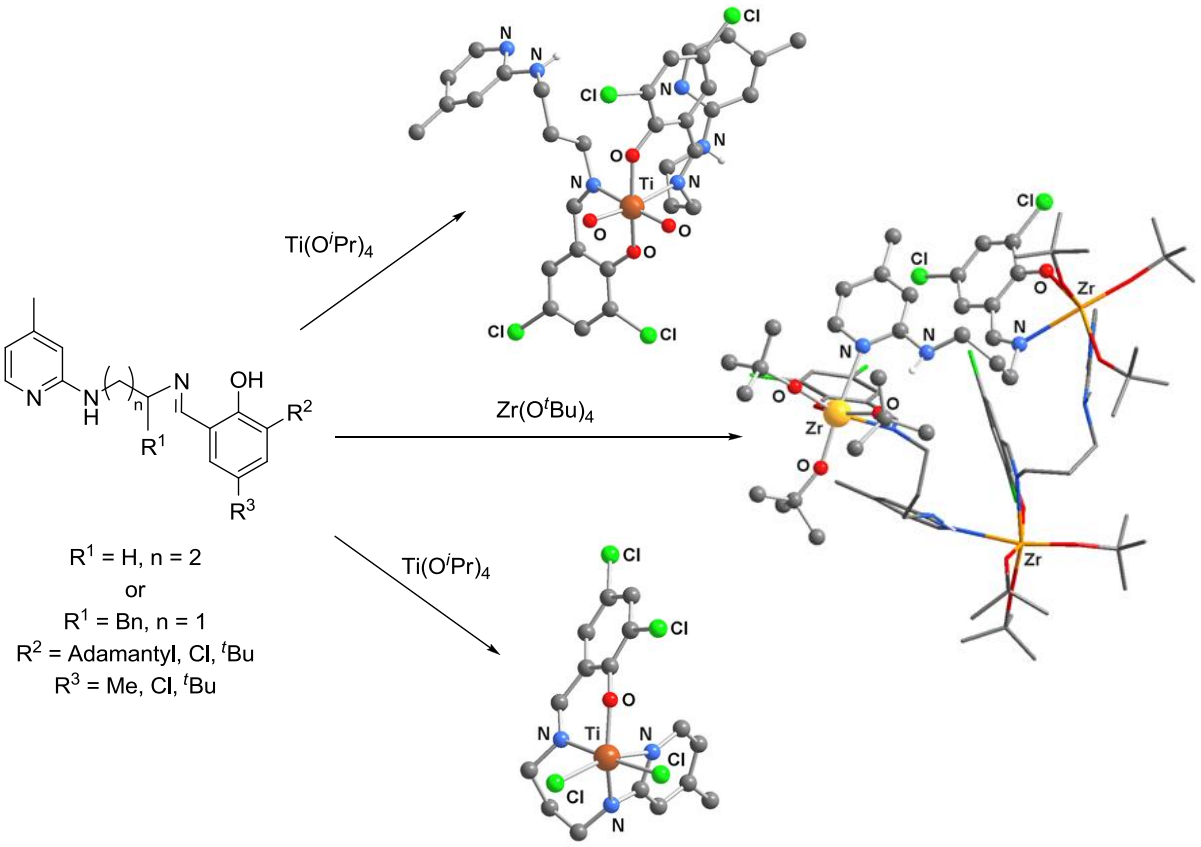


Based on the two well established aminopyridine (Ap) and phenoxy-imine (FI) ligand systems, an interesting new Ap-FI hybrid ligand system was developed. Mono-*N*-arylated aliphatic diamines, representing the Ap part of the new ligand, were synthesized via Ir-catalyzed alkylation of aromatic amines using unprotected amino alcohols as alkylating agents. This protocol was developed independently in our group four years ago. The phenoxy-imine part was either commercially available or synthesized according to published procedures. After a simple condensation reaction which combines both parts, four different Ap-FI hybrid ligands were achieved. They feature 3-adamantyl-5-methyl, 3,5-di-chloro or 3,5-di-*tert*-butyl substitution on the phenolate ring of the FI part, a methyl group at 4-position of the Ap part and either a propylene or a substituted ethylene bridge between the two nitrogen donors. Reaction of hafnium tetrabenzyl with all four Ap-FI hybrid ligands exclusively led to mono(Ap-FI) complexes of the type [(Ap-FI)$HfBn_2$]. After characterization of the new complexes, they were tested in polymerization of 1-hexene. Upon activation with tris(pentafluorophenyl)borane some of the hafnium dibenzyl complexes polymerize 1-hexene in a living fashion to highly isospecific poly(1-hexene) ([*mmmm*] = 92%) at room temperature. Moreover, ultra-high molecular weights (up to

M_n = 1,500,000 g·mol^{-1}) and extremely narrow polydispersities (PDI = 1.02) suggest the living nature of the polymerization process.

Interestingly, an imine alkylated deactivation product of one of the hafnium dibenzyl complexes was characterized by X-ray structure analysis. These findings showed that the hafnium dibenzyl catalyst precursors were not long term stable in solution and the ligand has a high tendency to undergo alkylation of the imine function at its phenoxy-imine part. However, the coordination mode of the ligand was clarified through a titanium model complex. Thereby the Ap-FI ligand showed its desirable *fac-mer* coordination mode which is essential for the *cis*-standing of the two substituents at the metal center.

3.5 Coordination Chemistry of Ap-FI Hybrids with Titanium and Zirconium and their Ethylene Homopolymerization Performance



Upon further variation of the metal precursors used for the syntheses of Ap-FI stabilized group IV complexes different coordination modes of the Ap-FI ligand were observed. Mono(Ap-FI) complexes of the type [(Ap-FI)Ti(O*i*Pr)$_2$] or [(Ap-FI)TiCl$_2$] were obtained from the sterically demanding adamantyl-substituted Ap-FI hybrid ligand or the chloro-substituted Ap-FI hybrid ligand when treated with titanium(IV) isopropoxide or bis(dimethylamido) titanium(IV) dichloride. In both cases, the ligands act as a tetradentate dianionic chelate. By changing the steric or electronic properties of the ligands, multi(ApH-FI) complexes of the type [(ApH-FI)$_2$Ti(O*i*Pr)$_2$] or [(ApH-FI)Zr(O*t*Bu)$_3$]$_3$ were synthesized which feature the ligands in their monoanionic form. The new titanium and zirconium complexes were all characterized by elemental analysis, NMR spectroscopy and to some extent by X-ray crystal structure analysis. The titanium complexes with the promising *fac-mer* coordination mode of the respective Ap-FI ligand were tested in ethylene polymerization experiments. The results showed that the new catalyst systems are able to polymerize ethylene with MAO and d-MAO as activators. However, in the presence of trimethylaluminum bimodal molecular weight distributions were observed. This may be due to the noninnocent nature of the Ap-FI ligand which inhibits access to a highly controlled polymerization process. By the use of d-MAO as activator undesirable side reactions were

suppressed and monomodal molecular weight distributions as well as high molecular weights were obtained.

3.6 Individual Contribution to Joint Publications

The results presented in this thesis were obtained in collaboration with others and are published, submitted for publication or are 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 respective corresponding author.

Chapter 4

This work is published in *Organometallics* **2011**, *30*, 4854–4861, with the title

"Synthesis of Alumina-Terminated Linear PE with a Hafnium Aminopyridinate Catalyst"
Isabelle Haas, Winfried P. Kretschmer, and Rhett Kempe*

I synthesized and characterized all complexes presented in this work and carried out the NMR experiments, the X-ray analyses and crystal structure solutions as well as the ethylene polymerization experiments. Also, the publication was written by me. Winfried P. Kretschmer performed the GPC analyses. Rhett Kempe supervised this work and was as well as Winfried P. Kretschmer involved in scientific discussions, comments and correction of the manuscript.

Chapter 5

This work is to be submitted to *J. Am. Chem. Soc.* with the title

"Flipping the Switch from Polymerization to Oligomerization with a Monoanionic η^1-Imidazolidiniminate as Ancillary π-Donor Ligand"
Isabelle Haas, Winfried P. Kretschmer, and Rhett Kempe*

All the complex syntheses and characterizations as well as three X-ray structure analyses and crystal structure solutions were done by me. I also did the polymerization experiments, oligomerization experiments and α-olefin analyses. The manuscript also was written by me. Auke Meetsma measured one X-ray structure and did the crystal structure solution. Winfried P. Kretschmer performed the GPC analyses. Rhett Kempe supervised this work and was involved as well as Winfried P. Kretschmer in scientific discussions, comments and correction of the manuscript.

This work is filed in as a patent application with the No. *EP* 13158550 (11.03.2013) and the title

"Complexes for the Catalytic Oligomerization of Olefins"

Inventors: Isabelle Haas, Winfried P. Kretschmer, and Rhett Kempe

Applicant: Universität Bayreuth

The application text was written by the patent attorneys Stefan Fickert (*Vossius & Partner*), Edith Kinder (*Bayrische Patentallianz*), Sarah Krüger (*Bayrische Patentallianz*), Winfried P. Kretschmer (*Universität Bayreuth*) and me (*Universität Bayreuth*). Rhett Kempe (*Universität Bayreuth*) supervised this work and was involved in scientific discussions and comments on the manuscript.

Chapter 6

This work has been accepted for publication in *Chem. Eur. J.* (doi: 10.1002/chem.201301176) with the title

"A Highly Efficient Titanium Catalyst for the Synthesis of Ultra-High Molecular Weight Polyethylene (UHMWPE)"

Isabelle Haas, Christian Hübner, Winfried P. Kretschmer, and Rhett Kempe*

I synthesized and characterized all of the compounds presented in this work and the publication was written by me. The X-ray analyses and crystal structure solutions were also done by me. Christian Hübner helped with the synthesis of the complexes and with the development of the polymerization protocol in the course of his B. Sc. thesis in our group. Winfried P. Kretschmer supervised this work and did the ethylene polymerization experiments and analyses. Rhett Kempe was involved in scientific discussions, comments and correction of the manuscript.

Chapter 7

This work is submitted to *Chem. Eur. J.* with the title

"Aminopyridinate-FI hybrids, their Hafnium and Titanium Complexes and Living 1-Hexene Polymerization"

Isabelle Haas, Thomas Dietel, Konstantin Press, Moshe Kol*, and Rhett Kempe*

I developed and prepared all ligands and complexes presented in this work and carried out the characterizations as well as the X-ray analyses and the crystal structure solutions. Also, the publication was written by me. Thomas Dietel helped with the syntheses of the ligands and complexes in the

course of his B. Sc. thesis in our group. Konstantin Press performed the 1-hexene polymerization experiments and GPC analyses. Moshe Kol and Rhett Kempe supervised this work and were involved in scientific discussions, comments and correction of the manuscript.

Chapter 8

This work is to be submitted to *Eur. J. Inorg. Chem.* with the title

"Coordination Chemistry of Ap-FI Hybrids with Titanium and Zirconium and their Ethylene Homopolymerization Performance"

Isabelle Haas, Thomas Dietel, and Rhett Kempe*

I synthesized and characterized all of the compounds presented in this work and wrote the manuscript. Thomas Dietel helped with the syntheses and the development of the polymerization protocol during his B. Sc. thesis in our group. Winfried P. Kretschmer performed the GPC analyses. Rhett Kempe supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

4 Synthesis of Aluminum-Terminated Linear PE with a Hafnium Aminopyridinate Catalyst

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4.1 Abstract

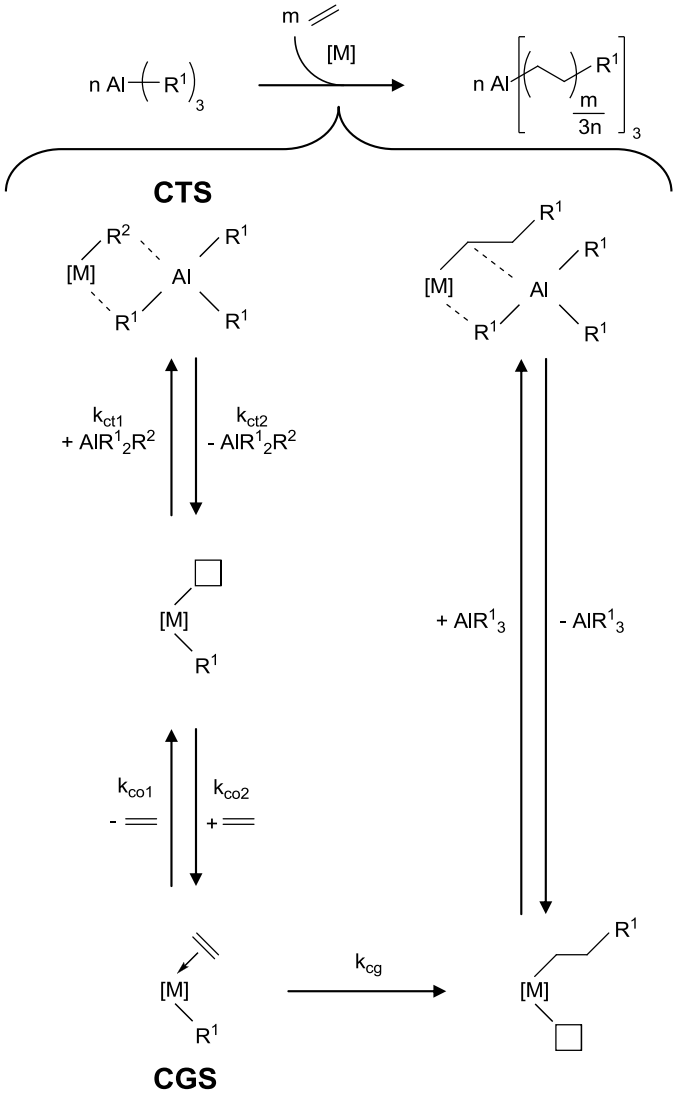
Five different Ap (aminopyridinato) ligand stabilized hafnium complexes were synthesized and characterized through NMR spectroscopy, elemental analysis, and (to some extent) by X-ray crystal structure analysis. Moreover, a tunable ethylene polymerization catalyst system based on these complexes was tested in CCTP (coordinative chain transfer polymerization) with TEA (triethylaluminum) as the chain transfer agent. The catalyst precursor giving the highest degree of control, [Cp*Hf(ApHDIP)Me_2] (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, Ap_HDIP-H = *N*-(2,6-diisopropylphenyl)pyridine-2-amine, Me = methyl), in the presence of high amounts of TEA was investigated regarding different parameters: e.g., temperature, ethylene pressure, catalyst/chain transfer agent ratio, and reaction time. The results showed that the new catalyst system is able to tolerate up to 5000 equiv of TEA and was able to produce linear aluminum-terminated polyethylene with polydispersities down to 1.2.

4.2 Introduction

Zieglers "Aufbaureaktion",[1] the rather slow insertion of ethylene into Al-C bonds or the *syn* addition of Al alkyls to ethylene (carboalumination), is an industrial process of great importance. This process gains access to long-chain Al alkyls, which can easily be transformed to the corresponding alcohols via oxidation with O_2. These aliphatic alcohols have a chain length of (for instance) 6–22 carbon atoms and are called Ziegler or fatty alcohols. Fatty alcohols have wide applications in areas such as personal care and polymer/leather/metal processing as well as agriculture and are used in cosmetics, flavors, fragrances, plastics (as softener), paints, coatings, industrial cleaning materials, and biocides.[2] A further

expansion of the described wide range of application would be possible if fatty alcohols with chain lengths significantly higher than 22 carbon atoms were efficiently accessible. A polymerization method which is able to produce longer chain Al alkyls (in a highly controlled fashion) is CCTP (coordinative chain transfer polymerization).[3,4]

Since Eisenberg and Samsel[5] as well as Mortreux and coworkers[6] cleared the way for CCTP in the early 1990s, a few very interesting ethylene/propylene CCTP systems across the ranks of RE (rare earth metals) and transition metals with different CTAs (chain transfer agents), such as Mg,[6] Zn[7,8,9] and Al alkyls,[10,11] have been discovered. Furthermore, enhancements of the CCTP concept such as "chain shuttling"[9] and "ternary CCTP"[12] have been developed already. A simplified mechanism of CCTP is shown in Scheme 1.



Scheme 1. Net Reaction and Mechanism of CCTP: Top: CTS (Chain Transfer State); bottom: CGS (Chain Growing State); [M] = cationic or neutral transition metal or RE complex; R^1, R^2 = alkyl moiety.

k_{ct1}, k_{ct2}, k_{co1}, k_{co2} and k_{cg} are rate constants. *n, m* = natural numbers. *β*-H elimination termination steps must be suppressed. Intermolecular chain exchange is preferred over intramolecular (CTS).[13]

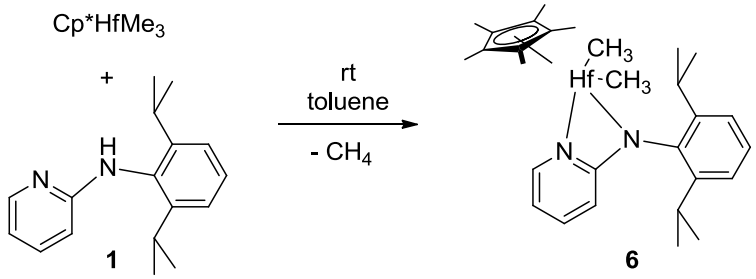
The CGS elongates the polymer chain. The CTS is used to transfer the polymer chain between the catalyst and the CTA. At the CTA chain growth is very slow and polymerization is of low relevance as long as the CTA bears the polymer chain. Bochmann and Lancaster first reported that the exchange of alkyl chains between Hf (or Zr) cations and Al occurs via the formation of a Hf/Al (or Zr/Al) bimetallic complex (CTS).[14] Rate constants k_{ct} (Scheme 1) for a variety of metallocene cations (Ti, Zr, and Hf) and trimethylaluminum were reported by Norton and Petros in 2004.[13] Recently Norton and coworkers reported a detailed mechanistic picture of the zirconium complex catalyzed chain growth of Al alkyls.[15] The kinetics of chain growth have been studied when catalyzed by [(EBI)Zr(μ-Me)$_2$AlMe$_2$][B(C_6F_5)$_4$] (EBI = ethylene-bridged bis(indenyl), Me = methyl). The reaction is first order in [olefin] and [catalyst] and inverse first order in [AlR_3].[15] Thus, high amounts of Al alkyl result in poor overall CCTP activity. On the other hand, high Al to catalyst ratios are desired to minimize (process) costs. A possibility to solve this problem is the design of a new catalyst system undergoing a relatively slow chain exchange or a fast but not too fast chain growth in comparison to chain exchange that still suppresses *β*-H eliminiation and transfer processes. Under these conditions the influence of the added amount of Al alkyl still reduces activity but due to multiple insertions a certain overall chain growth activity is observed.

Herein, we present an ethylene polymerization catalyst system based on Ap (aminopyridinato) ligand[16,17,18,19] stabilized hafnium Cp* complexes and its behavior in CCTP with TEA (triethylaluminum). The effect of changing different parameters, e.g. temperature, ethylene pressure, catalyst/CTA ratio, and reaction time is discussed.

4.3 Results and Discussion

Synthesis and Structure of the Hafnium Complexes

The applied Ap ligands **1** (Ap_HDIP-H = *N*-(2,6-diisopropylphenyl)pyridine-2-amine), **2** (Ap_{Me}DIP-H = *N*-(2,6-diisopropylphenyl)-6-methylpyridine-2-amine), **3** (Ap_{Br}DIP-H = 6-bromo-*N*-(2,6-diisopropylphenyl)pyridine-2-amine), **4** (Ap_{Cl}DIP-H = 6-chloro-*N*-(2,6-diisopropylphenyl)pyridine-2-amine), and **5** (Ap_HTMA-H = *N*-mesityl-4-methylpyridine-2-amine) were prepared as reported.[20,21,22,23,24] [Cp*$HfMe_3$] was synthesized according to published procedures.[22,25,26] Reaction of one equiv of **1** with [Cp*$HfMe_3$] in toluene at room temperature results in the formation of **6** by methane elimination (Scheme 2).



Scheme 2. Synthesis of the Hafnium Catalyst Precursor **6**.

The compounds **7–10** were synthesized analogously to **6** using **2–5**, respectively, instead of **1**. Recrystallization of the raw product in hexane gave access to good yields of complexes **6–10** as yellow crystalline materials. Figure 1 shows the synthesized hafnium catalyst precursors.

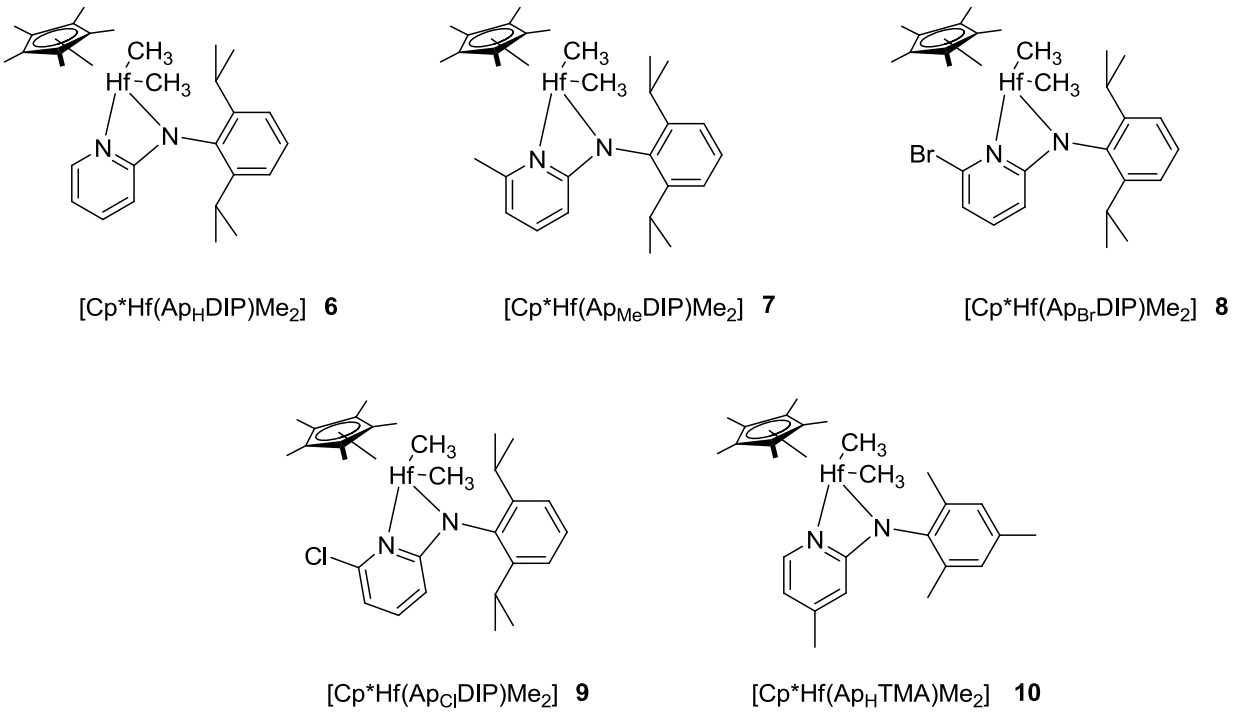


Figure 1. Synthesized catalyst precursors.

All compounds were characterized by NMR spectroscopy and elemental analysis. Crystals of complexes **6**, **7**, and **9** suitable for X-ray analysis were grown from hexane solutions. The molecular structure of **6** is shown in Figure 2. For the molecular structures of **7** and **9** as well as details of the X-ray crystal structure analyses of all three complexes, see the Supporting Information.

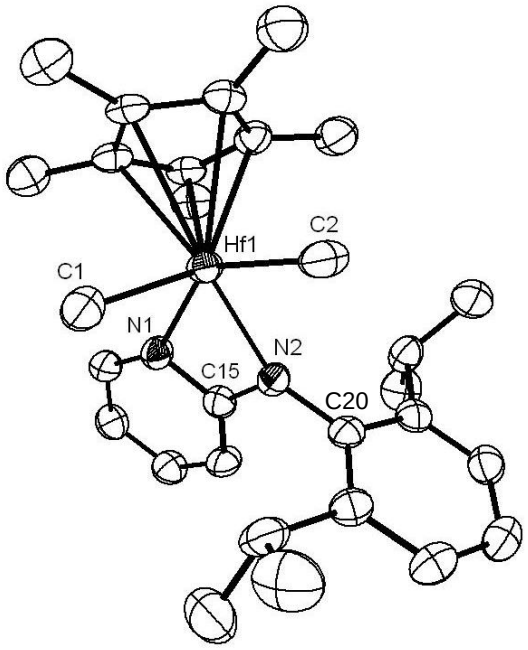


Figure 2. Molecular structure (40% thermal ellipsoids) of compound **6**. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and angles [°]: Hf1–N2 2.195(4), Hf1–N1 2.359(4), N1–C15 1.357(6), N2–C15 1.357(6), Hf1–C1 2.221(5), Hf1–C2 2.238(5); Hf1–N1–C15 92.0(3), Hf1–N2–C15 99.4(3), N1–C15–N2 110.2(4), N1–Hf1–N2 58.39(14), C1–Hf1–C2 96.0(2), C15–N2–C20 118.7(4).

All obtained crystal structures of the aminopyridinato ligand stabilized Hf complexes feature a nearly 58° N1–Hf–N2 Ap angle (58.39(14)° for **6**, 58.63(14)° for **7** and 58.1(3)° for **9**). In contrast the C1–Hf–C2 angle varies from 90° to 96°, depending on the steric demand of the substituent at the 6-position of the pyridine ring (90.9(2)° for **7**, 93.2(3) for **9** and 96.0(2) for **6**). The mean Hf–C bond length (2.222 Å) of all the three compounds is comparable to the expected value of a Hf–C bond of a methyl ligand (2.261 Å).[27] The dialkyl **6** formes organohafnium cations in the presence of activators such as ammonium borates ($[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$) or $[PhNMe_2H]^+[B(C_6F_5)_4]^-$) and trityl borate $[(C_6H_5)_3C]^+[B(C_6F_5)_4]^-$ (BF_{20}). The reaction of **6** with BF_{20} gave rise to **11**. Figure 3 shows the ^1H NMR spectra of catalyst precursor **6** and its activation with BF_{20}.

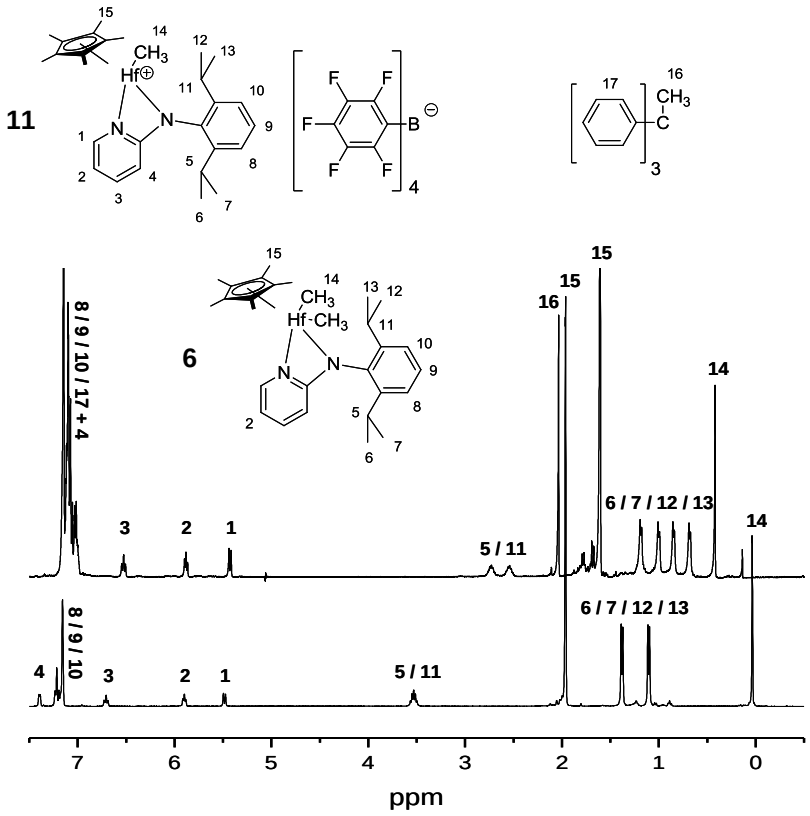


Figure 3. ^{1}H NMR spectra (C_6D_6): Bottom: spectrum of catalyst precursor **6**; top: spectrum after the activation of **6** with BF_{20}.

The NMR spectroscopic investigations of the organohafnium cation **11** revealed a single signal set as observed for **6**. The abstraction of one methyl group by the activator BF_{20} leads to a further splitting of the three isopropyl signals (5/11, 6/7/12/13) due to a decrease in symmetry of the complex.

Ethylene Polymerization Studies

For the polymerization of ethylene with the Ap ligand stabilized organohafnium cations the presence of aluminum alkyls is essential (Table 1, entry 1).

Only the catalyst precursor **6** is able to reach a polydispersity lower than 2 (Table 1, entry 2). The precatalysts **8** and **9** do not show any activity under the tested ethylene polymerization conditions of 50 °C and 15 min. reaction time (Table 1, entries 4 and 6). Polymer formation can be observed at higher reaction temperatures or longer reaction times (Table 1, entries 5 and 7). The organohafnium cations based on **6** gave the best polymerization results, and we proceeded to explore this catalyst system in more detail.

Table 1. Comparison of the Ethylene Polymerization of All Synthesized Organohafnium Catalyst Precursors **6–10**.[a]

entry	precursor	Al/Hf (amt of TEA [mmol])	time [min]	temp [°C]	yield [g]	activity [kg·mol^{-1}·h^{-1}·bar^{-1}]	M_w [g/mol]	PDI	N_{exptl}/N_{theor} [%][b]
1	**6–10**	0 (0)	90	50	0	0	n.d.	n.d.	-
2	**6**	10 000 (20)	15	50	0.62	630	380	1.3	4
3	**7**	10 000 (20)	15	50	0.74	740	2 500	2.5	13
4	**8**	10 000 (20)	15	50	0	0	n.d.	n.d.	-
5	**8**	10 000 (20)	90	50	2.69	450	58 000	3.8	<1
6	**9**	10 000 (20)	15	50	0	0	n.d.	n.d.	-
7	**9**	10 000 (20)	15	80	2.64	2 600	5 000	3.5	3
8	**10**	10 000 (20)	15	50	0.14	140	36 000	27.6	2

[a] Conditions: dialkyl (**6–10**); 2 μmol; ammonium borate, $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$); Hf/B = 1/1.1; aluminum alkyl, TEA; 290 mL toluene; pressure, 2 bar. [b] N_{exptl}, experimental chain number [yield PE (in g)/M_n]; N_{theor}, theoretical chain number, considering three growing chains per Al atom.

Termination Reaction Study

NMR spectroscopy of the polymers obtained (after hydrolytic workup) revealed saturated polymers (Figure 4).

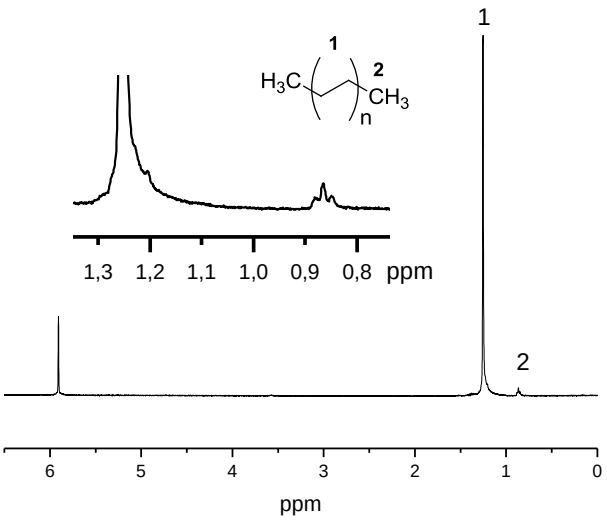


Figure 4. ^{1}H NMR spectrum of the obtained polymer of entry 2 in Table 1. The inset shows the signal of the methyl end groups.

The ^{1}H NMR spectra of the polymeric product of entry 2 (Table 1) shows no signals for olefinic protons. No β-H elimination seems to occur during the polymerization process.

Temperature and Pressure Dependence of the Organohafnium-Catalyzed Ethylene Polymerization

Temperature plays a very sensitive role in CCTP. Temperature influences the insertion rate and the transfer rate (Scheme 1), but not necessarily to the same extent. Furthermore, with growing chain length the PE chains become more and more insoluble, which causes precipitation at some stage. This precipitation blocks the transfer of the growing chain which is essential for the CCTP mechanism, and a bimodal distribution is observed (temporarily).[6c,10] Entries 1–3 in Table 2 show the effect of temperature, and entries 2 and 4 in Table 2 show the effect of pressure on the organohafnium catalyst system based on **6**.

Table 2. Temperature and Pressure Dependence of Ethylene Polymerization Using Organohafnium Cations Based on **6**.[a]

entry	pressure [bar]	temp. [°C]	activity [kg·mol^{-1}·h^{-1}·bar^{-1}]	productivity [g(PE)/g(cat.)]	yield [g]	M_w [g/mol]	PDI	N_{exptl}/N_{theor} [%][c]
1	2	30	240	200	0.24	1010	1.9	2
2	2	50	430	360	0.43	880	1.2	2
3	2	80	1960	1640	1.96	8000	12.1[b]	10

4	5	50	700	1460	1.74	1020	2.1	12

[a] Conditions: dialkyl (**6**), 2 μmol; ammonium borate, $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$); Hf/B = 1/1.1; aluminum alkyl, TEA; Hf/Al = 1/5000; 290 mL toluene; time, 15 min. [b] Bimodal distribution: (1) peak M_w 45 000, PDI 1.8; (2) peak M_w 1100, PDI 2.2. [c] N_{exptl} = experimental chain number [yield PE (in g)/M_n]; N_{theor} = theoretical chain number, considering three growing chains per Al atom.

The rise in temperature (entry 1–3, Table 2) goes along with an increase in activity and productivity. At 80 °C a bimodal distribution and substantial amounts of precipitated polymer were observed. Chain growth can proceed more quickly at 80 °C, which is in accordance with the increase in activity. This increase in activity might have a much stronger effect than the increased polymer solubility at 80 °C so that precipitation takes place and a bimodal distribution is observed.[6c,10] Pressure is also an important parameter to influence the polymerization result. Due to an increase in ethylene solubility[28] at higher pressures the insertion rate is increased independently from the chain transfer rate, leading to an increase in polydispersity, molecular weight, and activity. At higher pressure, an increase in activity, an increase of the molecular weight, and an increase in polydispersity is observed (entries 2 and 4, Table 2).

In order to optimize the polymerization process with respect to the highest control, it was decided to use 50 °C and 2 bar as reaction conditions for the following studies.

Effect of the Al Concentration

Mainly CCTP catalyst systems which handle CTA/catalyst ratios between 50 and 100 are described in the literature. Only one example of Mortreux and coworkers[6c] gives an experiment with an Mg/Sm ratio of 1000, and one work by Gibson and coworkers[7c] gives an experiment with a Zn/Zr ratio of 2800. The great advantage of the Hf system described here is the tolerance to very high amounts of aluminum alkyls. Table 3 summarizes the results concerning the variation of the Al/Hf ratio in CCTP of ethylene with the organohafnium cations based on **6**.

Table 3. Dependence of the Ethylene Polymerization on the Aluminum to Hafnium Ratio.[a]

entry	Al/Hf (amt of TEA [mmol])	activity [kg·mol^{-1}·h^{-1}·bar^{-1}]	yield [g]	M_w [g/mol]	PDI	N_{exptl}/N_{theor} [%][c]
1	0 (0.0)	0	0	n.d.	n.d.	-
2	50 (0.1)	110	0.84	618 000	12.4	6

3	100 (0.2)	2800	2.80	22 000	3.2	66
4	500 (1.0)	550	0.55	2 500	1.5	12
5	1 000 (2.0)	400	0.40	1 570	1.4	6
6	5 000 (10.0)	430	0.43	880	1.2	2
7[b]	(20.0)	0	0	n.d.	n.d.	-

[a] Conditions: dialkyl (**6**), 2 μmol; ammonium borate, $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$); Hf/B = 1/1.1; aluminum alkyl, TEA; 290 mL of toluene; pressure, 2 bar; temperature, 50 °C; time, 15 min. [b] No catalyst precursor. [c] N_{exptl} = experimental chain number [yield PE (in g)/M_n]; N_{theor} = theoretical chain number, considering three growing chains per Al atom.

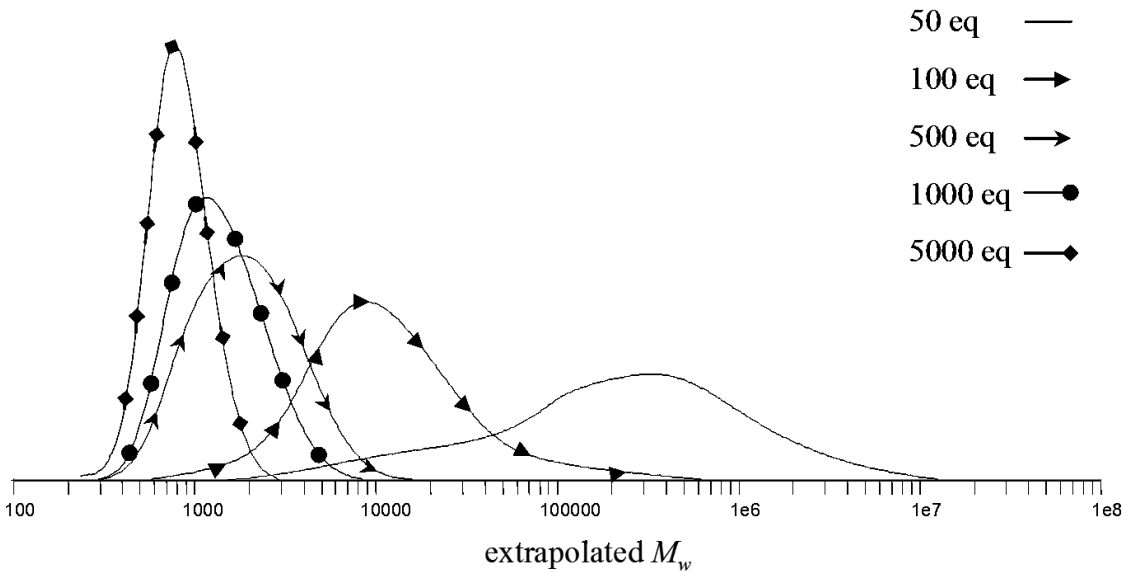


Figure 5. Molecular weight distribution (GPC) of the polymerization experiments listed in Table 3.

For this catalyst system monomodal molecular weight distributions with a polydispersity between 1.2 and 3.2 and M_w between 400 and 22 000 (Figure 5) were observed. Whereas narrow dispersities and low molecular weights were observed with high amounts of TEA, broad polydispersities and high molecular weights were observed with low amounts of TEA. In entry 3 of Table 3, two elongated alkyl chains per Al atom are observed with a rather broad PDI. The higher PDI may result from the relatively high molecular weight (far behind the precipitation point).[6c,10] A higher amount of CTA (Table 3, entries 4–6) results in lower molecular weights and lower PDI. Low to very low amounts of extended chains are observed at high Al to Hf ratios. Aluminum cations stabilized by aminopyridinato

ligands are nearly inactive in ethylene polymerization.[10,29] If no **6** is added, no polymerization takes place (entry 7, Table 3).

Time Dependence of the Organohafnium-Catalyzed Ethylene Polymerization

The observation of the polymerization results with increasing time gives important information on the nature of the chain transfer. If very fast chain transfer takes place during polymerization, the level of control is very high and it is possible to produce polymeric materials over a large range of molecular weights with nearly the same narrow polydispersities.[8a,10] With the Hf catalyst system described here, this is not the case. Table 4 shows the time dependence of the catalyst system based on **6**, and Figure 6 gives the molecular weight distribution of the experiments in Table 4. An increase in yield and activity with increasing time takes place as well as the formation of a bimodal distribution.

Table 4. Time Dependence of the Ethylene Polymerization Using Organohafnium Cations Based on **6**.[a]

entry	time [min]	activity [kg·mol^{-1}·h^{-1}·bar^{-1}]	yield [g]	ethylene consumption [g]	M_n [g/mol]	PDI	N_{exptl}/N_{theor} [%][b]	N_{exptl}/N_{theor} [%][c]
1	15	430	0.43	1.46	760	1.2	6	2
2	30	720	1.45	4.01	910	20.7	15	
peak 1					810	1.3		6
peak 2					900	23.5		
3	45	940	2.82	6.26	1 070	44.9	20	
peak 1					820	1.3		11
peak 2					22 000	6.8		
4	60	1440	5.77	8.51	1 340	152.0	21	
peak 1					730	1.6		26
peak 2					31 000	14.5		

[a] Conditions: dialkyl (**6**), 2 μmol; ammonium borate, $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$); Hf/B = 1/1.1; aluminum alkyl, TEA; Hf/Al = 1/5000; 290 mL of toluene; pressure, 2 bar; time, 15 min. [b] N_{exptl} = experimental chain number [ethylene consumption (in g, determined by a Bronkhorst HIGH-TECH EL-FLOW mass flow controller)/M_n]; N_{theor} = theoretical chain number,

considering three growing chains per Al atom. [c] N_{exptl} = experimental chain number [yield (in g)/M_n]; N_{theor} = theoretical chain number, considering three growing chains per Al atom.

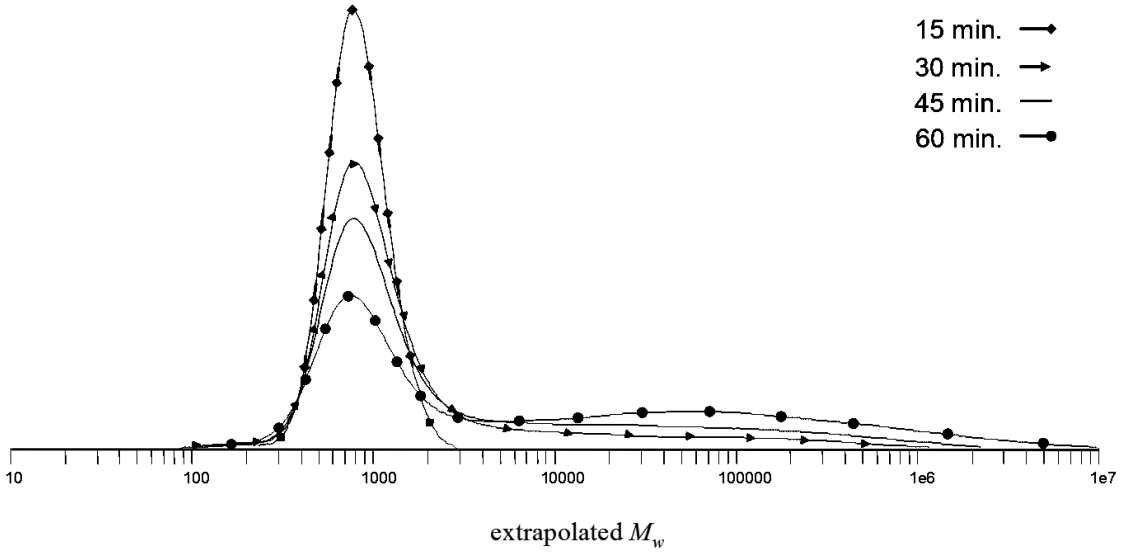


Figure 6. Molecular weight distribution (GPC) of the polymerization experiments listed in Table 4.

The second peak could be explained by a transformation of the first catalytically active species into a second, yet unknown, catalyst species (**6a**) during polymerization. This new species does not carry out chain transfer but produces high molecular weight polymers (Table 4, entries 2–4, peak 2). The first peak nearly remains at its molecular weight and shows just a slight increase in PDI (Table 4, entries 1–4, peak 1). Furthermore, the amount of extended chains increases. A very long polymerization time is necessary to elongate all theoretically possible chains if such a high amount of Al alkyl is present during polymerization. Because of the transformation of the CCTP catalyst species derived from **6** to **6a**, it is impossible to observe a quantitative Al alkyl chain elongation here. If we add high Al amounts to traditional ethylene CCTP catalysts such as the aminopyridinato and amidinato yttrium catalyst system,[11f] the catalysts are inactive already at Al/Y ratios of about 400.

4.4 Conclusion

A few conclusions can be drawn from the studies discussed here. First, aminopyridines react cleanly with [Cp*$HfMe_3$] to form mixed Cp*/Ap dimethyl complexes. Second, these Hf complexes can be activated with borates to undergo chain transfer polymerization with ethylene in the presence of large amounts of aluminum alkyls. Linear PE with saturated end groups is observed after hydrolysis. Most likely, relatively slow chain transfer (in relation to chain growth) leads to multiple insertions and a lesser

degree of control in comparison to traditional CCTP catalyst systems. Third, the transformation of the active chain transfer catalyst into a second (polymerization active) species which produces a higher molecular weight PE fraction is assumed. The formation of this species prevents quantitative chain elongation.

Further efforts should be directed towards the development of more stable catalysts able to tolerate high amounts of Al alkyls and to achieve quantitative chain elongation.

4.5 Experimental Section

General Comments. All manipulations of air- or moisture-sensitive compounds were carried out under N_2 and Ar using glove-box, standard Schlenk, or vacuum-line techniques. Solvents and reagents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy, or sodium benzophenone ketyl under nitrogen immediately before use. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxyen 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). Elemental analyses were carried out with a Vario elementar EL III apparatus.

NMR Spectroscopy. NMR spectra were recorded on a Varian INOVA 400 (^{1}H, 400 MHz; ^{13}C, 100.5 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 23 °C, were referenced internally using the residual solvent resonances, and the chemical shifts (δ) are reported in ppm. The polymer sample was prepared by dissolving 15 mg of the polymer in 0.5 mL $C_2D_2Cl_4$ at 100 °C for 3 h before measuring.

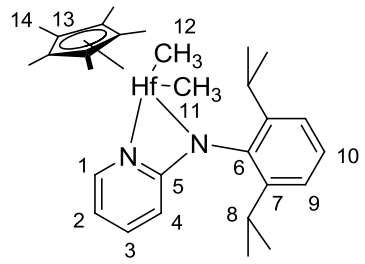
Gel Permeation Chromatography. GPC analysis was carried out on a Polymer Laboratories Ltd. (PL-GPC220) chromatograph at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% weight/volume) in the mobile-phase solvent in an external oven and were run without filtration. The molecular weight was referenced against linear polyethylene (M_w = 120 – 3 000 000 g/mol) and polystyrene (M_w = 510 – 3 200 000 g/mol) standards. The reported values are the average of at least two independent determinations.

X-ray Crystallography. X-ray crystal structure analyses were performed with a STOE-IPDS II diffractometer equipped with an Oxford Cryostream low-temperature unit (λ(MoK) = 0.71073 Å). Structure solution and refinement were accomplished using SIR97,[30] SHELXL-97,[31] and WinGX.[32] Selected details of the X-ray crystal structure analyses are given in the Supporting Information.

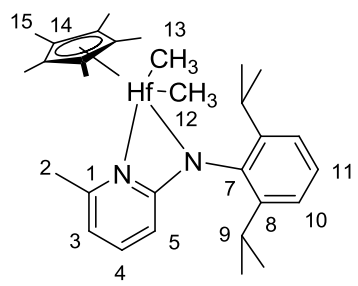
Ligand and Complex Synthesis. *N*,*N*,*N*-Trialkylammonium tetrakis(pentafluorophenyl)-borate ($[R_2NMeH][B(C_6F_5)_4]$, R = $C_{16}H_{31}$–$C_{18}H_{35}$, 6.2 wt.-% $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals) and triethylaluminum (TEA, 25 wt.-% in toluene, Aldrich) were used as received.

The precursor materials $[Cp^*HfCl_3]$[22,25] and $[Cp^*HfMe_3]$[26] as well as the ligands Ap_HDIP-H (*N*-(2,6-diisopropylphenyl)pyridine-2-amine),[20] Ap_{Me}DIP-H (*N*-(2,6-diisopropylphenyl)-6-methylpyridin-2-amine),[21] Ap_{Br}DIP-H (6-bromo-*N*-(2,6-diisopropylphenyl)pyridine-2-amine),[22] Ap_{Cl}DIP-H (6-chloro-*N*-(2,6-diisopropylphenyl)pyridine-2-amine)[23] and Ap_HTMA-H (*N*-mesityl-4-methylpyridine-2-amine)[24] were prepared according to published procedures.

Preparation of [Cp*Hf(Ap_HDIP)Me_2]. Ap_HDIP-H (0.200 g, 0.786 mmol) and $[Cp^*HfMe_3]$ (0.282 g, 0.786 mmol) were dissolved in toluene (15 mL), and the mixture was stirred overnight. All volatiles were removed under reduced pressure, and the residue was suspended in hexane (10 mL). The overlaying orange solution was filtrated, and the residue was extracted with hexane (2 × 5 mL). Removal of the solvent afforded **6** as a yellow, spectroscopically pure compound (0.324 g, 69%). Crystals suitable for an X-ray analysis were available through crystallization out of a saturated hexane solution at -22 °C. Anal. Calcd for $C_{29}H_{42}HfN_2$ (598.28): C, 58.33; H, 7.09; N, 4.69. Found: C, 58.57; H, 7.51; N, 4.61. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.40 (dd, ^3J = 4.6 Hz, 1H, H^1), 7.26 – 7.18 (m, 3H, H^9, H^{10}), 6.71 (dd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, 1H, H^3), 5.90 (dd, ^3J = 6.6 Hz, ^3J = 6.6 Hz, 1H, H^2), 5.49 (d, ^3J = 8.5 Hz, 1H, H^4), 3.53 (sept, ^3J = 6.8 Hz, 2H, H^8), 1.96 (s, 15H, H^{14}), 1.38 (d, ^3J = 6.9 Hz, 6H, $H_{CH_3i\text{-}Pr}$), 1.10 (d, ^3J = 6.7 Hz, 6H, $H_{CH_3i\text{-}Pr}$), 0.03 (s, 6H, H11, H^{12}) ppm. ^{13}C NMR (400 MHz, C_6D_6, 298 K): δ = 180.0 (s, 1C, C^5), 144.5 (s, 2C, C^7), 143.2 (s, 1C, C^1), 143.1 (s, 1C, C^6), 140.8 (s, 2C, C^8), 125.9 (s, 1C, C^3), 124.2 (s, 1C, C^{11}), 119.2 (s, 5C, C^{13}), 109.6 (s, 1C, C^4), 107.0 (s, 1C, C^2), 52.3 (s, 1C, C^{11}), 52.2 (m, 1C, C^{12}), 28.5 (s, 1C, C^{10}), 25.4 (s, 2C, $C_{CH_3i\text{-}Pr}$), 24.2 (s, 2C, $C_{CH_3i\text{-}Pr}$), 11.5 (s, 5C, C^{14}) ppm.

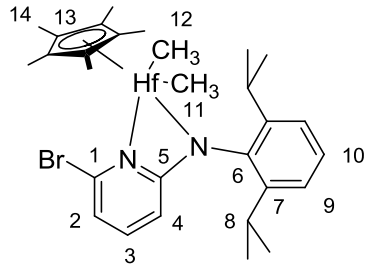


Preparation of [Cp*Hf(Ap_{Me}DIP)Me_2]. Ap_{Me}DIP-H (0.100 g, 0.373 mmol) and $[Cp^*HfMe_3]$ (0.134 g, 0.373 mmol) were dissolved in toluene (10 mL) and stirred overnight. All volatiles were removed under reduced pressure, and the residue was suspended in hexane (8 mL). The overlaying orange solution was filtrated, and the residue was extracted with hexane (2 × 5 mL). Removal of the solvent afforded **7** as a yellow, spectroscopically pure compound (0.137 g, 61%). Crystals suitable for an X-ray analysis were available through crystallization out of a saturated hexane solution at -22 °C. Anal. Calcd for $C_{30}H_{44}HfN_2$ (612.30): C, 58.96; H, 7.26; N, 4.58; Found: C, 59.17; H, 6.91; N, 4.60. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.23

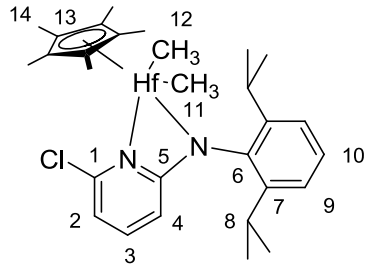


– 7.18 (m, 3H, H^{10}, H^{11}), 6.70 (dd, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 1H, H^4), 5.90 (d, ^3J = 7.6 Hz, 1H, H^3), 5.35 (d, ^3J = 8.6 Hz, 1H, H^5), 3.49 (sept, ^3J = 6.9 Hz, 2H, H^9), 2.06 (s, 3H, H^2), 1.97 (s, 15H, H^{15}), 1.38 (d, ^3J = 6.9 Hz, 6H, $H_{CH_3i\text{-}Pr}$), 1.10 (d, ^3J = 6.7 Hz, 6H, $H_{CH_3i\text{-}Pr}$), 0.12 (s, 6H, H^{12}, H^{13}) ppm. ^{13}C NMR (400 MHz, C_6D_6, 298 K): δ = 169.7 (s, 1C, C^6), 154.1 (s, 1C, C^1), 144.7 (s, 2C, C^8), 143.9 (s, 1C, C^7), 140.8 (s, 2C, C^9), 125.8 (s, 1C, C^4), 124.2 (s, 2C, C^{10}), 119.4 (s, 5C, C^{14}), 111.3 (s, 1C, C^5), 104.4 (s, 1C, C^3), 53.1 (s, 1C, C^{12}), 53.0 (s, 1C, C^{13}), 28.4 (s, 1C, C^{11}), 25.6 (s, 2C, $C_{CH_3i\text{-}Pr}$), 24.2 (s, 2C, $C_{CH_3i\text{-}Pr}$), 22.9 (s, 1C, C^2), 11.6 (s, 5C, C^{15}) ppm.

Preparation of [Cp*Hf(Ap_{Br}DIP)Me_2]. Ap_{Br}DIP-H (0.200 g, 0.602 mmol) and [Cp*$HfMe_3$] (0.216 g, 0.602 mmol) were dissolved in toluene (10 mL) and stirred overnight. All volatiles were removed under reduced pressure, and the residue was suspended in hexane (8 mL). The overlaying orange solution was filtrated, and the residue was extracted with hexane (2 × 5 mL). Removal of the solvent afforded **8** as a yellow, spectroscopically pure compound (0.273 g, 67%). Anal. Calcd for $C_{29}H_{41}BrHfN_2$ (676.19): C, 51.52; H, 6.11; N, 4.14. Found: C, 51.83; H, 6.23; N, 4.04. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.18 – 7.16 (m, 3H, H^9, H^{10}), 6.29 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 1H, H^3), 6.21 (d, ^3J = 7.4 Hz, 1H, H^2), 5.29 (d, ^3J = 8.1 Hz, 1H, H^4), 3.38 (sept, ^3J = 6.7 Hz, 2H, H^8), 2.05 (s, 15H, H^{14}), 1.34 (d, ^3J = 7.1 Hz, 6H, $H_{CH_3i\text{-}Pr}$), 1.02 (d, ^3J = 6.7 Hz, 6H, $H_{CH_3i\text{-}Pr}$), 0.24 (s, 6H, H^{11}, H^{12}) ppm. ^{13}C NMR (400 MHz, C_6D_6, 298 K): δ = 170.6 (s, 1C, C^5), 144.3 (s, 2C, C^7), 143.0 (s, 1C, C^1), 141.6 (s, 2C, C^8), 137.1 (s, 1C, C^6), 126.2 (s, 1C, C^3), 124.4 (s, 2C, C^9), 120.1 (s, 5C, C^{13}), 114.8 (s, 1C, C^4), 106.2 (s, 1C, C^2), 54.9 (s, 1C, C^{11}), 54.8 (s, 1C, C^{12}), 28.5 (s, 1C, C^{10}), 25.5 (s, 2C, $C_{CH_3i\text{-}Pr}$), 24.1 (s, 2C, $C_{CH_3i\text{-}Pr}$), 11.8 (s, 5C, C^{14}) ppm.

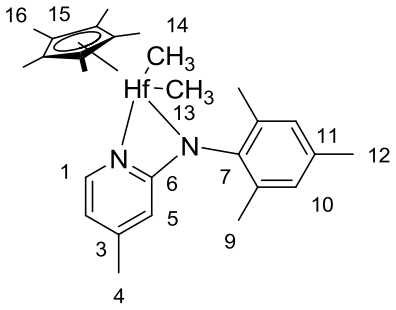


Preparation of [Cp*Hf(Ap_{Cl}DIP)Me_2]. Ap_{Cl}DIP-H (0.113 g, 0.392 mmol) and [Cp*$HfMe_3$] (0.141 g, 0.392 mmol) were dissolved in toluene (10 mL) and stirred overnight. All volatiles were removed under reduced pressure, and the residue was suspended in hexane (8 mL). The overlaying orange solution was filtrated, and the residue was extracted with hexane (2 × 5 mL). Removal of the solvent afforded **9** as a yellow, spectroscopically pure compound (0.161 g, 65%). Crystals suitable for an X-ray analysis were available through slow vaporization of the solvent hexane out of a saturated solution at room temperature. Anal. Calcd for $C_{29}H_{41}ClHfN_2$ (632.24): C, 55.15; H, 6.54; N, 4.44. Found: C, 55.54; H, 6.56; N, 4.54. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.18 – 7.16 (m, 3H, H^9, H^{10}), 6.40 (dd, ^3J = 8.5 Hz, ^3J = 8.5 Hz, 1H, H^3), 6.01 (d, ^3J = 7.7 Hz, 1H, H^2), 5.27 (d, ^3J = 8.5 Hz, 1H, H^4), 3.41 (sept, ^3J = 6.8 Hz, 2H, H^8), 2.04 (s, 15H, H^{14}), 1.35 (d, ^3J = 6.8 Hz, 6H, $H_{CH_3i\text{-}Pr}$), 1.04 (d, ^3J = 6.8 Hz, 6H, $H_{CH_3i\text{-}Pr}$), 0.20 (s, 6H, H^{11}, H^{12})



ppm. ^{13}C NMR (400 MHz, C_6D_6, 298 K): δ = 170.4 (s, 1C, C^5), 144.3 (s, 2C, C^7), 142.9 (s, 1C, C^1), 142.0 (s, 2C, C^8), 140.0 (s, 1C, C^6), 126.2 (s, 1C, C^3), 124.4 (s, 2C, C^9), 120.1 (s, 5C, C^{13}), 110.4 (s, 1C, C^4), 105.7 (s, 1C, C^2), 54.6 (s, 1C, C^{11}), 54.5 (s, 1C, C^{12}), 28.5 (s, 1C, C^{10}), 25.5 (s, 2C, $C_{CH_3i\text{-}Pr}$), 24.2 (s, 2C, $C_{CH_3i\text{-}Pr}$), 11.7 (s, 5C, C^{14}) ppm.

Preparation of [Cp*Hf(Ap_HTMA)Me_2]. Ap_HTMA-H (0.200 g, 0.884 mmol) and [Cp*$HfMe_3$] (0.141 g, 0.392 mmol) were dissolved in toluene (10 mL) and stirred overnight. All volatiles were removed under reduced pressure, and the residue was suspended in hexane (8 mL). The overlaying orange solution was filtrated, and the residue was extracted with hexane (4 × 10 mL). Removal of the solvent afforded **10** as a pale yellow, spectroscopically pure compound (0.261 g, 52%). Anal. Calcd for $C_{27}H_{38}HfN_2$ (570.25): C, 56.98; H, 6.73; N, 4.92. Found: C, 55.74; H, 7.05; N, 4.93. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.40 (d, ^3J = 5.2 Hz, 1H, H^1), 6.94 (s, 2H, H^{10}), 5.86 (d, ^3J = 5.4 Hz, 1H, H^2), 5.54 (s, 1H, H^5), 2.40 (s, 6H, H^9), 2.22 (s, 3H, H^{12}), 1.98 (s, 15H, H^{16}), 1.54 (s, 3H, H^4), 0.08 (s, 6H, H^{13}, H^{14}) ppm. ^{13}C NMR (400 MHz, C_6D_6, 298 K): δ = 168.5 (s, 1C, C^6), 153.2 (s, 1C, C^1), 143.1 (s, 1C, C^3), 143.0 (s, 1C, C^7), 133.9 (s, 2C, C^8), 133.7 (s, 1C, C^{11}), 129.7 (s, 2C, C^{10}), 119.0 (s, 5C, C^{15}), 111.7 (s, 1C, C^5), 105.2 (s, 1C, C^2), 51.8 (s, 1C, C^{13}), 51.8 (s, 1C, C^{14}), 21.5 (s, 1C, C^4), 20.9 (s, 1C, C^{12}), 19.1 (s, 2C, C^9), 11.6 (s, 5C, C^{16}) ppm.



Synthesis of the Catalyst Stock Solutions. Complexes **6–10** were prepared as described above. For catalytic ethylene conversion the intense yellow residues were dissolved in toluene (10 mL) and used without further purification.

Polymerization Studies: General Description of Polymerization Experiments. The catalytic ethylene polymerization reactions were performed in a 1 L stainless steel autoclave (Versoclave, Büchiglasuster) equipped with a mechanical stirrer in semibatch mode (ethylene was added by replenishing the flow to keep the pressure constant). The reactor was temperature- and pressure-controlled and equipped with separate toluene and catalyst/cocatalyst injection systems. During a polymerization run, the pressure, ethylene flow, inner and outer reactor temperature, and stirrer speed were monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 h at 120 °C prior to use. The reactor was then brought to the desired temperature, stirred at 600 rpm, and charged with 270 mL of toluene together with the activator *N,N,N*-trialkylammonium tetrakis(pentafluorophenyl)borate (2.2 μmol, 24.5 mg, 11% stock solution in Isopar) and the required amount of trialkylaluminum. After pressurization with ethylene to reach the desired total pressure, the

autoclave was equilibrated for 5 min. Subsequently [Cp*Hf(Ap_HDIP)Me_2] (2 mL, 0.001 M stock solution in toluene) together with toluene (18 mL) was injected to start the reaction. During the run the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by replenishing the flow. After the desired reaction time the reactor was vented and the residual aluminum alkyls were destroyed by addition of ethanol (100 mL). The precipitated polymeric product was collected, stirred for 30 min. in acidified ethanol, and rinsed with ethanol on a glass frit. The polymer was initially dried at 80 °C to a constant weight.

Supporting Information. Figures giving the molecular structures of **7** and **9** and CIF files and a table giving the parameters of the X-ray analysis of **6–8** and detailed information on the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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4.6 References

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4.7 Supporting Information

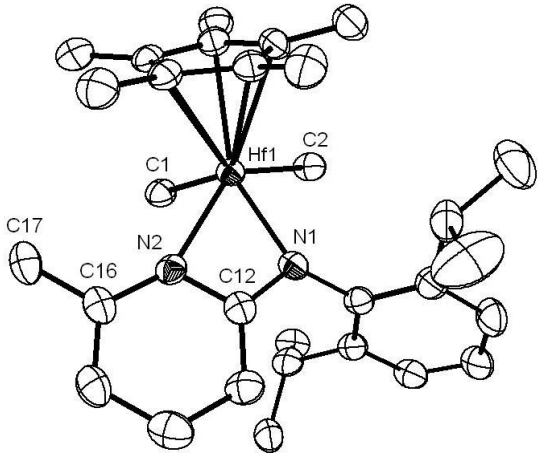

Figure S1. Molecular structure (40% thermal ellipsoids) of compound **7**. Hydrogen atoms have been removed for clarity. One independent molecule was found per asymmetric unit; selected bond lengths [Å] and angles [°]: Hf1-N2 2.347(4), Hf1-N1 2.188(4), N1-C12 1.358(6), N2-C12 1.362(6), Hf1-C1 2.212(5), Hf1-C2 2.226(5), C16-N2 1.356(6), C16-C17 1.491(7); Hf1-N1-C12 99.4(3), Hf1-N2-C12 92.1(3), N1-C12-N2 109.8(4), N1-Hf1-N2 58.63(14), C1-Hf1-C2 90.9(2), C12-N2-C16 120.0(4), N2-C16-C17 117.7(5).

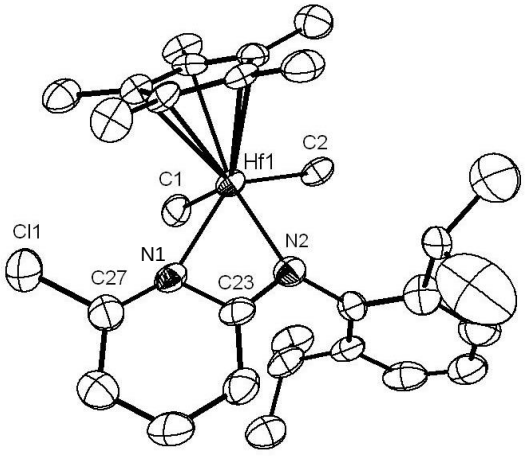

Figure S2. Molecular structure (40% thermal ellipsoids) of compound **9**. Hydrogen atoms have been removed for clarity. Two independent molecules were found per asymmetric unit; selected bond lengths [Å] and angles [°]: Hf1-N2 2.199(7), Hf1-N1 2.395(8), N1-C23 1.360(10), N2-C23 1.350(10), Hf1-C1 2.184(10), Hf1-C2 2.251(8), N1-C27 1.312(11), C27-Cl1 1.733(9); Hf1-N1-C23 90.6(5), Hf1-N2-C23 99.7(5), N1-C23-N2 111.4(8), N1-Hf1-N2 58.1(3), C1-Hf1-C2 93.2(3), N1-C27-Cl1 117.9(7).

Table S1. Parameters of the X-ray analysis of **6**, **7** and **9**.

Compound	**6**	**7**	**9**
Formula	$C_{29}H_{42}HfN_2$	$C_{30}H_{44}HfN_2$	$C_{29}H_{41}ClHfN_2$
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	10.8830(9)	8.6800(3)	10.9958(5)
b [Å]	10.9470(8)	22.7530(9)	15.6539(8)
c [Å]	12.2890(10)	14.6140(5)	17.5454(9)
α [°]	84.443(6)	90.00	95.571(4)
β [°]	86.082(7)	103.735(3)	103.256(4)
γ [°]	70.284(6)	90.00	99.838(4)
V [Å^3]	1370.77(19)	2803.67(18)	2867.0(2)
Z	2	4	4
Crystal size [mm^3]	0.52×0.48×0.32	0.22×0.14×0.10	0.24×0.14×0.13
$\varrho_{ber.}$ [g·cm^{-3}]	1.447	1.448	1.463
μ [mm^{-1}] (Mo-K$_\alpha$)	3.823	3.740	3.750
T [K]	133(2)	133(2)	133(2)
θ range [°]	1.67–25.73	1.69–25.70	1.67–25.76
Reflections unique	5162	5297	10810
Refl. Obs. [$I > 2\sigma(I)$]	4361	3496	5486
Parameters	289	298	609
wR_2 (all data)	0.070	0.056	0.081
R_1 value [$I > 2\sigma(I)$]	0.028	0.027	0.040
Largest diff. peak and hole [e·Å^{-3}]	1.560/-0.632	0.993/-0.669	1.241/-0.953

5 Flipping the Switch from Polymerization to Oligomerization with a Monoanionic η^1-Imidazolidiniminate as Ancillary π-Donor Ligand

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5.1 Abstract

Mixed η^2-aminopyridinato zirconium complexes of the type [ApLZr($CH_2Ph)_2$] (Ap = aminopyridinate and L = η^1-imidazolidiniminate or phenoxide) have been prepared from the monoanionic donor ligand and the corresponding mono(aminopyridinato) zirconium tribenzyl complex by toluene elimination. These compounds were characterized by spectroscopic methods, X-ray diffraction and elemental analysis. The different coordination modes of the benzyl moieties in solution and in the solid state were discussed. Furthermore, their behavior as catalyst precursors in ethylene oligomerization and polymerization was explored. The introduction of the additional η^1-guanidinato at the metal center transforms the catalytic properties of the mono(aminopyridinato) zirconium tribenzyl complexes from polymerization to oligomerization. Activation of the catalyst precursors with ammonium borate or MAO leads to highly efficient oligomerization catalysts which produce α-olefins in the range of C_4 to C_{30}. By introduction of a phenoxide ligand instead of the guanidinate this transformation failed and even ligand transfer occurred.

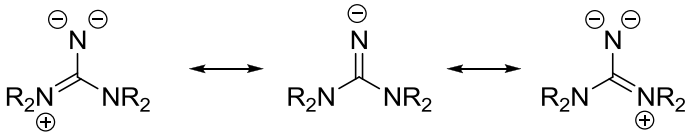
Keywords: Aminopyridinate ligands • Imidazolidiniminate • Zirconium • Oligomerization • α-Olefins

5.2 Introduction

Aminopyridinato ligand (Ap) stabilized complexes[1] have been used in a multiplicity of catalytic reactions.[2] There are many reasons for the use of aminopyridinate ligands as stabilizing or directing ligands in catalysis, for example, their relatively simple and high yield synthesis combined with easy modification of steric and electronic properties of the precursor aminopyridines.[3] In comparison to the

widely used cyclopentadienyl ligand, Ap ligands are promising alternatives with bigger steric demand[4] for better protection of the catalytic center in homogenous catalysis and especially in polymerization catalysis.[5]

Half-titanocenes containing imidazolidin-2-iminato ligands are known to exhibit high catalytic activities for ethylene polymerization.[6] Their success is first based on the ability of the Cp ligand to stabilize the transition metal and secondly on the unique ability of the imidazolidin-2-iminato ligand to act as a strong 2σ,4π-electron donor.[7] Imidazolidin-2-iminato ligands can be regarded as pseudo-isolobal to cyclopentadienyl ligands[8] but they occupy only one coordination site, while the Cp ligand needs three such sites. Moreover, the availability of a zwitterionic resonance structure of the imidazolidin-2-iminato ligands increases the negative charge on the nitrogen atom and therefore improves the π-donor capability (Scheme 1).



Scheme 1. Enhanced π-donation due to zwitterionic resonance contributors.

As a combination of the beneficial properties of Ap and imidazolidin-2-iminato ligands, we tried to substitute the stabilizing part, i.e., the Cp ligand by an Ap ligand whereas the imidazolidin-2-iminato ligand is kept.

We have already reported mono(aminopyridinato) zirconium tribenzyl complexes as effective polymerization catalysts.[9] Group 4 metal alkyls stabilized by other ligands together with aminopyridinates are unknown. Inspired by the high yield synthesis of the tribenzyl precursors, here we report on the straightforward synthesis and the structure of dibenzyl zirconium aminopyridinates additionally stabilized by imidazolidiniminate ligands. To the best of our knowledge this is the first use of aminopyridinato ligand stabilized catalyst precursors in an oligomerization process.

5.3 Results and Discussion

Concept Behind the Catalyst Design

On the one hand mono(aminopyridinato) zirconium tribenzyl complexes activated with ammonium borate give highly active ethylene polymerization catalysts. However, multimodal distribution of the resulting polymer suggests that the catalyst is rather ill defined. Application of this system to ethylene-propylene copolymerization gives rise to high regioselectivity including alternating ethylene-propylene units.[9] On the other hand a series of half-titanocenes containing 1,3-disubstituted imidazolidin-2-

iminato ligands show remarkable catalytic activity in syndiospecific styrene polymerization. These complexes are also active in ethylene homopolymerization as well as in efficient comonomer incorporation of 1-hexene and styrene in the presence of MAO.[6]

Combination of the stabilizing and protecting effect of the very bulky aminopyridinato ligand and the directing effect of the 1,3-disubstituted imidazolidin-2-iminato ligand should lead to promising catalyst precursors (Figure 1).

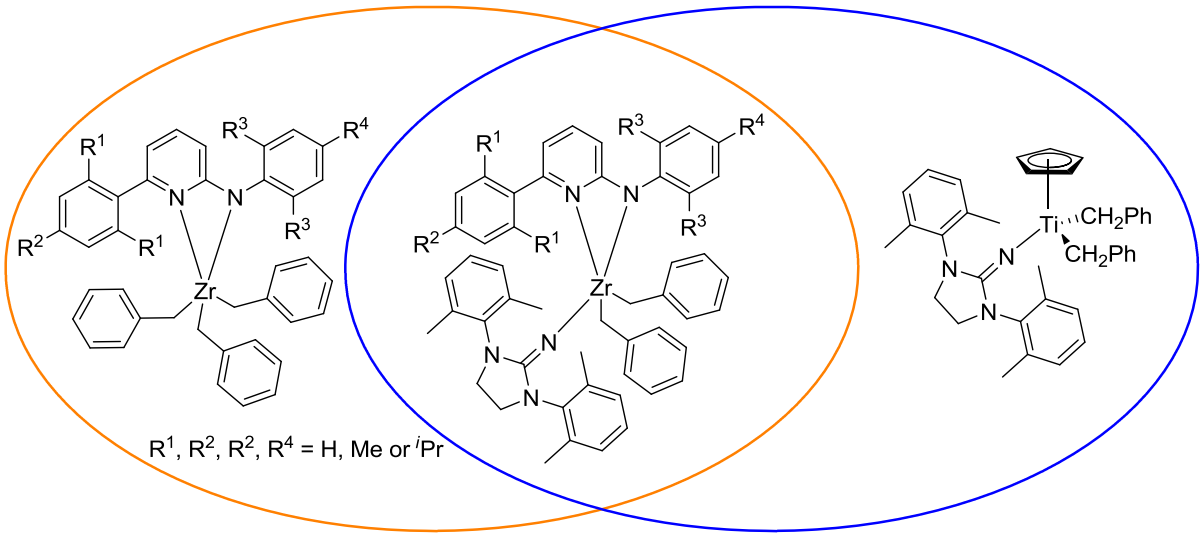
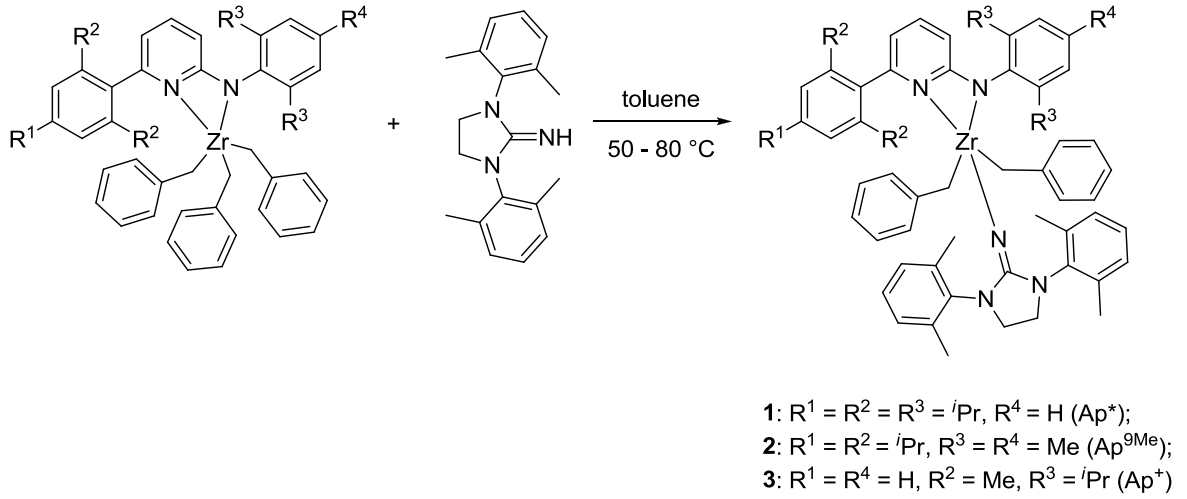


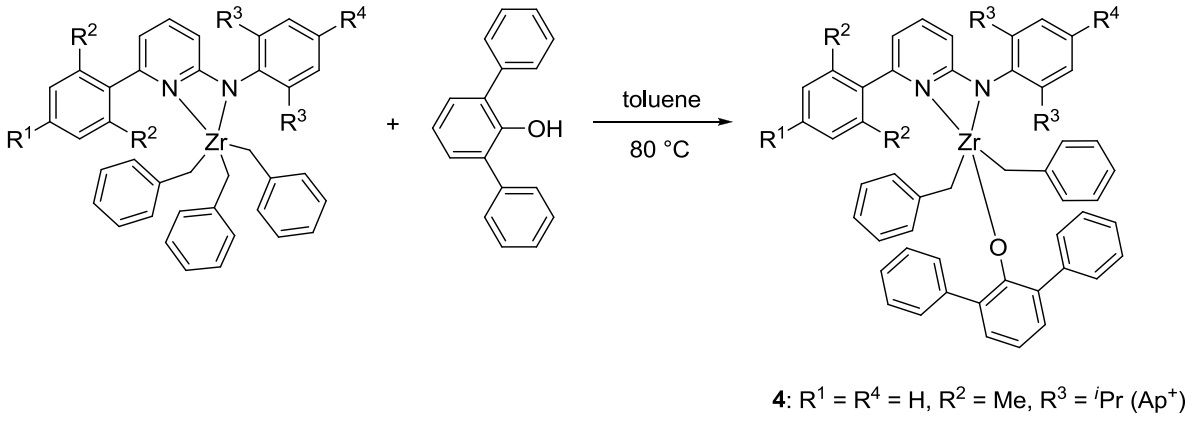
Figure 1. Formal combination of mono(aminopyridinato) zirconium tribenzyl complexes (left)[9] and half-titanocenes (right)[10] to yield new mixed dibenzyl zirconum species (middle).

Synthesis and Structure of the Mixed Aminopyridinate and Imidazolidiniminate Dibenzyl Zirconium Complexes

The mono(aminopyridinato) zirconium tribenzyl complexes were synthesized by alkane elimination[7] from $Zr(CH_2Ph)_4$ and the corresponding aminopyridine ligand, while the 1,3-diarylimidazolidiniminate [1,3-(2',6'-$Me_2C_6H_3)_2(CH_2N)_2C$=NH] was prepared from 1,2-dianilinoethane and cyanogen bromide in toluene according to literature procedures.[11]



Scheme 2. Synthesis of the mixed aminopyridinato/imidazolidin-2-iminato complexes **1**, **2** and **3**.



Scheme 3. Synthesis of the mixed aminopyridinato/phenoxido complex **4**.

Treatment of one equivalent of the neutral imidazolidinimine with the corresponding precursor [ApZr($CH_2Ph)_3$] in toluene at 50–80 °C leads to the dialkyl complexes [Ap*[1,3-(2',6'-$Me_2C_6H_3)_2(CH_2N)_2C$=N]Zr($CH_2Ph)_2$] **1**, [Ap^{9Me}[1,3-(2',6'- $Me_2C_6H_3)_2(CH_2N)_2C$=N]Zr($CH_2Ph)_2$] **2** and [Ap^+[1,3-(2',6'-$Me_2C_6H_3)_2(CH_2N)_2C$=N]Zr($CH_2Ph)_2$] **3**, respectively, owing to elimination of one equiv of toluene (Scheme 2). Using 2,6-diphenylphenol instead of the imidazolidinimine at a temperature of 80 °C yields [Ap^+(2,6-$Ph_2C_6H_3O$)Zr($CH_2Ph)_2$] **4** (Scheme 3). The resultant complexes were identified by their ^{1}H and ^{13}C NMR spectra and elemental analyses. Crystals suitable for X-ray analysis of **1**, **2** and **3** were grown by layering a saturated toluene solution with *n*-hexane while crystals of **4** were obtained by recrystallization from toluene. Selected bond distances and angles are summarized in Table 1.

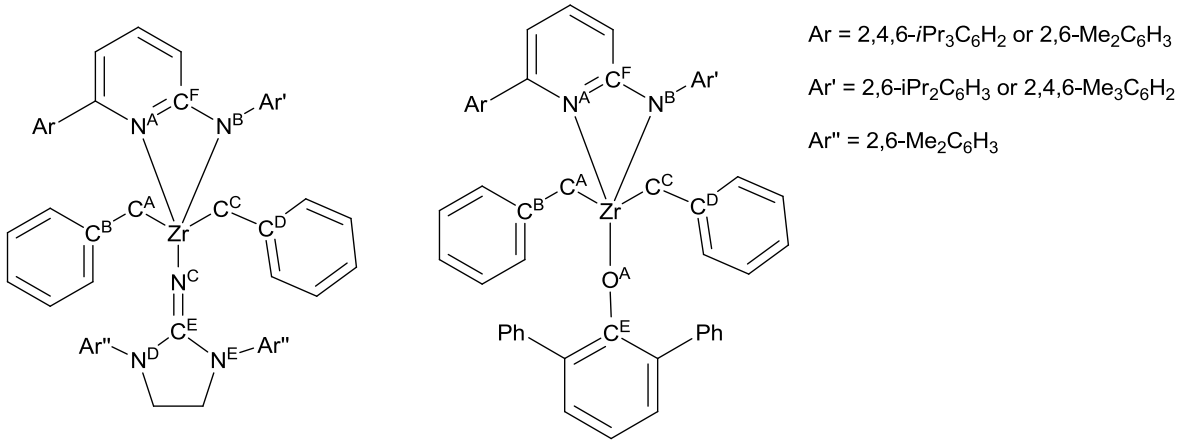


Figure 2. Labeling of the discussed crystal structures of complexes **1–4**.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1–4**.[a]

	1	**2**	**3**	**4**
C^A-Zr	2.268(5)	2.273(2)	2.283(3)	2. 2483(5)
C^B-Zr	3.039(64)	2.7444(2)	3.0077(31)	2.8419(7)
C^C-Zr	2.276(5)	2.269(1)	2.279(3)	2. 2778(4)
C^D-Zr	3.214(49)	3.1964(3)	3.178(24)	3.2128(5)
N^A-Zr	2.569(4)	2.477(2)	2.518(2)	2.4380(5)
N^B-Zr	2.116(4)	2.158(2)	2.135(2)	2.1279(3)
$N^C(O^A)$-Zr	1.956(4)	1.965(1)	1.969(2)	1.9478(4)
N^CO^A-C^E	1.309(6)	1.274(1)	1.292(3)	1.3873(3)
N^D-C^E	1.412(6)	1.383(1)	1.385(3)	-
N^E-C^E	1.388(6)	1.392(1)	1.372(3)	-
C^D-C^C-Zr	115.6(3)	115.4(4)	113.38(17)	115.088(10)
C^B-C^A-Zr	106.5(3)	91.5(4)	103.78(19)	97.177(11)
N^A-C^F-N^B	110.2(4)	111.8(5)	112.0(2)	111.137(14)
C^E-$N^C(O^A)$-Zr	170.7(4)	168.8(7)	169.6(2)	172.079(15)-
N^A-Zr-N^B	56.81(13)	57.7(3)	57.42(7)	59.107(7)

[a]Detailed crystallographic data, including CIF files for complexes **1**, **2**, **3** and **4**, are given in the Supporting Information.

The structures of **1** and **3** (Figure 3) show a strongly distorted trigonal-bipyramidal geometry around the metal center with the pyridine nitrogen atom and the imido or phenoxide ligand at the axial positions and an equatorial plane consisting of the two CH_2-groups of the benzyl moieties and the Ap ligand's amide nitrogen atom. The distortion can likely attributed to the strained η^2-coordination of the

aminopyridinate ligands [56.81(13)° for **1** and 57.42(7)° for **3**].[12] The angle N_{Py}-C-N_{amido} of 110.2(4)° for **1** and 112.0(2)° for **3** instead of the expected 120° verifies the strained bonding mode.[13] The difference between bond angles C^D-C^C-Zr [115.6(3)°] and C^B-C^A-Zr [106.5(3)] in **1** may be responsible for the different distances between Zr and C_{ipso} atoms [Zr-C^D, 3.214 (49) Å and Zr-C^B, 3.039 (64) Å]. This trend is also observed for complex **3**. The average Zr-CH_2 distance is 2.276 Å which is slightly shorter than the corresponding distances in the bis(aminopyridinato) zirconium dibenzyl complexes (2.287 Å).[14] The short distance C^E-N^C [1.309(6) Å] compared to C^E-N^D [1.412(6) Å] and C^E-N^E [1.388(6) Å] in **1** for the imidazolidiniminato ligand suggests extensive localization of the π character, which is also confirmed by the nearly linear conformation of Zr-N_{imido}-C_{imido} with an angle of 170.7(4)° and 169.6(2)° for complex **1** and **3**, respectively.

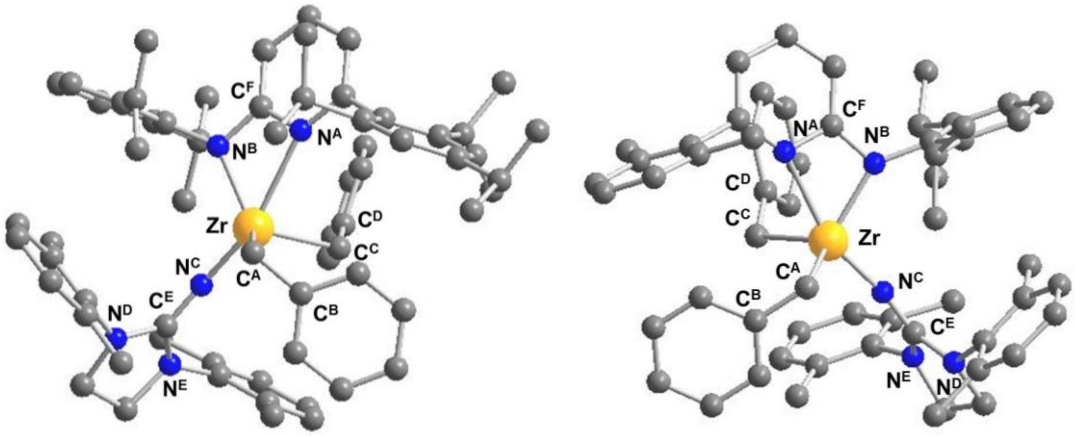


Figure 3. Molecular structure of complexes **1** (left) and **3** (right); hydrogen atoms and solvent molecules are omitted for clarity. Details are given in the Supporting Information.

Proton NMR spectra of complexes **1** and **3** showed two doublets appropriate for an AB spin system assigned to the benzylic methylene protons and a singlet assigned to the four equivalent methylene protons present on the imidazolidiniminate ligand backbone.

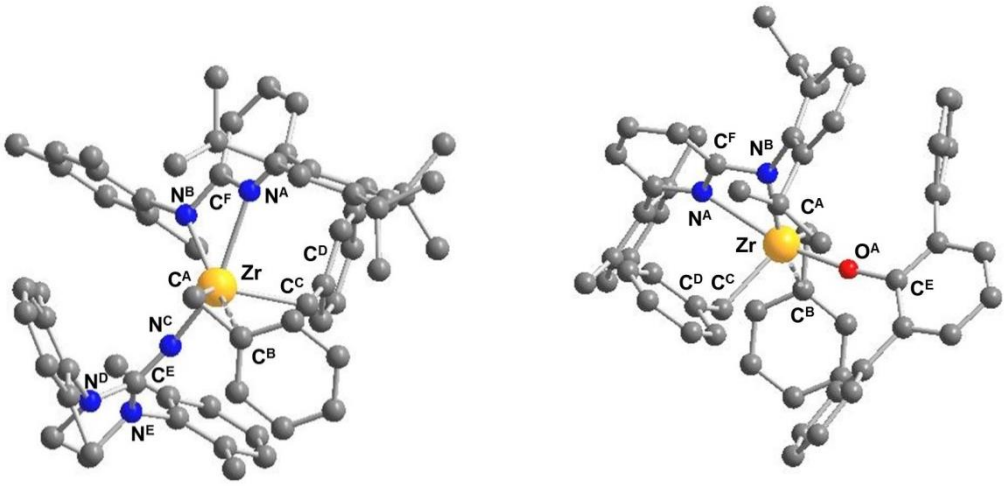


Figure 4. Molecular structure of complexes **2** (left) and **4** (right); hydrogen atoms and solvent molecules are omitted for clarity. Details are given in the Supporting Information.

The molecular structures of **2** and **4** are shown in Figure 4. The coordination pattern around the Zr atom is the same as was observed for **1** and **3,** however a difference is found in the coordination modes of the two benzyl ligands. In complexes **2** and **4** one of the benzyl ligands is bound to the metal in an η^1-manner [C^D-C^C-Zr amounts to 115.4(4)° for **2** and to 115.088(10)° for **4**] while the second one displays an acute angle Zr-C-C_{ipso} consistent with an η^2-coordination [C^B-C^A-Zr is 91.5(4)° for **2** and 97.177(11)° for **4**]. The distance between the metal and the *ipso*-carbon atom of the first benzyl [C^D-Zr] is 3.1964(3) Å for **2** and 3.2128(5) Å for **4** while a short distance of 2.7444(2) Å for **2** and 2.8419(7) Å for **4** observed for the latter [C^B-Zr] is consistent with a η^2-coordinated benzyl group. These angles as well as the η^1- or η^2-binding modes are quite sensitive to packing forces. However, in proton NMR spectra we observed two doublets for the benzylic methylene protons demonstrating their equivalency in solution.

Ethylene Oligomerization Using [Ap[1,3-(2',6'-$Me_2C_6H_3)_2(CH_2N)_2C$=N]Zr($CH_2Ph)_2$]–Borate Catalysts

The ethylene oligomerization results using **1–3** are summarized in Table 2–4. In contrast to their tribenzyl analogs (Table 2–4; entries 1, 6 and 11), complexes **1–3** are highly efficient oligomerization catalysts. Their catalyst performance has been explored in terms of temperature dependence and the cocatalyst used for the generation of the cationic species.

Table 2 shows the catalytic performance of catalyst precursor **1** after activation with ammonium borate ([R_2NMeH]-[$B(C_6F_5)_4$], R= $C_{16}H_{33}$-$C_{18}H_{37}$; entries 2–4) and $B(C_6F_5)_3$ (entry 5).

Table 2. Temperature and activator dependence of the ethylene oligomerization catalyzed by precursor **1**.[a]

Entry	Cat. [nmol]	Temp. [°C]	Yield [g]	Activity [kg·mol^{-1}·h^{-1}·bar^{-1}]	wt.-% C_4	wt.-% C_6	wt.-% > C_6	Purity C_6 fraction [% 1-hexene]
1[b]	2000	50	0.29	288	M_w: 105600 g/mol; PDI: 46 (monomodal)			
2[c]	200	30	4.88	48750	32	29	39 (C_8-C_{22})	> 99
3[c]	200	50	3.63	36250	23	27	50 (C_8-C_{24})	> 99
4[c]	200	70	1.30	13000	18	24	59 (C_8-C_{14})	> 99
5[d]	200	50	0.00	0	0	0	0	0

[a] Ethylene: 2 bar; activator: ammonium borate (1.1 eq); scavenger: TIBA (triisobutylaluminum; 100 μmol); 15 min; yield by ethylene flow. [b] Cat.: [Ap*Zr($CH_2Ph)_3$]. [c] Wt.-% and purity by GC and GCMS analysis. [d] Activator: tris(pentafluorophenyl)borane (1.1 eq).

Catalyst precursor **1** showed the highest catalytic activity of all tested complexes with about 49×10^3 kg·mol^{-1}·h^{-1}·bar^{-1} (entry 2). With increasing temperature activity decreased and the product distribution became smaller. This might be understandable because chain termination via β-H elimination is favored at higher temperatures. After activation of **1** with $B(C_6F_5)_3$ no ethylene conversion was observed.

Table 3 shows the catalytic performance of catalyst precursor **2** after activation with ammonium borate (entries 7–9) and $B(C_6F_5)_3$ (entry 10).

Table 3. Temperature and activator dependence of the ethylene oligomerization catalyzed by precursor **2**.[a]

Entry	Cat. [nmol]	Temp. [°C]	Yield [g]	Activity [kg·mol^{-1}·h^{-1}·bar^{-1}]	wt.-% C_4	wt.-% C_6	wt.-% > C_6	Purity C_6 fraction [% 1-hexene]
6[b]	2000	50	0.31	313	M_w: 416032 g/mol; PDI: 93 (bimodal)			
7[c]	200	30	1.99	19875	62	27	11 (C_8-C_{12})	> 99
8[c]	200	50	2.03	20250	45	31	24 (C_8-C_{18})	> 99
9[c]	200	70	0.98	9750	31	30	40 (C_8-C_{14})	> 99
10[d]	200	50	0.00	0	0	0	0	0

[a] Ethylene: 2 bar; activator: ammonium borate (1.1 eq); scavenger: TIBA (100 μmol); 15 min; yield by ethylene flow. [b] Cat.: [Ap^{9Me}Zr($CH_2Ph)_3$]. [c] Wt.-% and purity by GC and GCMS analysis. [d] Activator: tris(pentafluorophenyl)borane (1.1 eq).

Activation of catalyst precursor **2** with ammonium borate gave a highly active ethylene oligomerization system in contrast to the activation with borane. Increasing the temperature from 30 °C to 50 °C did not have a pronounced effect on the catalytic activity but leads to a notable shift of the product maximum from C_4 to higher oligomers. The oligomerization performance of catalyst precursor **2** showed a dropdown to nearly half of its catalytic activity by raising the temperature to 70 °C, whereas the product distribution between C_4, C_6 and higher oligomers is nearly balanced.

Besides regarding temperature and activator dependence, catalyst precursor **3** was also tested to figure out to which extent variation of ethylene pressure influences the oligomer product spectrum (Table 4).

Table 4. Temperature, activator, and pressure dependence of the ethylene oligomerization catalyzed by precursor **3**.[a]

Entry	Cat. [nmol]	Temp. [°C]	Yield [g]	Activity [kg·mol^{-1}·h^{-1}·bar^{-1}]	wt.-% C_4	wt.-% C_6	wt.-% > C_6	Purity C_6 fraction [% 1-hexene]
11[b]	2000	50	0.14	138	M_w: 242961 g/mol; PDI: 37 (bimodal)			
12[c]	200	30	2.41	24125	15	20	65 (C_8-C_{24})	> 99
13[c]	200	50	2.73	27250	16	20	64 (C_8-C_{24})	> 99
14[c]	200	70	3.55	35500	17	18	65 (C_8-C_{30})	> 99
15[d]	200	50	0.00	0	0	0	0	0
16[e]	200	50	0.33	3250	14	17	69 (C_8-C_{20})	> 99
17[f]	200	50	0.48	9500	17	21	62 (C_8-C_{22})	> 99
18[g]	200	50	2.65	13250	17	22	61 (C_8-C_{26})	> 99

[a] Ethylene: 2 bar; activator: ammonium borate (1.1 eq); scavenger: TIBA (100 μmol); 15 min; yield by ethylene flow. [b] Cat.: [Ap$^+$Zr(CH_2Ph)$_3$]. [c] Wt.-% and purity by GC and GCMS analysis. [d] Activator: tris(pentafluorophenyl)borane (1.1 eq). [e] Activator: d-MAO (1000 eq). [f] Ethylene: 1 bar. [g] Ethylene: 4 bar.

For the sterically less crowded system **3** the activity increased with increase in temperature, but interestingly the oligomer distribution nearly stays the same.

To get more insight into this catalytic behavior and to study different activation mechanisms of this catalyst system, we switched to methylaluminoxane (MAO) as the activator. Even MAO is able to abstract one of the benzyl groups and to generate a cationic catalyst species which oligomerizes ethylene without polymeric byproduct. However, the immense dropdown in activity may be due to the free trimethylaluminum (TMA). TMA is always present while using MAO as activator and therefore ligand transfer to aluminum can occur. The pressure experiments with 1 bar and 4 bar (entries 17 and

18) both show lower activities of the catalyst system but nearly the same product distribution as the run with 2 bar ethylene pressure (entry 13).

Ethylene Polymerization Using [Ap$^+$(2,6-Ph$_2$C$_6$H$_3$O)Zr(CH$_2$Ph)$_2$]–Borate Catalyst

GCMS analysis of the reaction mixture's soluble fraction after polymerization experiments with catalyst precursor **4** did not show any oligomeric product. Table 5 shows the catalytic performance of catalyst precursor **4** after activation with ammonium borate (entries 19–21).

Table 5. Temperature dependence of the ethylene polymerization catalyzed by precursor 4.[a]

Entry	Cat. [nmol]	Temp. [°C]	Yield [g]	Activity [$kg_{PE}\cdot mol^{-1}\cdot h^{-1}\cdot bar^{-1}$]	M_w [g/mol]	PDI
19	2000	30	traces	n.d.	n.d.	n.d.
20	2000	50	0.10	98	156525	21.2
21	2000	70	0.13	128	117274	40.1

[a] Cat.: [Ap$^+$(2,6-Ph$_2$C$_6$H$_3$O)Zr(CH$_2$Ph)$_2$]; ethylene: 2 bar; activator: ammonium borate (1.1 eq); scavenger: TIBA (100 µmol); 15 min; yield by ethylene-flow.

The catalyst system based on **4** showed low activities and high molecular weight polyethylene compared to its imidazolidiniminate analog. Activity increased with increasing temperature but the multimodal distributed PE indicates different active sites.

Comparison of the GPC spectra of entry 20 and entry 11 (polymerization run with [Ap$^+$Zr(CH$_2$Ph)$_2$]) shows an interesting concordance. Both the low molecular weight fraction and the high molecular weight fraction of the **4**/B(C$_6$F$_5$)$_4^-$ system are roughly in accord with the bimodal distribution of the [Ap$^+$Zr(CH$_2$Ph)$_3$]/ B(C$_6$F$_5$)$_4^-$ system (Figure 5).

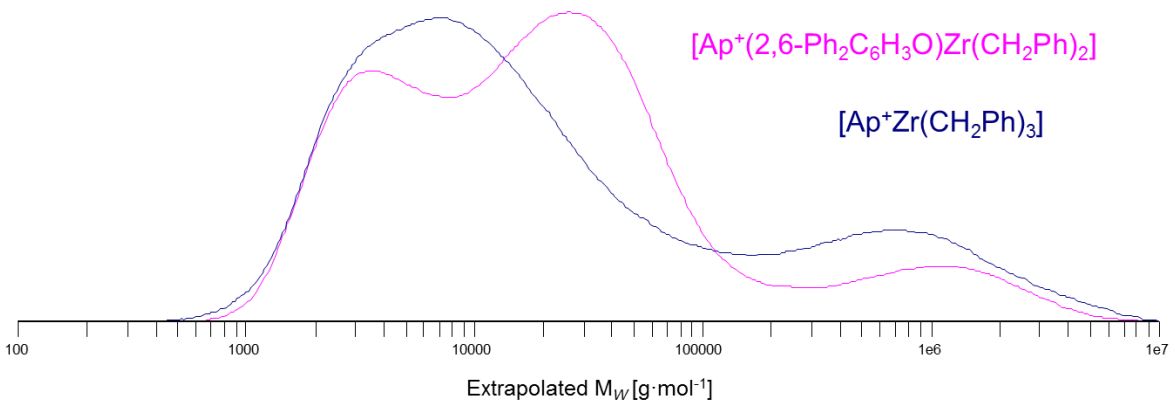


Figure 5. Molecular weight distribution (GPC) of the polymerization experiments 11 and 20.

This observation suggests that the polymeric product with a molecular weight of about 50,000 g·mol^{-1} resulted from catalyst precursor **4**. However, the additional anionic donor 2,6-$Ph_2C_6H_3O^-$ is lost during the polymerization process and the polymeric products with about 90,000 g·mol^{-1} and 1,000,000 g·mol^{-1} resulted from a cationic $[Ap^+Zr(CH_2Ph)_2]^+$ species. In case of the tribenzyl systems the same bimodal distributions were observed because the recoordination of the abstracted benzyl seems to interfere with the polymerization process or anion exchange occurs after double activation.[9]

5.4 Conclusion

Mixed aminopyridinato/imidazolidiniminato or phenoxido zirconium dibenzyl complexes can be prepared by toluene elimination in high yield if the aminopyridinato tribenzyl metal precursor is treated with one equivalent of the ligand. In solution all complexes show equivalent benzyl moieties whereas in complexes **2** and **4** one of the two benzylgroups is η^2-coordinated and the other is η^1-coordinated to the electron deficient metal center. In contrast to their tribenzyl analogs, the synthesized mixed aminopyridinato/imidazolidiniminato zirconium dibenzyl complexes were highly active in oligomerization of ethylene after activation with ammonium borate. Oligomerization studies revealed a very clean product spectrum of α-olefins in the range of C_4 to C_{30}. If activation of the dibenzyls occurs with MAO instead of ammonium borate, less oligomerization activity was observed. Activation with borane instead of ammonium borate leads to inactive catalyst species. The synthesized mixed aminopyridinato/phenoxido zirconium dibenzyl catalyst precursor only showed low polymerization activity without any oligomer production. On the basis of the GPC spectra it is obvious that the ancillary phenoxide ligand is not stable at the metal center during the polymerization process.
In summary, we changed an active polymerization system into a highly active oligomerization system by attaching an additional anionic donor ligand to the metal center.

Supporting Information Available

Detailed synthesis and characterization data of all ligands and complexes. Descriptions of the oligomerization and polymerization experiments.

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5.6 Supporting Information

General Procedure: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenktype glassware on a dual manifold Schlenk line or in a nitrogen or argon filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1 ppm O_2). Deuterated solvents were obtained from Cambridge Isotope Laboratories. Solvents and reagents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy, or sodium ketyl of benzophenone under nitrogen immediately before use.

Toluene for polymerization (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), a BASF R3-11 supported Cu oxyen 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 tetrakis(pentafluorophenyl)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 isoparaffin., DOW Chemicals) and triisobutylaluminum (TIBA, 1.0 M in toluene, Aldrich) were used as received.

Commercial benzylchloride, 2,6-diphenylphenol and zirconium(IV) chloride were used as received from Sigma-Aldrich. The ligand precursors 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-ylideneamine,[11] Ap*H,[4] $Ap^{9Me}H$,[15] Ap^+H[4] and the metal precursors tetrabenzyl zirconium[16], $[Ap^*ZrBz_3]$,[17] $[Ap^{9Me}ZrBz_3]$[17] and $[Ap^+ZrBz_3]$[17] were prepared according to published procedures.

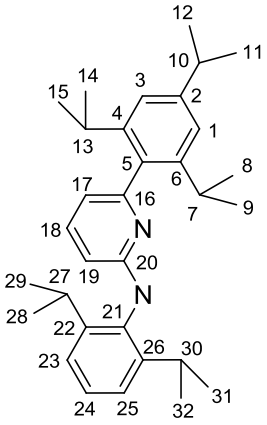
Gas Chromatography (GC): GC analysis was performed with an Agilent 6850 gas chromatograph equipped with an Agilent 19095J-323E capillary column (HP-5; 5% phenyl methyl siloxane; 30 m; film 1.5 μm, diameter 0.53 mm) and a flame ionization detector.

NMR Spectroscopy: NMR spectra were recorded on a Varian INOVA 300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 25 °C, were referenced internally using the residual solvent resonances; chemical shifts (δ) are reported in ppm.

Gel Permeation Chromatography (GPC): Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories Ltd. PL-GPC 220 high temperature chromatographic unit equipped with DP and RI detectors and two linear mixed bed columns (Olexis, 13 micron particle size). GPC analysis was performed 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 the solutions were run without filtration. The molecular weights of the samples were referenced to polyethylene (M_w = 520–3200000 g·mol^{-1}) and polystyrene (M_w = 580–2800000 g·mol^{-1}) standards. The reported values are the average of at least two independent determinations.

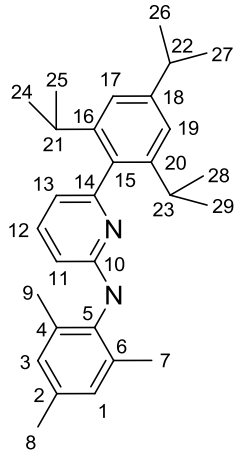
Elemental Analysis (C,H,N): Elemental analyses (C,H,N) were carried out with a Vario elementar EL III instrument.

Synthesis of [Ap*[1,3-(2',6'-$Me_2C_6H_3)_2(CH_2$ N)$_2$C=N]Zr($CH_2Ph)_2$] (1). [Ap*Zr($CH_2Ph)_3$] (300 mg, 0.366 mmol) in toluene (5 mL) was added to 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-ylideneamine



(107 mg, 0.366 mmol) in toluene (5 mL) at room temperature. The reaction mixture was stirred at 50 °C for 12 h. The mixture was evaporated to dryness and the product was washed with hexane (2 mL) to give the yellow product **1**. Suitable crystals for X-ray analysis were obtained by layering a saturated toluene solution with hexane. Yield 280 mg (76%). Elemental analysis for $C_{65}H_{79}N_5Zr$ (1021.58): calcd. C 76.42, H 7.79, N 6.86; found C 75.29, H 7.68, N 6.67. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.80 – 1.28 (m, 30H, $H^{8,9,11,12,14,15,28,29,31,32}$), 1.98 (s, 12H, CH_3), 1.99 – 2.10 (m, 4H, PhCH_2), 2.59 – 2.72 (m, 3H, $H^{7,10,13}$), 2.86 (s, 4H, NCH_2), 3.28 (sept, 2H, $J_{H,H}$ = 6.7 Hz, $H^{27,30}$), 5.50 (dd, 1H, J_{HH} = 9.7 Hz, H^{19}), 6.04 (d, 4H, J_{HH} = 8.7 Hz, o-$C_5H_5CH_2$), 6.38 (dd, 1H, J_{HH} = 8.3 Hz, H^{17}), 6.76 – 7.15 (m, 18H, $H^{1,3,18,23,24,25}$, p-$C_6H_5CH_2$, m-$C_6H_5CH_2$, C_6H_3) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 18.1 (s, 4C, CH_3), 22.9 (s, 2C, CH_3), 23.7 (s, 2C, CH_3), 24.0 (s, 2C, CH_3), 25.5 (s, 2C, CH_3), 26.6 (s, 2C, CH_3), 28.4 (s, 2C, *C*H), 30.8 (s, 2C, *C*H), 34.7 (s, 1C, *C*H), 44.9 (s, 2C, CH_2), 64.3 (s, 2C, PhCH_2), 107.1 (s, 1C, *C*H), 115.2 (s, 1C, *C*H), 119.8 (s, 1C, Ph), 121.3 (s, 1C, Ph), 125.5 (s, 1C, *C*), 127.6 (s, 2C, *C*H), 128.1 (s, 4C, Ph), 128.3 (s, 4C, Ph), 128.9 (s, 2C, *C*H), 129.2 (s, 2C, *C*H), 129.9 (s, 2C, *C*), 135.6 (s, 1C, *C*), 137.5 (s, 6C, C_6H_3), 138.3 (s, 2C, N*C*), 139.6 (s, 1C, *C*), 144.0 (s, 1C, *C*), 145.6 (s, 2C, *C*), 146.7 (s, 2C, *C*), 147.2 (s, 1C, *C*), 147.6 (s, 2C, *C*), 149.8 (s, 1C, *C*), 157.4 (s, 1C, *C*), 168.3 (s, 1C, *C*N) ppm.

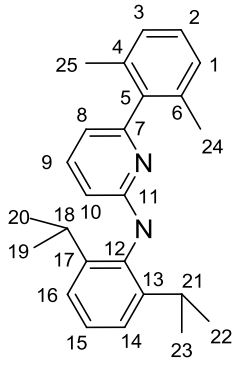
Synthesis of [Ap^{9Me}[1,3-(2',6'-$Me_2C_6H_3)_2(CH_2$ N)$_2$C=N]Zr($CH_2Ph)_2$] (2). Toluene (30 mL) was added to a mixture of [Ap^{9Me}Zr($CH_2Ph)_3$] (300 mg, 0.39 mmol) and 1,3-bis(2,6-dimethyl-



phenyl)imidazolidin-2-ylideneamine (113 mg, 0.39 mmol) at room temperature. The resulting solution was stirred for 3 h at 80 °C. The mixture was evaporated to dryness and the resulting residue was washed with hexane (2 mL) affording **2** as a yellow solid. X-ray quality crystals were obtained by adding a few drops of *n*-hexane to a concentrated toluene solution at room temperature. Yield 310 mg (82%). Elemental analysis for $C_{62}H_{73}N_5Zr$ (979.50): calcd. C 76.02, H 7.51, N 7.15; found C 76.53, H 7.79, N 6.69. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.07 (d, 6H, J_{HH} = 7.4 Hz, $H^{24,25}$), 1.16 (d, J_{HH} = 7.7 Hz, $H^{26,27}$), 1.25 (d, 6H, J_{HH} = 7.4 Hz, $H^{28,29}$), 1.51 (d, 2H, J_{HH} = 7.8 Hz, PhCH_2), 1.60 (s, 6H, $H^{7,9}$), 1.67 (d, 2H, J_{HH} =

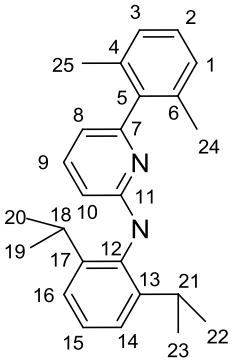
7.9 Hz, PhCH_2), 2.01 (s, 12H, CH_3), 2.20 (s, 3H, H[8]), 2.75 (sept, 1H, J_{HH} = 6.8 Hz, H[22]), 2.90 (s, 4H, NCH_2), 3.15 (sept, 2H, J_{HH} = 6.8 Hz, H[21,23]), 5.35 (d, 1H, J_{HH} = 9.3 Hz, H[11]), 6.00 (d, 4H, J_{HH} = 8.3 Hz, o-$C_6H_5CH_2$), 6.27 (d, 1H, J_{HH} = 8.0 Hz, H[13]), 6.70 – 7.16 (m, 17H, H[1,3,12,17,19], m-$C_6H_5CH_2$, p-$C_6H_5CH_2$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 18.3 (s, 4C, *C*H_3), 19.0 (s, 2C, *C*H_3), 21.2 (s, 1C, *C*H_3), 22.6 (s, 2C, *C*H_3), 24.5 (s, 2C, *C*H_3), 26.6 (s, 2C, *C*H_3), 31.0 (s, 2C, *C*H), 35.0 (s, 1C, *C*H), 45.2 (s, 2C, N*C*H_2), 63.1 (s, 2C, Ph*C*H_2), 104.9 (s, 1C, *C*H), 115.1 (s, 1C, *C*H), 120.7 (s, 1C, Ph), 121.4 (s, 1C, Ph), 125.7 (s, 1C, *C*), 127.7 (s, 2C, *C*H), 128.1 (s, 4C, Ph), 128.4 (s, 4C, Ph), 129.0 (s, 2C, *C*H), 129.3 (s, 2C, C), 129.4 (s, 1C, *C*H), 133.3 (s, 1C, *C*), 134.4 (s, 2C, *C*), 136.1 (s, 1C, *C*), 137.9 (s, 6C, C_6H_3), 138.0 (s, 2C, N*C*), 140.1 (s, 1C, *C*), 144.6 (s, 1C, *C*), 145.6 (s, 1C, *C*), 146.0 (s, 2C, *C*), 147.2 (s, 2C, *C*), 149.9 (s, 1C, *C*), 157.1 (s, 1C, *C*), 167.7 (s, 1C, *C*N) ppm.

Synthesis of [Ap$^+$[1,3-(2',6'-$Me_2C_6H_3)_2$(CH_2 N)$_2$C=N]Zr($CH_2Ph)_2$] (3). To a toluene solution (7 mL) containing [Ap$^+$Zr($CH_2Ph)_3$] (202 mg, 0.28 mmol) was added 1,3-bis(2,6-dimethyl-phenyl)imidazolidin-2-ylideneamine (82 mg, 0.28 mmol) in toluene (7 mL) at room temperature. The reaction mixture was stirred at 50 °C for 12 h. The mixture was evaporated to dryness and the product was washed with hexane (2 mL) to give the yellow product **3**. Suitable crystals for X-ray analysis were obtained by layering a saturated toluene solution with hexane. Yield 241 mg (93%). Elemental analysis for $C_{58}H_{65}N_5Zr$ (923.39): calcd. C 74.44, H 7.10, N 7.58; found C 75.35, H 6,83, N 7.57. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.91 (d, 6H, J_{HH} = 7.4 Hz, H[22,23]), 1.00 (d, 6H, J_{HH} = 7.4 Hz, H[19,20]), 2.05 (s, 12H, CH_3), 2.08 (d, 2H, J_{HH} = 10.6 Hz, PhCH_2), 2.21 (d, 2H, J_{HH} = 10.6 Hz, PhCH_2), 2.29 (s, 6H, H[24,25]), 2.72 (sept, 2H, J_{HH} = 6.8 Hz, H[18,21]), 2.93 (s, 4H, NCH_2), 5.51 (d, 1H, J_{HH} = 9.1 Hz, H[10]), 6.09 (d, 1H, J_{HH} = 8.1 Hz, H[8]), 6.19 (d, 4H, J_{HH} = 8.4 Hz, o-$C_6H_5CH_2$), 6.83 – 7.20 (m, 19H, H[1,2,3,9,14,15,16], C_6H_3, p-$C_6H_5CH_2$, m-$C_6H_5CH_2$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 18.3 (s, 4C, *C*H_3), 20.7 (s, 2C, *C*H_3), 24.8 (s, 2C, *C*H_3), 25.2 (s, 2C, *C*H_3), 28.3 (s, 2C, *C*H), 45.7 (s, 2C, *C*H_2), 65.9 (s, 2C, *C*H_2), 106.5 (s, 1C, *C*H), 113.3 (s, 1C, *C*H), 120.5 (s, 1C, *C*H), 124.2 (s, 1C, *C*H), 125.5 (s, 1C, *C*), 127.4 (s, 2C, *C*H), 128.1 (s, 3C, *C*H), 128.3 (s, 4C, *C*H), 128.5 (s, 4C, *C*H), 129.0 (s, 2C, *C*H), 129.5 (s, 2C, *C*), 134.8 (s, 1C, *C*), 136.7 (s, 2C, *C*), 137.8 (s, 6C, C_6H_3), 138.2 (s, 2C, N*C*), 140.8 (s, 1C, *C*), 143.0 (s, 1C, *C*), 145.0 (s, 2C, *C*), 146.7 (s, 2C, *C*), 149.8 (s, 1C, *C*), 156.8 (s, 1C, *C*), 172.9 (s, 1C, *C*N) ppm.



Synthesis of [Ap$^+$(2,6-$Ph_2C_6H_3O$)Zr($CH_2Ph)_2$] (4). Toluene (10 mL) was added to [Ap$^+$Zr($CH_2Ph)_3$] (100 mg, 0.138 mmol) and 2,6-diphenylphenol (34 mg, 0.138 mmol) at room temperature. The reaction mixture was stirred at 80 °C for 12 h. The mixture was evaporated to dryness and the product was washed with hexane (5 mL) affording **4** as a light yellow, spectroscopically pure compound. Suitable

crystals for X-ray analysis were obtained by refluxing a saturated toluene solution for 15 min. and subsequent cooling the solution to room temperature. Yield 114 mg (94%). Elemental analysis for $C_{57}H_{56}N_2OZr$ (876.29): calcd. C 78.13, H 6.44, N 3.20; found C 77.85, H 6.57, N 3.13. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.85 (d, 3H, J_{HH} = 7.5 Hz, H^{23}), 1.00 (d, 3H, J_{HH} = 7.6 Hz, H^{22}), 1.14 (dd, 6H, J_{HH} = 7.5, 7.4 Hz, $H^{19,20}$), 1.95 – 2.03 (m, 10H, $H^{24,25}$,PhCH_2), 3.22 (sept, 1H, J_{HH} = 7.1 Hz, H^{21}), 3.55 (sept, 1H, J_{HH} = 6.9 Hz, H^{18}), 5.63 (d, 1H, J_{HH} = 8.0 Hz, H^{10}), 6.16 (d, 1H, J_{HH} = 8.7 Hz, H^8), 6.34 (d, 4H, J_{HH} = 10.8 Hz, o-$C_6H_5CH_2$), 6.67 (t, 2H, J_{HH} = 7.3 Hz, p-$C_6H_5CH_2$), 6.75 – 7.11 (m, 24H, $H^{1,2,3,9,14,15,16}$, m-$C_6H_5CH_2$, $Ph_2C_6H_3$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 19.9 (s, 2C, CH_3), 23.9 (s, 2C, CH_3), 25.4 (s, 2C, CH_3), 28.9 (s, 2C, *C*H), 80.1 (s, 2C, CH_2), 105.6 (s, 1C, *C*H), 114.5 (s, 1C, *C*H), 121.6 (s, 1C, *C*H), 122.2 (s, 1C, *C*H), 124.1 (s, 1C, *C*H), 124.4 (s, 2C, *C*H), 124.6 (s, 1C, *C*), 127.3 (s, 1C, *C*), 127.7 (s, 3C, *C*H), 128.1 (s, 4C, *C*H), 128.2 (s, 2C, *C*H), 128.4 (s, 4C, *C*H), 128.8 (s, 2C, *C*H), 128.9 (s, 4C, *C*H), 129.8 (s, 4C, *C*H), 130.2 (s, 2C, *C*H), 132.7 (s, 2C, *C*), 135.8 (s, 1C, *C*), 137.7 (s, 1C, *C*), 139.8 (s, 2C, *C*), 142.9 (s, 1C, *C*), 143.1 (s, 1C, *C*), 144.7 (s, 1C, *C*), 147.9 (s, 1C, *C*), 156.1 (s, 1C, *C*), 160.4 (s, 1C, *C*), 172.7 (s, 1C, *C*) ppm.



Synthesis of the Catalyst Stock Solutions: The complexes **1–4** were prepared as described above. For catalytic ethylene conversion the acute yellow residue was dissolved in toluene (10 mL) and used without further purification.

Oligomerization of Ethylene: The catalytic ethylene oligomerization reactions were performed in a 250 mL glass autoclave (Büchi) equipped with a mechanical stirrer in semibatch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature- and pressure-controlled and equipped with separated toluene, catalyst and cocatalyst injection systems. During a oligomerization run, the pressure, the ethylene flow, the inner and outer reactor temperature and the stirrer speed were monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 h at 80 °C prior to use. The reactor was then brought to the desired temperature, stirred at 1000 rpm and charged with 150 mL of toluene together with the activator *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)borate (2.2 nmol, 2.45 mg, 11% stock solution in isoparaffin), the required amount of TIBA (triisobutylaluminum, 0.1 mL of a 1.0 M solution) (Zr/Al = 1:500) and 1 g cumene was added as an internal standard, unless mentioned different in the text. After pressurizing with ethylene to reach a total pressure of 1, 2 or 4 bar, the autoclave was equilibrated for 5 min. Subsequently, 0.1 mL of a 0.002 M catalyst stock solution in toluene was injected to start the reaction. During the run, the ethylene pressure was kept constant to within 0.1 bar of the initial

pressure by replenishing the gas flow. After a 15 min. reaction time, the reactor was cooled down to 0 °C, vented, and the solution was then analyzed by GC to determinate the activity and the product distribution.

Polymerization of Ethylene: The polymerization experiments were performed as described above for oligomerization runs. After a 15 min. reaction time, the reactor was vented and the polymerization process was immediately stopped by addition of 100 mL of ethanol. The polymeric product was collected, stirred for 30 min. in acidified ethanol and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and subsequently in vacuo at 80 °C.

Table 6. Crystal data and collection parameters of **1–4**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{137}H_{166}N_{10}Zr_2$	$C_{65}H_{78}N_5O_{0.75}Zr$	$C_{58}H_{65}N_5Zr$	$C_{57}H_{56}N_2OZr$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	$P2_1/c$	$P2_1/n$	$P2_1/n$
a [Å]	39.7250(12)	13.5850(1)	20.3060(8)	11.383(2)
b [Å]	17.2110(10)	15.0030(12)	11.5250(5)	25.624(6)
c [Å]	18.7540(11)	28.688(2)	21.2750(9)	15.794(4)
α [°]	90.00	90.00	90.00	90.00
β [°]	109.235(4)	101.604(6)	104.797(3)	94.315(3)
γ [°]	90.00	90.00	90.00	90.00
V [Å^3]	12106.4(11)	5727.6(8)	4813.8(3)	4593.7(18)
Z	4	4	4	4
Crystal size [mm^3]	0.73×0.49×0.41	0.14×0.08×0.08	0.51×0.23×0.21	0.33×0.28×0.09
$\varrho_{calcd.}$ [g·cm^{-3}]	1.171	1.197	1.274	1.267
μ [mm^{-1}] (Mo-K$_\alpha$)	0.225	0.237	0.272	2.81
T [K]	133(2)	133(2)	133(2)	100(1)
θ range [°]	1.09–24.84	1.45–25.77	1.24–24.65	2.59–23.38
Reflections unique	10130	10391	8089	28698

Refl. Obs. [$I > 2\sigma(I)$]	4405	4986	5942	7260
Parameters	692	658	587	556
wR_2 (all data)	0.1017	0.1527	0.0871	0.1589
R_1 value [$I > 2\sigma(I)$]	0.0557	0.0681	0.0393	0.0586
Largest diff. peak and hole [e·Å^{-3}]	0.449/-0.316	0.888/-0.588	0.619/-0.550	0.81/-0.85

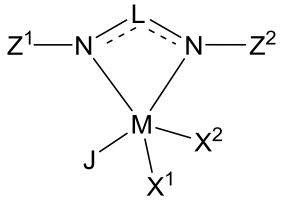
Crystallographic Analysis: X-ray crystal structure analyses were performed with a STOE-IPDS II instrument equipped with an Oxford Cryostream low-temperature unit and a Bruker SMART APEX CCD diffractometer (platform with full three-circle goniometer; $\lambda(MoK_\alpha)$ = 0.71073 Å). Structure solution and refinement were accomplished using SIR97,[18] SHELXL-97[19] and WinGX.[20] Details of the X-ray crystal structure analyses are listed in Table 6.

5.7 Patent Application 'Complexes for the Catalytic Oligomerization of Olefins'

Isabelle Haas, Winfried P. Kretschmer, and Rhett Kempe

EP 13158550, **2013**. (Patent Application)
Applicant: Universität Bayreuth
BayPat Ref.: B72249 EP
Vossius & Partner Ref.: W1086 EP

Abstract
The invention concerns transition metal complexes of the formula (I) which provide active and selective catalysts for the oligomerization of olefins, in particular ethylene, as well as methods for the oligomerization of olefins using the transition metal complexes.



(I)

Complexes for the Catalytic Oligomerization of Olefins

The invention relates to the oligomerization of olefins, in particular the oligomerization of ethylene, and to metal complexes which are able to provide catalyst compositions which efficiently and selectively catalyse the oligomerization.

5.8 Technical Background

There is an increasing demand for linear α-olefins (LAO's), in particular for olefins having 4 to 10 carbon atoms (C_4-C_{10} range). The high demand for LAO's is based on their broad spectrum of applications as additives or starting materials in other chemical processes. In addition, linear α-olefins are found as endproducts in various applications. For example, the light fractions 1-butene, 1-hexene and 1-octene are used as comonomers in the rapidly growing polymer market, in particular for the production of LLDPE (Linear Low Density Polyethylene). The middle fractions, such as 1-decene, 1-

dodecene and 1-tetradecene are raw materials for synthetic oils, detergents and shampoos. Heavy fractions can be used as additives for lubricating oils, tensides, oil field chemicals, and as waxes.
Alpha-olefins can be prepared via Fischer-Tropsch-Synthesis. Here, either the Coal-to-Liquid-process (CtL-process) or the Gas-to-Liquid-process (GtL-process) can be used. In the CtL-process, the coal is first reacted at very high temperatures (above 1000 °C) with water vapour and air or oxygen to form synthesis gas which, subsequent to the separation of nitrogen oxides and sulphur dioxide, is reacted via heterogeneous catalysis to form hydrocarbons including α-olefins and water. In the GtL-process, natural gas is reacted via addition of oxygen and water vapour to form synthesis gas, and the latter is transformed into hydrocarbons in a Fischer-Tropsch-Synthesis. Both processes have the disadvantage that, besides the desired α-olefins, a broad variety of products (paraffins and alcohols) is produced. This means that the pure α-olefins become only accessible after elaborate purification processes (e.g. *DE* 10022466 A1).

Other industrial-scale procedures for the preparation of α-olefins are the cracking of paraffins, the dehydration of paraffins and the dehydrogenisation of alcohols, or chain growth reactions including the oligomerization of ethylene (W. Keim, A. Behr, G. Schmitt, Grundlagen der Industriellen Chemie – Technische Produkte und Prozesse, 1. Auflage; Otto Salle Verlag GmbH und Co.: Frankfurt am Main, Germany, **1986**; pp. 126 – 150). Since ethylene represents an easily accessible raw material source, the first types of reactions play hardly any role for the industrial production today. In addition, the production of α-olefins via oligomerization of ethylene provides exclusively olefins with an even number of C-atoms which have the highest value for commercial applications (cf. J. Skupinska, *Chem. Rev.* **1991***, 91,* 613–648; G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1204). Some of the most important industrially used production processes for LAO's which are based on the oligomerization of ethylene are the following (A. Forestière, H. Olivier-Bourbigou, L. Saussine, *Oil Gas Sci. Technol.* **2009**, *64*, 649–667):

- the Shell Higher-Olefin-Process (SHOP; cf. W. Keim, *Angew. Chem. Int. Ed. Engl.* **1990***, 29,* 235–244; D. Vogt, Oligomerization of Ethylen to Higher Linear α-Olefins, in *Applied Homogeneous Catalysis with Organometallic Compounds*; B. Cornils, W. A. Hermann; VCH: New York, **1996**; Vol. 1, pp. 245–258; G. R. Lappin, J. D. Sauer, *Alphaolefins Applications Handbook*; Marcel Decker Inc.: Berkeley, CA, **1989**) using a nickel complex;

- the α-Sablin-process (*European Chemical News*, 5–11 November **2001**, p. 27; P. M. Fritz, H. V. Boelt, *Process Worldwide* **2005**, *8*, 26–28; P. M. Fritz, H. V. Boelt, *Linde Technology* **2004**, *2*, 38–45) which uses a

zirconia salt as a precatalyst;

- the Chevron-Phillips-Gulf-process and the INEOS-ethyl-process (D. Vogt, Oligomerization of Ethylen to Higher Linear α-Olefins, in *Applied Homogeneous Catalysis with Organometallic Compounds*; B. Cornils, W. A. Hermann; VCH: New York, **1996**; Vol. 1, pp. 245–258; G. R. Lappin, J. D. Sauer, *Alphaolefins Applications Handbook*; Marcel Decker Inc.: Berkeley, CA, **1989**; *Alpha Olefins* (06/07-5), PERP Report, Nexant ChemSystems, **2008**) which rely on the aluminum alkyl mediated oligomerization of ethylene.

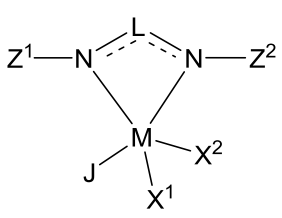
In addition to the above processes, which yield more or less broad distribution of α-olefins having different chain lengths, there are processes which selectively produce a single α-olefin in high purity. They include the Chevron-Phillips trimerisation process for the production of 1-hexene (cf. Sami Matar, Lewis F. Hatch, *Chemistry of Petrochemical Processes,* Gulf Publishing Company, **2000**, 2nd Edition, p. 209sqq.), the Sasol tri- and tetramerisation process yielding 1-hexene and 1-octene (e.g. *US* 8,076,523 B2) and the Axens/Sabic Alphabutol-process yielding 1-butene (A. Mortreux, F. Petit, *Industrial applications of homogeneous catalysis,* Kluwer, Dordrecht, **1988**, p. 190).

Further approaches for complex catalyzed oligomerization reactions to form α-olefins are disclosed in *EP* 1 362 837 A1, *EP* 2 070 593 A1, *US* 2010/0286349 A1 or *WO* 2012/080588 A1.

However, a need remains for metal complexes which provide highly active and thus efficient catalyst system which lead to the selective production of α-olefins at mild reaction conditions and with a high yield.

5.9 Summary of the Invention

The present invention provides complexes of the following formula (I), as well as catalyst systems using these complexes:



(I)

wherein

M is a metal selected from Zr and Hf;

X^1 and X^2 are independently selected from Cl, Br, I, F, H, alkyl, -alkyl-O-alkyl, -alkyl-O-aryl, alkoxy, aryloxy, aralkyl, -alkyl-$SiR^aR^bR^c$ and NR^1R^2, wherein any alkyl group is optionally substituted by one or more substituents selected from OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and $N(C1\text{-}8\ alkyl)_2$, and any aryl group is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and $N(C1\text{-}8\ alkyl)_2$;

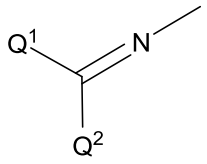
L is selected from CZ^3, N, and PR^3R^4;

Z^1 and Z^2 are independently selected from alkyl, cycloalkyl, heterocycloalkyl, alkenyl, aryl, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl, wherein any alkyl group, alone or as part of another group, and any alkenyl group is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and any aryl group, alone or as part of another group, and any heteroaryl group is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br, and $N(C1\text{-}8\ alkyl)_2$;

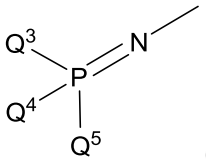
Z^3 is selected from H, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, alkoxy, aryl, aryloxy, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl, F, Cl, Br, NR^1R^2, and PR^3R^4, wherein any alkyl group, alone or as part of another group, and any alkenyl group is optionally substituted by one or more substituents selected from F, Cl, Br, and $N(C1\text{-}8\ alkyl)_2$ and wherein any aryl group, alone or as part of another group, and any heteroaryl group is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br, NH_2 and $N(C1\text{-}8\ alkyl)_2$;

or any suitable groups Z^1 and Z^3 or Z^2 and Z^3 as defined above may be linked to form an optionally substituted five- to seven-membered heterocyclic ring incorporating the nitrogen atom to which Z^1 is attached or the nitrogen atom to which Z^2 is attached;

J is selected from a ligand of the formula (II) or (III):



(II)



(III),

wherein

Q^1 to Q^5 are independently selected from alkyl, cycloalkyl, heterocycloalkyl, alkenyl, alkoxy, aryl, aryloxy, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl and NR^5R^6, wherein any alkyl group, alone or as part of another group, and any alkenyl group is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and wherein any aryl group , alone or as part of another

group, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$;

or any suitable groups Q^1 and Q^2 as defined above may be linked to form a five- to seven-membered, carbocyclic or heterocyclic, saturated or unsaturated ring together with the carbon atom to which they are attached, or any suitable groups Q^3 and Q^4 as defined above or Q^4 and Q^5 as defined above may be linked to form a five- to seven-membered, heterocyclic, saturated or unsaturated ring together with the P-atom to which they are attached;

R^a, R^b and R^c are independently selected from alkyl and aryl; and

R^1, R^2, R^3, R^4, R^5 and R^6 are independently selected from H, alkyl, cycloalkyl, alkenyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$;

or any suitable groups R^1 and R^2 as defined above, R^3 and R^4 as defined above or R^5 and R^6 as defined above may be linked to form an optionally substituted five or six-membered heterocyclic ring including the N or P atom to which they are attached; or, where Q^1 and Q^2, Q^3 and Q^4 or Q^4 and Q^5 are NR^5R^6, two groups R^5 or two groups R^6 as defined above may be linked to form an optionally substituted saturated or unsaturated heterocycle including the two N atoms of the groups NR^5R^6;

or one of Q^1 to Q^5 as defined above may be linked with one of Z^1 or Z^2 as defined above to form a metallacycle including M.

In addition, the invention relates to processes for the oligomerization of olefins, in particular of ethylene, which are catalyzed by the complexes or catalyst systems in accordance with the invention.

The complexes in accordance with the invention are able to provide highly active catalyst systems for the selective synthesis of α-olefins, in particular short chain α-olefins in the C_4-C_{10} range. The complexes can be conveniently prepared form starting compounds described in the literature, and they catalyze the oligomerization of olefins under conditions which are significantly milder in terms of their high selectivity at lower temperatures and at a lower pressure compared to known industrial processes. Moreover, the amounts of catalysts which are required in order to achieve a satisfactory yield are very low, such that large amounts of products can be prepared using small amounts of catalysts. In comparison with systems previously described in the literature and used in industry, the catalyst system in accordance with the invention has the additional advantage that a narrow product distribution of the α-olefins results.

5.10 Detailed Description

A "catalyst composition" as referred to herein refers to a composition comprising the complex of the invention (i.e. the complex of formula (I) or any preferred embodiment thereof) as such or in an activated form obtainable by reacting the complex with an activator, which system can be contacted with the reactants to be subjected to the catalyzed reaction. Typical examples are a solution or a dispersion of the complex or the activated complex, or a carrier on which the complex or the activated complex is immobilized, e.g. via adsorption.

The complex of the invention (i.e. the complex of formula (I) or any preferred embodiment thereof) can also be referred to as a "precatalyst" herein. In accordance with the practice in the art, the term "precatalyst" refers to a complex in a form which is converted into the catalytically active species, e.g. via abstraction of a ligand, during the course of the catalyzed reaction. The activation can be assisted by an activator or a co-catalyst.

Oligomerization, in accordance with the understanding in polymer chemistry, relates to a process wherein monomers are covalently linked to each other to form a product (oligomer) containing a limited number of subunits derived from these monomers. Generally, the total number of subunits in an oligomer does not exceed 100. In the oligomers provided by the complexes and methods in accordance with the invention, a number of monomer subunits of 2 to 20 is preferred, a number of 2 to 15 is more preferred, and a number of 2 to 12 is further preferred and a number of 2 to 10 is particularly preferred. It will be understood that oligomer mixtures obtained in an oligomerization reaction as carried out in the context of the invention show a distribution with respect to their chain lengths. Generally, the peak (or peaks) of such a product distribution indicating the relative weight ratio of oligomers in the mixture versus the number of subunits contained in the oligomer (e.g. determined via gas chromatography) lies in the range of 2 to 5, in particular 2 to 3.

As used herein, "alkyl" represents a straight or branched chain saturated hydrocarbon residue which does not comprise any carbon-to-carbon double bonds or carbon-to-carbon triple bonds. Unless otherwise defined in a specific context, alkyl groups with 1 to 8 carbon atoms are generally preferred in the context of the invention. As exemplary groups, methyl, ethyl, propyl and butyl are mentioned.

As used herein, "alkenyl" represents a straight or branched chain unsaturated hydrocarbon residue comprising one or more than one (such as two or three) carbon-to-carbon double bond(s) which does not comprise any carbon-to-carbon triple bonds. Unless otherwise defined in a specific context, alkenyl

groups with 1 to 8 carbon atoms and one or two double bonds are generally preferred in the context of the invention.

As used herein, "aryl" represents an aromatic hydrocarbon ring, in particular a 6 to 10 membered ring (unless a different number of ring members is indicated in a specific context), including bridged ring or fused ring systems containing at least one aromatic ring. "Aryl" may, for example, refer to phenyl or naphthyl. Preferred as aryl groups are monocyclic groups with 6 or fused bicyclic groups with 9 or 10 ring members. Thus, generally preferred embodiments of "aryl" are phenyl or naphthyl, and particularly preferred is phenyl.

As used herein, "aralkyl" represents an alkyl group as defined above, wherein one or more, preferably one hydrogen atom is replaced by an aryl group, preferably a phenyl group. A particularly preferred aralkyl group is benzyl.

The term "–alkyl-O-alkyl" refers to an alkyl group as defined above, wherein one hydrogen atom is replaced by an alkoxy group. Likewise, the term "–alkyl-O-aryl" refers to an alkyl group as defined above, wherein one hydrogen atom is replaced by an aryloxy group.
As used herein, a "heterocycle" is a ring comprising one or more (such as, e.g., one, two, or three) ring heteroatoms which may be selected from O, S, and N, including bridged ring or fused ring systems. A heterocycle may be saturated or unsaturated, such that the term encompasses heteroalkyl rings as well as heteroraryl rings. Preferred are 5 - 14 membered rings, and particular preference is given to monocyclic groups with 5 or 6 members and fused bicyclic groups with 8 to 10 ring members.

As used herein, "heteroaryl" represents an aromatic ring, preferably a 5-14 membered ring (unless a different number of ring members is indicated in a specific context), including bridged ring or fused ring systems containing at least one aromatic ring, comprising one or more (such as, e.g., one, two, or three) ring heteroatoms independently selected from O, S, and N. Particularly preferred as heteroaryl groups are monocyclic groups with 5 or 6 members and fused bicyclic groups with 8 to 10 ring members. "Heteroaryl" may, for example, refer to thienyl (thiophenyl), benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, furyl (furanyl), isobenzofuranyl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl (including, without limitation, 2H-pyrrolyl), imidazolyl, pyrazolyl, pyridyl (pyridinyl; including, without limitation, 2-pyridyl, 3-pyridyl, and 4-pyridyl), pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyl, isoindolyl, indolyl (including, without limitation, 3H-indolyl), indazolyl, purinyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, cinnolinyl, pteridinyl, carbazolyl, beta-carbolinyl, phenanthridinyl, acridinyl, phenanthrolinyl (including, without limitation, [1,10]phenanthrolinyl, [1,7]phenanthro-linyl,

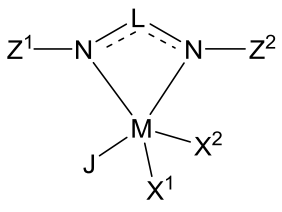
and [4,7]phenanthrolinyl), phenazinyl, isothiazolyl, phenothiazinyl, oxazolyl, isoxazolyl, furazanyl, phenoxazinyl, pyrazolo[1,5-a]pyrimidinyl (including, without limitation, pyrazolo[1,5-a]pyrimidin-3-yl), 1,2-benzoisoxazol-3-yl, or benzimidazolyl.

As used herein, "cycloalkyl" represents a saturated hydrocarbon ring, preferably a 3-11 membered ring (unless a different number of ring members is indicated in a specific context), including bridged ring, spiro ring or fused ring systems. "Cycloalkyl" may, for example, refer to cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, or cycloheptyl. Preferred as cycloalkyl groups are monocyclic groups with 5 or 6 ring members or fused bicyclic groups with 9 or 10 ring members.

As used herein, "heterocycloalkyl" represents a saturated ring, preferably a 3-11 membered ring (unless a different number of ring members is indicated in a specific context), including bridged ring, spiro ring or fused ring systems, containing one or more (such as, e.g., one, two, or three) ring heteroatoms independently selected from O, S, and N. Particularly preferred as heterocycloalkyl groups are monocyclic groups with 5 or 6 members and fused bicyclic groups with 8 to 10 ring members. "Heterocycloalkyl" may, for example, refer to oxetanyl, tetrahydrofuranyl, piperidinyl, piperazinyl, aziridinyl, azetidinyl, pyrrolidinyl, imidazolidinyl, morpholinyl, pyrazolidinyl, tetrahydrothienyl, octahydroquinolinyl, octahydroisoquinolinyl, oxazolidinyl, isoxazolidinyl, azepanyl, diazepanyl, oxazepanyl or 2-oxa-5-aza-bicyclo[2.2.1]hept-5-yl.

As far as the compounds and complexes used herein allow two suitable groups to be linked to form a ring, it will be understood by the skilled person that the concerned groups should, in combination, be sufficiently long such that the resulting ring system can be stable. In addition, it will be understood that two groups can be linked if they contain atoms between which a bond (including single or double bonds) can be formed. As example, a link can be formed between two carbon atoms in different groups via replacement of one or two hydrogen atom in each of the groups by a bond or a double bond between the groups.

As defined above, the present invention provides in accordance with a first aspect complexes of the following formula (I):



(I)

wherein

M is a metal selected from Zr and Hf;

X^1 and X^2 are independently selected from Cl, Br, I, F, H, alkyl, -alkyl-O-alkyl, -alkyl-O-aryl, alkoxy, aryloxy, aralkyl, -alkyl-$SiR^aR^bR^c$, and NR^1R^2, wherein any alkyl group, alone or as part of another group such as -alkyl-O-alkyl, alkoxy or aralkyl, is optionally substituted by one or more substituents selected from OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and $N(C1\text{-}8\ alkyl)_2$, and any aryl group, alone or as part of another group such as -alkyl-O-aryl, aralkyl or aryloxy, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and $N(C1\text{-}8\ alkyl)_2$;

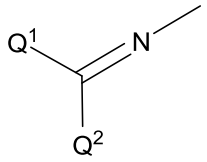
L is selected from CZ^3, N, and PR^3R^4;

Z^1 and Z^2 are independently selected from alkyl, cycloalkyl, heterocycloalkyl, alkenyl, aryl, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl, wherein any alkyl group, alone or as part of another group such as -alkyl-O-alkyl or aralkyl, and any alkenyl group, is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and any aryl group, alone or as part of another group, such as -alkyl-O-aryl or aralkyl, and any heteroaryl group, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$;

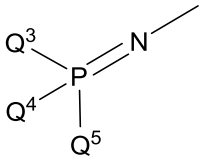
Z^3 is selected from alkyl, cycloalkyl, heterocycloalkyl, alkenyl, alkoxy, aryl, aryloxy, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl, F, Cl, Br, NR^1R^2, and PR^3R^4, wherein any alkyl group, alone or as part of another group such as -alkyl-O-alkyl, alkoxy or aralkyl, and any alkenyl group, is optionally substituted by one or more substituents selected from OH, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and wherein any aryl group, alone or as part of another group such as -alkyl-O-aryl, aralkyl or aryloxy, and any heteroaryl group, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$;

or any suitable groups Z^1 and Z^3 or Z^2 and Z^3 as defined above may be linked to form an optionally substituted five- to seven-membered heterocyclic ring incorporating the nitrogen atom to which Z^1 is attached or the nitrogen atom to which Z^2 is attached;

J is selected from a ligand of the formula (II) or (III):



(II)



(III),

wherein

Q^1 to Q^5 are independently selected from alkyl, cycloalkyl, heterocycloalkyl, alkenyl, alkoxy, aryl, aryloxy, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl and NR^5R^6, wherein any alkyl group, alone or as part of another group, and any alkenyl group is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group , alone or as part of another group, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$;

or any suitable groups Q^1 and Q^2 as defined above may be linked to form a five- to seven-membered, carbocyclic or heterocyclic, saturated or unsaturated ring together with the carbon atom to which they are attached, or any suitable groups Q^3 and Q^4 as defined above or Q^4 and Q^5 as defined above may be linked to form a five- to seven-membered, heterocyclic, saturated or unsaturated ring together with the P-atom to which they are attached;

R^a, R^b and R^c are independently selected from alkyl and aryl; and

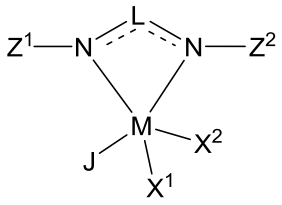
R^1, R^2, R^3, R^4, R^5 and R^6 are independently selected from H, alkyl, cycloalkyl, alkenyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br, NH_2, NH(C1-8 alkyl) and N(C1-8 alkyl)$_2$;

or any suitable groups R^1 and R^2 as defined above, R^3 and R^4 as defined above or R^5 and R^6 as defined above may be linked to form an optionally substituted five or six-membered heterocyclic ring including the N or P atom to which they are attached;

or, where Q^1 and Q^2, Q^3 and Q^4 or Q^4 and Q^5 are NR^5R^6, two groups R^5 or two groups R^6 as defined above may be linked to form an optionally substituted, saturated or unsaturated heterocycle including the two N atoms of the groups NR^5R^6;

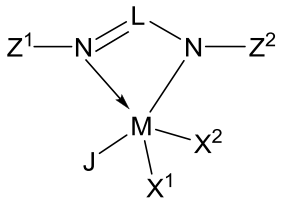
or one of Q^1 to Q^5 as defined above may be linked with one of Z^1 or Z^2 as defined above to form a metallacycle including M.

As regards the ligand formed by Z^1, N, L, N and Z^2, it will be understood that the delocalization of the electrons in the ligand indicated by the dashed bonds in the formula (I)

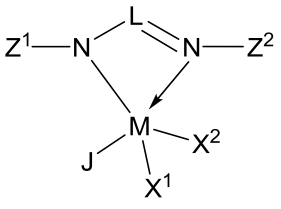


(I)

is influenced by the electron structure of the groups Z^1, Z^2 and L. Thus, a strongly delocalized system will be formed if L is a group CZ^3 and the concerned ligand is symmetrical with respect to L. In this case, the bonds formed by the nitrogen atoms to the metal center are equivalent. However, the structure of the complexes of formula (I) embraces constellations wherein the delocalization would be less pronounced, such that one of the N atoms can be considered as an anionic atom which binds with the metal, the other one as a neutral atom coordinating with an electron lone pair, as illustrated in the following formulae (I') and (I").



(I')



(I")

As noted above, the electron structure of the nitrogen metal bonds will be ultimately determined by the nature of associated groups Z^1, L, and Z^2, and the actual structure will frequently be an intermediate between the idealized resonance structures (I) and (I') or (I"). Thus, the indication of a resonance structure such as (I), (I') or (I") for any complexes described herein is not to be seen as limiting the concerned compounds to the illustrated equivalent or non-equivalent types of nitrogen-metal bonds in accordance with the common practice in the art.

In the ligand containing Z^1, L and Z^2, the following are preferred meanings of these variables.

L is preferably CZ^3.

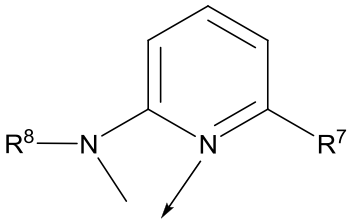
Z^1 and Z^2 are preferably selected from alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, -alkyl-O-alkyl, and -alkyl-O-aryl, wherein any alkyl group, alone or as part of another group such as aralkyl, -alkyl-O-alkyl, and -alkyl-O-aryl, is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and any aryl group, alone or as part of another group, such as aralkyl and -alkyl-O-aryl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$. It is particularly preferred that Z^1 and Z^2 are selected from alkyl, cycloalkyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$. Preferably, the alkyl group is not substituted and the aryl group is not substituted or substituted by one or more C1-8 alkyl groups.

Z^3 is preferably selected from H, alkyl, cycloalkyl, aryl, aralkyl, and NR^1R^2, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$. Preferably, the alkyl and the aryl group is not substituted.

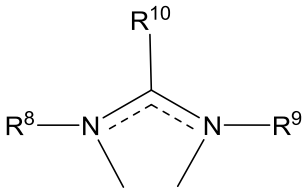
According to another preferred embodiment, Z^1 and Z^3 or Z^2 and Z^3 are taken together to form a pyridine ring including the nitrogen atom to which Z^1 or Z^2, respectively, is attached, which pyridine ring is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$. Preferably, it is unsubstituted. The group Z^1 or Z^2 which is not involved in the formation of the pyridine ring is defined in accordance with the preferred options listed above.

R^1 and R^2 are preferably independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$; or R^1 and R^2 as defined above may be linked to form an optionally substituted five or six-membered heterocyclic ring including the N atom to which they are attached. More preferably R^1 and R^2 are independently selected from H, alkyl, aryl, and aralkyl, and are in particular independently selected from H and C1-8 alkyl.

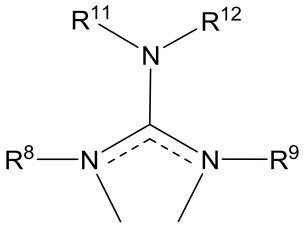
In a particularly preferred embodiment, the ligand containing Z^1, L and Z^2 is selected from one of the following formulae (IVa) to (IVc):



(IVa)



(IVb)



(IVc).

In these formulae, the variables have the following general and preferred meanings.

R^7, R^8, and R^9 are independently selected from alkyl, cycloalkyl, aryl, and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$. Preferably, the aryl group is not substituted or substituted by one or more C1-8 alkyl groups.

It is preferred that R^7, R^8, and R^9 are independently selected from aryl and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups. It is particularly preferred that R^7, R^8, and R^9 are independently phenyl, optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups.

R^{10} is selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$. Preferably, the aryl group is not substituted or substituted by one or more C1-8 alkyl groups.

It is preferred that R^{10} is selected from aryl and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups. It

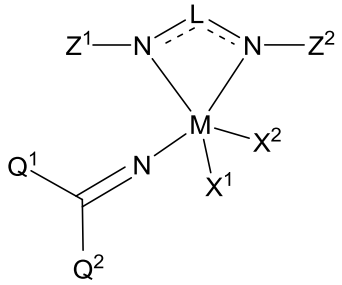
is particularly preferred that R^{10} is phenyl, optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups.

R^{11} and R^{12} are independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$; or R^{11} and R^{12} as defined above may be linked to form an optionally substituted five or six-membered heterocyclic ring including the N atom to which they are attached. Preferably R^{11} and R^{12} are independently selected from H, alkyl, aryl, and aralkyl, and are in particular independently selected from H and C1-8 alkyl.

Among the ligands of formulae (IVa) to (IVc), particular preference is given in the context of the invention to ligands of formula (IVa).

Among the ligands of formulae (II) and (III) as J, preference is given to the ones of formula (II).

For a ligand J of formula (II), the compound of formula (I) has the following structure (Ia)



(Ia),

wherein the variables are defined as above, including preferred embodiments.

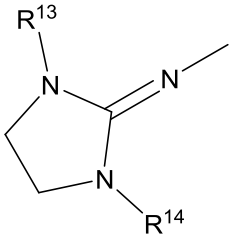
In the ligand containing Q^1 and Q^2, the following are preferred meanings for these variables.

Q^1 and Q^2 are preferably independently selected from alkyl, aryl, aralkyl, and NR^5R^6, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of another group such as -alkyl-O-aryl, aralkyl or aryloxy, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$.

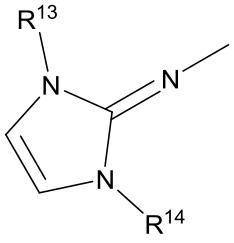
R^5 and R^6 are preferably independently selected from alkyl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$.

In accordance with a further preferred embodiment, Q^1 and Q^2 are both NR^5R^{6a}, wherein the groups R^5 are independently selected from the preferred options listed above, and the two groups R^{6a} are taken together to form a 5- or 6- membered, preferably 5 membered, saturated or unsaturated heterocycle containing the two N atoms of the NR^5R^{6a} groups as heteroatoms. In addition to the groups R^5, the heterocycle may carry one or more further substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. Preferably, these further substituents are absent.

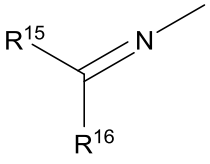
In a particularly preferred embodiment, the ligand of formula (II) is selected from one of the following formulae (IIa) to (IIe):



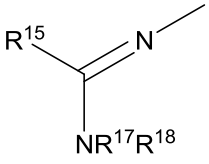
(IIa)



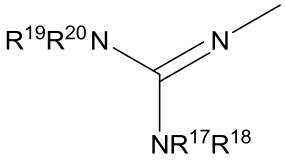
(IIb)



(IIc)



(IId)



(IIe)

The variables in these formulae are defined as follows:

R^{13} and R^{14} are independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. Preferably, the aryl group is not substituted or substituted by one or more C1-8 alkyl groups.

It is preferred that R^{13} and R^{14} are independently selected from aryl and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups. It is particularly preferred that R^{13} and R^{14} are independently phenyl, optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups.

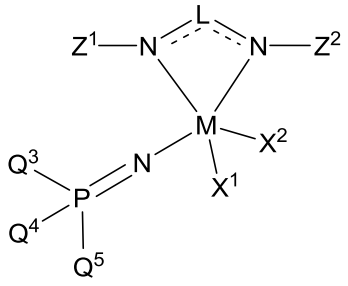
R^{15} and R^{16} are independently selected from alkyl, cycloalkyl, aryl, and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. Preferably, the aryl group is not substituted or substituted by one or more C1-8 alkyl groups.

It is preferred that R^{15} and R^{16} are independently selected from aryl and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups. It is particularly preferred that R^{15} and R^{16} are independently phenyl, optionally substituted in the ortho- and/or
para-position by one or more C1-8 alkyl groups.

R^{17}, R^{18}, R^{19} and R^{20} are independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$; or R^{17} and R^{18} or R^{19} and R^{20} as defined above may be linked to form an optionally substituted five or six-membered heterocyclic ring including the N atom to which they are attached. Preferably R^{17}, R^{18}, R^{19} and R^{20} are independently selected from H, alkyl, aryl, and aralkyl, and are in particular independently selected from H and C1-8 alkyl.

Among the ligands of formulae (IIa) to (IIe), particular preference is given in the context of the invention to ligands of formula (IIa) and (IIb).

For a ligand J of formula (III), the compound of formula (I) has the following structure (Ib)



(Ib),

wherein the variables are defined as above, including preferred embodiments.

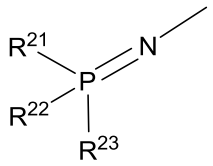
In the ligand containing Q^3, Q^4 and Q^5, the following are preferred meanings for these variables.

Q^3 to Q^5 are preferably independently selected from alkyl, aryl, aralkyl, and NR^5R^6, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of another group such as -alkyl-O-aryl, aralkyl or aryloxy, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$.

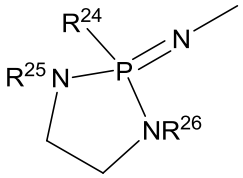
R^5 and R^6 are preferably independently selected from alkyl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$.

In accordance with a further preferred embodiment, one of Q^3 and Q^5 is defined in accordance with the above preferred embodiments of Q^3 to Q^5, and the other two, i.e. Q^3 and Q^4 or Q^4 and Q^5, are both NR^5R^{6a}, wherein the groups R^5 are independently selected from the preferred options listed above, and the two groups R^{6a} are taken together to form a 5- or 6- membered, preferably 5 membered, saturated or unsaturated heterocycle containing the two N atoms of the NR^5R^{6a} groups as heteroatoms. In addition to the groups R^5, the heterocycle may carry one or more further substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. Preferably, these further substituents are absent.

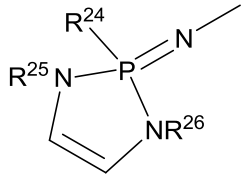
In a preferred embodiment, the ligand of formula (III) is selected from one of the following formulae (IIIa) to (IIId):



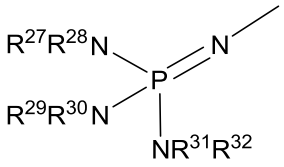
(IIIa)



(IIIb)



(IIIc)



(IIId)

The variables in these formulae are defined as follows.

R^{21} to R^{24} are independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. Preferably, the aryl group is not substituted or substituted by one or more C1-8 alkyl groups.

It is preferred that R^{21} to R^{24} are independently selected from alkyl, aryl and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups. It is particularly preferred that R^{13} and R^{14} are independently phenyl, optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups.

R^{21} to R^{24} are independently selected from alkyl, cycloalkyl, aryl, and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. Preferably, the aryl group is not substituted or substituted by one or more C1-8 alkyl groups.

It is preferred that R^{21} to R^{24} are independently selected from alkyl, aryl and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups. It is particularly preferred that R^{21} to R^{24} are independently t-butyl or phenyl.

R^{25} and R^{26} are independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F,

Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. Preferably, the aryl group is not substituted or substituted by one or more C1-8 alkyl groups.

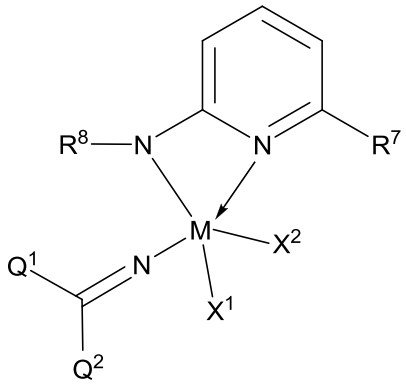
It is preferred that R^{25} and R^{26} are independently selected from alkyl, aryl and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups. It is particularly preferred that R^{25} and R^{26} are independently phenyl, optionally substituted in the ortho- and/or para-position by one or more C1-8 alkyl groups.

R^{27} to R^{32} are independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. Preferably R^{27} to R^{32} are independently selected from H, alkyl, aryl, and aralkyl, and are in particular independently selected from H and C1-8 alkyl.

Among the ligands of formulae (IIIa) to (IIId), particular preference is given in the context of the invention to ligands of formula (IIIa).

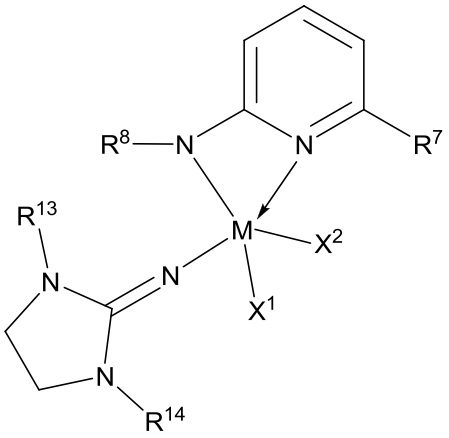
Regarding X^1 and X^2, it is preferred that these ligands are independently selected from Cl, Br, alkyl, -alkyl-Si$R^aR^bR^c$, alkoxy, aryloxy, and aralkyl, wherein any alkyl group, alone or as part of alkoxy or aralkyl, is optionally substituted by one or more substituents selected from OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and N(C1-8 alkyl)$_2$, and any aryl group, alone or as part of another group such as aralkyl or aryloxy, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and N(C1-8 alkyl)$_2$. It is more preferred that X^1 and X^2 are independently selected from Cl, Br, alkyl, aralkyl, and -alkyl-Si$R^aR^bR^c$. As alkyl, methyl is preferred. As aralkyl, benzyl is preferred. For -alkyl-Si$R^aR^bR^c$, it is preferred that -alkyl- is $-CH_2-$, and that R^a to R^c are independently selected from methyl and phenyl, and it is particularly preferred that -alkyl- is $-CH_2-$, and that R^a to R^c are all methyl (Me), or that two of them are methyl and one of them is phenyl (Ph). Thus, in a particularly preferred embodiment, X^1 and X^2 are independently selected from methyl, benzyl, $-CH_2-SiMe_3$ and $-CH_2-SiMe_2Ph$. Most preferred is benzyl.

In the light of the above, particularly preferred complexes in accordance with the invention have the following formula (Ic):

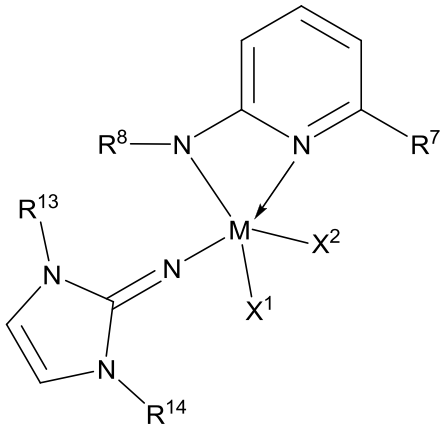


(Ic),

wherein the variables M, X^1, X^2, R^7, R^8, Q^1 and Q^2 have the meanings defined above, including preferred definitions thereof. More preferred are the complexes of the formulae (Id) and (Ie):



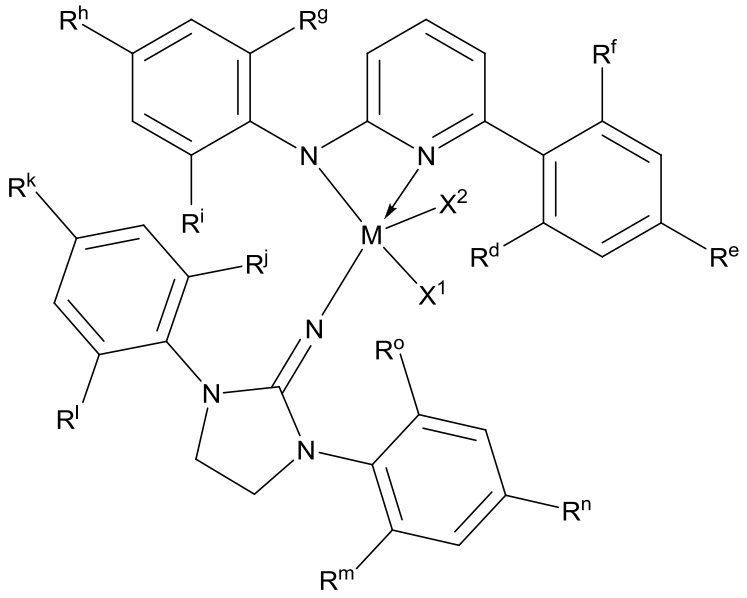
(Id)



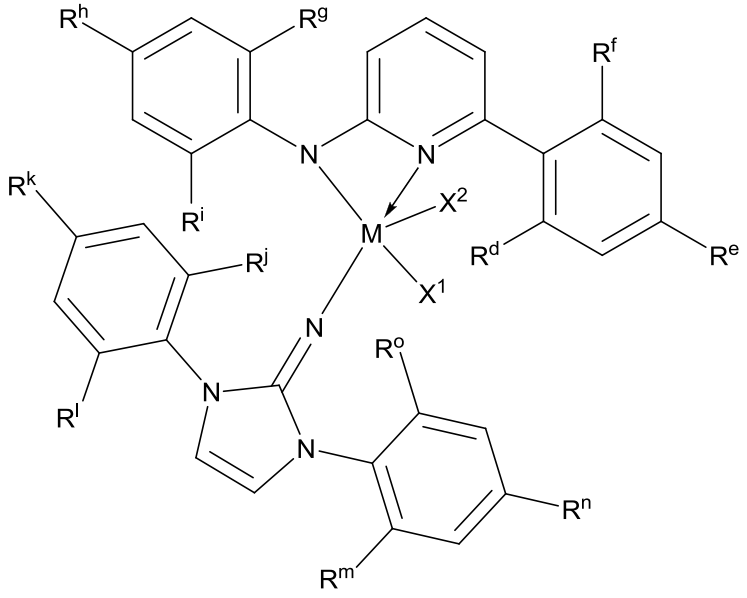
(Ie).

In these formulae, the variables M, X^1, X^2, R^7, R^8, R^{13} and R^{14} have the meanings defined above, including preferred definitions thereof.

In accordance with a yet further preferred embodiment, the complex in accordance with the invention has the formula (If) or (Ig) below.



(If)



(Ig)

wherein M is selected from Zr and Hf,

X^1 and X^2 are independently selected from Cl, Br, alkyl, alkoxy, aryloxy, aralkyl, and $-CH_2-SiR^aR^bR^c$, wherein R^a to R^c are independently selected from methyl and phenyl, and preferably from alkyl, especially methyl, and aralkyl, especially benzyl, and are most preferably benzyl,

and R^d to R^o are independently selected from H and C1-8 alkyl, and preferably R^d, R^f, R^g, R^i, R^j, R^l, R^m and R^o are independently selected from C1-8 alkyl and R^e, R^h, R^k and R^n are selected from H and C1-8 alkyl.

In a further aspect, the invention provides a method for the oligomerization of an olefin, especially ethylene, which method comprises the step of contacting the complex of formula (I), including its preferred embodiments, with an olefin. Preferably, the complex of formula (I) is contacted with the olefin in the presence of an activator.

Generally, the complex in accordance with the invention is used in the form of a catalyst composition. In order to provide a catalyst composition in accordance with the invention which can be conveniently contacted with an olefin as a reactant in an oligomerization reaction, a complex in accordance with the invention (or a mixture of two or more complexes of the invention) can be dissolved or dispersed in a solvent. Examples of suitable solvents include aromatic solvents, such as toluene, benzene and xylene, alkanes, such as the commercially available products Isopar® (Exxon) and Parafol® (SASOL), and cycloalkanes such as cyclohexane.

Alternatively, the complex can be supported on a carrier. This carrier can be, for example, a metal halide or a metal oxide. The metal oxide can be selected from alumina, boria, magnesia, thoria, zirconia, silica, or mixtures thereof. Furthermore, polymeric materials may be used.

Conveniently, the olefin to be oligomerized and the activator can be first charged into the reactor wherein the oligomerization reaction is carried out before the complex or the catalyst composition containing the complex in accordance with the invention is added to the reactor. However, the components (complex(es), activator(s) and reactants) can also be contacted in a different order or can be premixed before injection into the reactor. For example, an activator or an activator and a co-activator can be incorporated together with the complex of formula (I) into the catalyst composition in accordance with the invention, e.g. by combining the complex or complexes and the activator or activators in the solvent contained in the catalyst composition.

The activator can be reacted with the complex in accordance with the invention in order to transform the complex into a catalytically active cationic species which offers a coordination site for the olefin to be oligomerized. Generally, the transformation proceeds via removal of one of the ligands X^1 and X^2 as an anion from the complex of formula (I).

As an activator in accordance with the invention, an alumoxane can be used. An alumoxane component useful as an activator typically is a cyclic or linear oligomeric aluminum compound represented by the general formula $-(Al(R')-O)_n-$ (cyclic) or $R'-(Al(R')-O)_n-AlR'_2$ (linear), wherein R' is independently a C1-

C20 alkyl radical, for example, methyl, ethyl, propyl, butyl, or pentyl, and "n" is an integer from 3-50. Most preferably, R' is methyl and "n" is at least 4. Preferred examples of alumoxanes are methyl alumoxane (MAO), modified methyl alumoxane (MMAO), ethyl alumoxane, iso-butyl or dry-alumoxane from which all volatiles are removed. The amount of the alumoxane to be reacted with the complex in accordance with the invention generally ranges from 20 mol aluminoxane/mol complex to 10000 mol aluminoxane/mol complex, and preferably from 100 mol aluminoxane/mol complex to 500 mol aluminoxane/mol complex.

Furthermore, ionic activators can be used such as those which contain an anion selected from tetrakis-perfluorophenylborate, tetrakis-perfluoronaphthylborate, tetrakis-perfluorophenyl-aluminate or tetrakis-perfluor-m-xyleneborate. In accordance with a preferred embodiment, the ionic activators combine the above anion with a non-coordinating cation.

Examples of suitable ionic activators are dialkyl ammonium salts of the above anions, such as: di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, and dicyclohexylammonium tetrakis(pentafluorophenyl) borate; tri-substituted phosphonium salts of the above anions, such as: triphenylphosphonium tetrakis(pentafluorophenyl) borate, tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and tri(2,6-dimethylphenyl)phosphonium tetrakis-(pentafluorophenyl) borate; di-substituted oxonium salts of the above anions, such as: diphenyloxonium tetrakis(pentafluorophenyl) borate, di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and di(2,6-dimethylphenyl)oxonium tetrakis(pentafluorophenyl) borate; di-substituted sulfonium salts of the above anions, such as: diphenylsulfonium tetrakis(pentafluorophenyl) borate, di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and bis(2,6-dimethylphenyl)sulfonium tetrakis(pentafluorophenyl) borate; or imidazoliniumsalts of the above anions.

A further class of activators that can be used are Lewis acid activators, such as triphenyl boron, tris-perfluorophenyl boron, tris-perfluoronaphthylboron, tris-perfluor-m-xyleneboron or tris-perfluorophenyl aluminum.

The amount of the ionic activator or the Lewis acid activator to be reacted with the complex in accordance with the invention generally ranges from 1 mol activator/mol complex to 2 mol activator/mol complex, and preferably from 1 mol activator/mol complex to 1.1 mol activator/mol complex.

As a co-activator, a compound can be used which is capable of alkylating the transition metal complex, such that when used in combination with an activator such as a Lewis acid activator or an ionic activator, an active catalyst is formed. Co-activators include alumoxanes, such as methyl alumoxane,

modified alumoxanes such as modified methyl alumoxane, aluminum alkyls such trimethyl aluminum, tri-isobutyl aluminum, triethyl aluminum, and tri-isopropyl aluminum and aluminum alkyl halides. The amount of the co-activator is generally in the range of 1 mole to 1000 moles per mole of the complex in accordance with the invention, preferably in the range of 5 mole to 50 moles per mole of the complex in accordance with the invention.

In the method for oligomerizing an olefin in accordance with the invention, monomers selected from ethylene, propylene or an α-olefin, or mixtures of these monomers, can be oligomerized. Preferably, only ethylene is used as the monomer which is subjected to oligomerization.

The method comprises the step of contacting the monomer(s) to be oligomerized with the complex in accordance with the invention or with an activated complex obtainable by contacting the complex in accordance with the invention with an activator, and optionally a co-activator. For example, the monomers can be contacted first with an activator and optionally a co-activator, and subsequently with the complex of the invention, or the monomers are first contacted with the complex in accordance with the invention, and then with the activator and optionally a co-activator.

Frequently, it is advantageous to add a scavenger to the reaction mixture. Scavengers for oligomerization reactions are known in the art, and generally the same compounds can be used as they are used in polymerization reactions. Examples are aluminum alkyls, such as triisobutylaluminum (TIBA), alumoxanes or combinations thereof.

The reaction temperature during the oligomerization reaction is typically in the range of 0 to 100 °C, preferably 20 to 80 °C and in particular 30 to 70 °C. It is an advantage of the complexes in accordance with the invention that they are able to catalyze the oligomerization with a high activity favourably at reduced temperatures. The temperature can also be used to influence the composition of the oligomerized product. At lower temperatures, the formation of products with a lower degree of oligomerization is favoured, at higher temperatures, a higher ratio of products with a higher degree of oligomerization can be obtained.

An exemplary concentration of the monomer to be oligomerized, especially ethylene, in the reaction vessel (typically an autoclave) ranges from 0.1 to 5 MPa (1 – 50 bar), preferably from 0.2 to 1.0 MPa (2 – 10 bar) for a concentration of the complex of the invention of $1 \cdot 10^{-5}$ bis $1 \cdot 10^{-6}$ M (mol/l).

The complex of the invention is preferably used in a catalyst composition comprising a solvent, and the liquid phase of the catalyst composition can be contacted with the gaseous or liquid monomers. Since ethylene is a preferred monomer, the reaction usually proceeds by contact between the liquid catalyst composition and a gaseous monomer. In this case, the monomer can be conveniently oligomerized at an absolute pressure in the reactor (usually provided by the monomer) of 0.10 to 5.0 MPa, preferably 0.15 to 1.0 MPa, and more preferably 0.15 to 0.3 MPa. Advantageously, a high activity is achieved at relatively low pressures. The monomer pressure in the reactor can also be used to influence the composition of the oligomerized product. At lower pressures, the formation of products with a lower degree of oligomerization is favoured, at higher pressures, a higher ratio of products with a higher degree of oligomerization can be obtained.

The complexes and catalyst systems in accordance with the invention allow the production of oligomeric α-olefins with a high selectivity. In particular, the products show a narrow product distribution with respect to the number of monomers contained in the oligomers (i.e. the degree of oligomerization). For the oligomerization of ethylene, 1-butene, 1-hexene and 1-octene, in particular 1-butene and 1-hexene can be obtained as main products with a ratio of preferably more than 50 wt.-% of all oligomers produced. No polymeric side products are obtained. If the distribution of oligomer chain lengths in the product (as determined e.g. via gas chromatography) is described as a Flory-Schulz-distribution (H.H. Nijs, P.A. Jacobs, Journal of Catalysis, **1980**, *65*, 328–334), the K-value is usually between 0.2 and 0.7, preferably between 0.2 and 0.6. The K-value, as used herein, can be determined as disclosed in *"Oligomerization of Ethylene Using New Tridentate Iron Catalysts Bearing alpha-Diimine Ligands with Pendant S and P Donors"*, Brooke L. Small, Ray Rios, Eric R. Fernandez, Deidra L. Gerlach, Jason A. Halfen, and Michael J. Carney; Organometallics **2010**, *29*, 6723–6731.

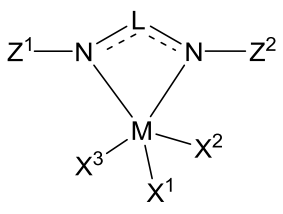
Also in terms of the structure of the obtained products, the complexes in accordance with the invention ensure a highly selective oligomerization. No incorporation of α-olefins already formed as products into the growing α-olefin chains has been observed. Thus, in the case of ethylene oligomerization, only linear (non-branched) oligomeric α-olefins are formed. Moreover, no isomerization of the products was observed, i.e. α-olefins having one double bond are provided with a high yield.

The complexes in accordance with the invention can be conveniently prepared according to synthetic methods known in the art.

The bidentate ligands containing two coordinating N-Atoms of the complexes in accordance with the invention, such as the aminopyridinato-ligands, are accessible via convenient routes of synthesis at high yields (z.B. Natalie M. Scott, Thomas Schareina, Oleg Tok, Rhett Kempe, *Eur. J. Inorg. Chem.* **2004**, 3297–3304 and the literature cited therein). The sterical and electronic properties of such ligands can be easily varied. The preparation of the ligand-metal complexes, such as the aminopyridinato complexes, is well documented especially in the field of polymerization catalysts (e.g. R. Kempe, *Eur. J. Inorg. Chem.* **2003**, 791–803; W. P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, *Chem. Eur. J.* **2006**, *12*, 8969–8978; W. P. Kretschmer, B. Hessen, A. Noor, N. M. Scott, R. Kempe, *J. Organomet. Chem.* **2007**, *692*, 4569–4579.; H. Fuhrmann, S. Brenner, P. Arndt, R. Kempe, *Inorg. Chem.* **1996**, *35*, 6742–6745; M. Hafeez, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2011**, 5512–5522; Ch. Döring, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2010**, 2853–2860; A. Noor, W. P. Kretschmer, G. Glatz, R. Kempe, *Inorg. Chem.* **2011**, 50, 4598–4606; N. M. Scott, T. Schareina, O. Tok, R. Kempe, *Eur. J. Inorg. Chem.* **2004**, 3297–3304). The preparation of amidinato complexes is disclosed, e.g. in C. Visser, PhD Thesis, University of Groningen, **2003**.

Also the monodentate ligand J can be prepared by methods known in the art. For example, the synthesis of the iminoimidazolidines is described in *DE* 2916140 A1 via reaction of the corresponding *N,N'*-diarylalkyl-1,2-diamine with cyanogene bromide in toluene. The 1,2-diamine can be prepared either from the corresponding arylamine and 1,2-dibromoethane, or via reduction of an α-diimine, the latter being prepared via condensation reaction between the corresponding arylamine and glyoxal. The synthesis of other ketimide ligands is described, e.g., in *US* 2004/0192541 and the literature cited therein. The coordination of the ligand to a metal center can be easily achieved (e.g. as described in *US* 2004/0192541). Regarding the synthesis and coordination of phosphinimide ligands J, reference can be made e.g. to W. P. Kretschmer, C. Dijkhuis, A. Meetsma, B. Hessen and J. Teuben, *Chem. Commun.*, **2002**, 608–609, *an*d to *WO* 2011/102989 and to D. W. Stephan, *Organometallics* **2005**, *24,* 2548–2560 and the literature cited in these documents.

As a general route of synthesis for the complexes in accordance with the invention, a complex precursor of formula (V):



(V)

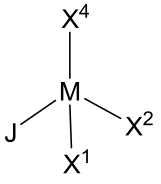
wherein Z^1, L, Z^2, X^1 and X^2 are defined as above, including preferred embodiments, and X^3 is selected from Cl, Br, I, F, H, alkyl, -alkyl-O-alkyl, -alkyl-O-aryl, alkoxy, aryloxy, aralkyl, -alkyl-$SiR^aR^bR^c$, and NR^1R^2, wherein any alkyl group, alone or as part of another group such as -alkyl-O-alkyl, alkoxy or aralkyl, is optionally substituted by one or more substituents selected from OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and N(C1-8 alkyl)$_2$, and any aryl group, alone or as part of another group such as -alkyl-O-aryl, aralkyl or aryloxy, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$, and R^a, R^b and R^c are independently selected from alkyl and aryl;
is reacted with a compound of the formula (VIa) or (VIb):

$Q^1Q^2N{=}NH$ (VIa)
$Q^3Q^4Q^5P{=}NH$ (VIb),

wherein Q^1 to Q^5 are independently defined as above, including preferred embodiments, or with a salt containing an anion of a compound of the formula (VIa) or (VIb) obtained by abstracting the proton indicated these formulae.

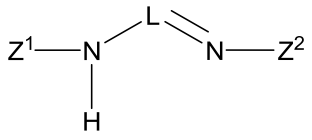
Typically, the molar ratio of the compounds of formula (V) and (VIa) or (VIb) in the reaction is about 1, such as 0.9 to 1.1, and is preferably 1.0. The reaction can be conveniently accomplished in a solvent, e.g. an aromatic solvent such as toluene, at moderate temperatures ranging e.g. from 25 to 70 °C, preferably from 40 to 60 °C. In the compounds of formula (V), X^3 is preferably selected from Cl, Br, alkyl, alkoxy, aryloxy, and aralkyl, wherein any alkyl group, alone or as part of alkoxy or aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br N(C1-8 alkyl)$_2$, and any aryl group, alone or as part of another group such as aralkyl or aryloxy, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$. It is more preferred that X^3 selected from Cl, Br, alkyl, especially methyl, and aralkyl, especially benzyl. Most preferred is benzyl.

Alternatively, the complexes in accordance with the invention can be prepared by reacting a complex precursor of formula (VII):

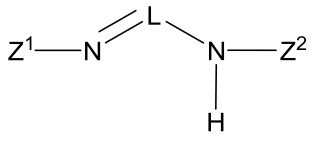


(VII)

wherein J, X^1 and X^2 are defined as above, including preferred embodiments, and X^4 is selected from Cl, Br, I, F, H, alkyl, -alkyl-O-alkyl, -alkyl-O-aryl, alkoxy, aryloxy, aralkyl, -alkyl-$SiR^aR^bR^c$, and NR^1R^2, wherein any alkyl group, alone or as part of another group such as -alkyl-O-alkyl, alkoxy or aralkyl, is optionally substituted by one or more substituents selected from OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and N(C1-8 alkyl)$_2$, and any aryl group, alone or as part of another group such as -alkyl-O-aryl, aralkyl or aryloxy, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$, and R^a, R^b and R^c are independently selected from alkyl and aryl; with a compound of the formula (VIIIa) or (VIIIb):



(VIIIa)



(VIIIb)

or with a salt containing an anion of a compound of the formula (VIIIa) or (VIIIb) obtained by abstracting the proton indicated these formulae.

A precursor of formula (V) can be conveniently prepared by reacting a compound of formula $MX^1X^2X^3X^4$, wherein X^1 to X^4 are defined as above, including preferred embodiments, with a compound of formula (VIIIa) or (VIIIb) as defined above, or with a salt containing an anion of a compound of the formula (VIIIa) or (VIIIb) obtained by abstracting the proton indicated these formulae. M(CH_2SiMe_3)$_4$ and M(CH_2SiMe_2Ph)$_4$ (M = Zr, Hf) (M. R. Collier, M. F. Lappert, R. Pearce, *J. Chem. Soc., Dalton Trans.* **1973**, 445.) and tetrabenzylzirconium as exemplary compounds of formula $MX^1X^2X^3X^4$ have been long known in literature.

A precursor of formula (VII) can be conveniently prepared by reacting a compound of formula $MX^1X^2X^3X^4$, wherein X^1 to X^4 are defined as above, including preferred embodiments, with a compound of formula (VIa) or (VIb) as defined above, or with a salt containing an anion of a compound of the formula (VIa) or (VIb) obtained by abstracting the proton indicated these formulae.

In this specification, a number of patent and non-patent documents are cited. The disclosure of these documents, while not considered relevant for the patentability of this invention, is herewith

incorporated by reference in its entirety. More specifically, all referenced documents are incorporated by reference to the same extent as if each individual document was specifically and individually indicated to be incorporated by reference.

The invention will now be described by reference to the following examples, which are merely illustrative and are not to be construed as a limitation of the scope of the present invention.

5.11 Examples

The following abbreviations are used:

Me	-	Methyl (CH_3)
Et	-	Ethyl (CH_3CH_2)
i-Pr	-	*iso*-Propyl (Me_2CH)
i-Bu	-	*iso*-Butyl (Me_2CHCH_2)
Bz	-	Benzyl (CH_2Ph)
MAO	-	Methylaluminumoxane [$(MeAlO)_n \cdot (Me_3Al)_{1/3\,n}$]
d-MAO	-	dry-Methylaluminoxane [$(MeAlO)_n$]
TIBA	-	Tri-*iso*-butylaluminum (*i*-Bu_3Al)
ApH	-	Aminopyridine[a]
Ap*H	-	N-(2,6-Diisopropylphenyl)-6-(2,4,6-triisopropylphenyl)pyridin-2-amine[a]
Ap^+H	-	N-(2,6-Diisopropylphenyl)-6-(2,6-dimethylphenyl)pyridin-2-amine[a]
$Ap^{9Me}H$	-	[N-Mesityl-6-(2,4,6-triisopropylphenyl)pyridin-2-amine[a]
ImH	-	1,3-Bis(2,6-dimethylphenyl)imidazolidin-2-imine[a]

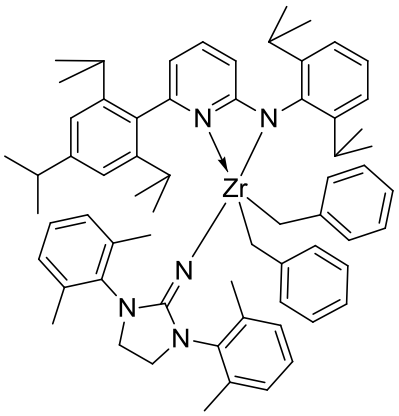
[a]In line with common practice in the art, the H in the abbreviation indicates the parent compound from which the corresponding anionic ligand (e.g. Ap – aminopyridinato ligand) is prepared via abstraction of a proton.

General: All manipulations of air- or moisture-sensitive compounds were carried out under N_2 using glove-box, standard Schlenk, or vacuum-line techniques. Solvents and reagents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy, or sodium ketyl of benzophenone under nitrogen immediately before use. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fisher Scientific), 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). NMR spectra were recorded on a Varian Inova 400 (^{1}H: 400 MHz, ^{13}C: 100.5 MHz) or Varian Inova 300 (1H: 300 MHz, 13C: 75.4 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 26°C, were referenced internally using the residual solvent resonances, and the chemical shifts (δ) reported in ppm. Gel permeation chromatography (GPC) analysis was carried out on a PL-GPC 220 (Agilent, Polymer Laboratories) high temperature chromatographic unit equipped with LS, DP and RI detectors and two linear mixed bed columns (Olexis, 13-micron particle size) at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.05 wt.-%, conc. = 1 mg/mL) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (M_w = 520 – 3,200,000 g·mol^{-1}) and polystyrene (M_w = 580–2,800,000 g·mol^{-1}) standards. The reported values are the average of at least two independent determinations. GC analysis was performed with an Agilent 6850 gas chromatograph equipped with an Agilent 19095J-323E capillary column (HP-5; 5% phenyl methyl siloxane; 30 m; film 1.5 μm, diameter 0.53 mm) and a flame ionization detector.

N,N-Dimethylanilinium (tetrapentafluorophenyl) borate ([PhNMe$_2$H][B(C$_6$F$_5$)$_4$], abcr GmbH & Co. KG), *N,N,N*-Trialkylammonium (tetrapentafluorophenyl) borate ([R$_2$NMeH][B(C$_6$F$_5$)$_4$] , R = C$_{16}$H$_{33}$ – C$_{18}$H$_{37}$, 6.2 wt.-% B(C$_6$F$_5$)$_4$ in Isopar, DOW Chemicals), Tri-*iso*-butyl aluminum (TIBA, 25 wt.-% in toluene, Aldrich), and EURECEN AI 5100-10-toluene (4.9 wt.-% in Al, Chemtura Organometallics) were used as received. dry-MAO was prepared by removal of volatiles from EURECEN AI 5100. Commercial benzylchloride, 2,6-diphenyl-phenol and zirconium(IV)chloride were used as received from Sigma-Aldrich. The ligand precursor 1,3-bis-(2,6-dimethyl-phenyl)imidazolidin-2-ylideneamine (*DE* 2916140 A1, *US* 2004/0192541 A1) and the metal precursors tetrabenzylzirconium (Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357), [N-(2,6-diisopropylphenyl)-6-(2,4,6-triisopropylphenyl)pyridin-2-amido]-tribenzylzirconium(VI) (Ap*ZrBz$_3$, **A**), [N-mesityl-6-(2,4,6-triisopropylphenyl)pyridin-2-amido]-dibenzylzirconium(VI) (Ap^{9Me}ZrBz$_3$, **B**), and [N-(2,6-diisopropylphenyl)-6-(2,6-dimethylphenyl)pyridin-2-amido]-tribenzylzirconium(IV) (Ap^{+}ZrBz$_3$, **C**) (A. Noor, W. P. Kretschmer, G. Glatz, A. Meetsma, R. Kempe, *Eur. J. Inorg. Chem.* **2008**, 5088) were prepared according to published procedures.

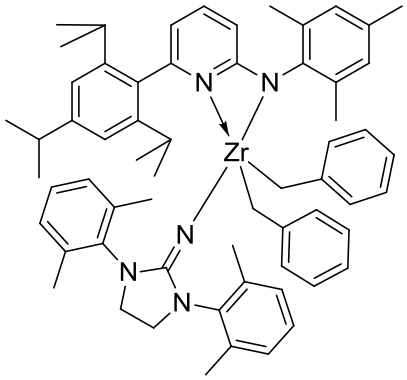
Example 1



Synthesis of [1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imido]-[N-(2,6-diisopropylphenyl)-6-(2,4,6-triisopropylphenyl)pyridin-2-amido]-dibenzylzirconium(IV); Ap*[1,3-(2',6'-$Me_2C_6H_3)_2(CH_2N)_2C{=}N]Zr(CH_2Ph)_2$; (Precatalyst **1**) (cf. Fig. 1)

Ap*$Zr(CH_2Ph)_3$ (300 mg, 0.366 mmol) in toluene (5 mL) was added to 1,3-bis-(2,6-dimethyl-phenyl)imidazolidin-2-ylideneamine (107 mg, 0.366 mmol) in toluene (5 mL) at room temperature. The reaction mixture was stirred at 50 °C for 12 h. Toluene was evaporated to dryness and the product was washed with hexane (2 mL) to give the yellow product 1. Suitable crystals for X-ray analysis can be obtained by overlaying a saturated toluene solution with hexane. The structure is shown in Fig. 1. Yield 280 mg (76%). Elemental analysis for $C_{65}H_{79}N_5Zr$ (1021.58): calcd. C 76.42, H 7.79, N 6.86; found C 75.29, H 7.68, N 6.67. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.80 – 1.28 (m, 30H, H), 1.98 (s, 12H, CH_3), 1.99 – 2.10 (m, 4H, $C_6H_5CH_2$), 2.59 – 2.72 (m, 3H, H), 2.86 (s, 4H, NCH_2), 3.28 (sept, 2H, H), 5.50 (dd, 1H, J_{HH} = 9.7 Hz, H), 6.04 (d 4H, J_{HH} = 8.7 Hz, o-$C_5H_5CH_2$), 6.38 (dd, 1H, J_{HH} = 8.3 Hz, H), 6.76 – 7.15 (m, 18H, H, p-$C_6H_5CH_2$, m-$C_6H_5CH_2$, C_6H_3) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 18.1 (s, 4C, *C*H_3), 22.9 (s, 2C, *C*H_3), 23.7 (s, 2C, *C*H_3), 24.0 (s, 2C, *C*H_3), 25.5 (s, 2C, *C*H_3), 26.6 (s, 2C, *C*H_3), 28.4 (s, 2C, *C*H), 30.8 (s, 2C, *C*H), 34.7 (s, 1C, *C*H), 44.9 (s, 2C, *C*H_2), 64.3 (s, 2C, Ph*C*H_2), 107.1 (s, 1C, *C*H), 115.2 (s, 1C, *C*H), 119.8 (s, 1C, Ph), 121.3 (s, 1C, Ph), 125.5 (s, 1C, *C*), 127.6 (s, 2C, *C*H), 128.1 (s, 4C, Ph), 128.3 (s, 4C, Ph), 128.9 (s, 2C, *C*H), 129.2 (s, 2C, *C*H), 129.9 (s, 2C, *C*), 135.6 (s, 1C, *C*), 137.5 (s, 6C, *C*$_6$H$_3$), 138.3 (s, 2C, N*C*), 139.6 (s, 1C, *C*), 144.0 (s, 1C, *C*), 145.6 (s, 2C, *C*), 146.7 (s, 2C, *C*), 147.2 (s, 1C, *C*), 147.6 (s, 2C, *C*), 149.8 (s, 1C, *C*), 157.4 (s, 1C, *C*), 168.3 (s, 1C, *C*N) ppm.

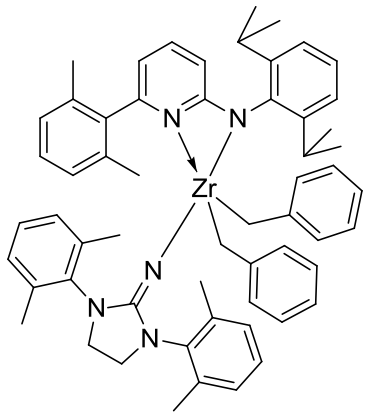
Example 2



Synthesis of [1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imido]-[N-mesityl-6-(2,4,6-triisopropylphenyl)pyridin-2-amido]-dibenzylzirconium(IV); Ap^{9Me}[1,3-(2',6'-$Me_2C_6H_3)_2$(CH_2 $N)_2C{=}N$]$Zr(CH_2Ph)_2$ (Precatalyst **2**).

Toluene (30 mL) was added to $Ap^{9Me}Zr(CH_2Ph)_3$ (300 mg, 0.39 mmol) and 1,3-bis-(2,6-dimethyl-phenyl)imidazolidin-2-ylideneamine (113 mg, 0.39 mmol) at room temperature. The resulting solution was stirred for 3 h at 80 °C with continous stirring. Toluene was evaporated to dryness and the resulting residue was washed with hexane (2 mL) affording **2** as a yellow solid. X-ray quality crystals can be obtained by adding a few drops of THF to a concentrated toluene solution at room temperature. Yield 310 mg (82%). Elemental analysis for $C_{62}H_{73}N_5Zr$ (979.50): calcd. C 76.02, H 7.51, N 7.15; found C 76.53, H 7.79, N 6.69. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 1.07 (d, 6H, J_{HH} = 7.4 Hz, H), 1.16 (d, J_{HH} = 7.7 Hz, H), 1.25 (d, 6H, J_{HH} = 7.4 Hz, H), 1.51 (d, 2H, J_{HH} = 10.2 Hz, $C_6H_5CH_2$), 1.60 (s, 6H, H), 1.67 (d, 2H, J_{HH} = 10.2 Hz, $C_6H_5CH_2$), 2.01 (s, 12H, CH_3), 2.20 (s, 3H, H), 2.75 (sept, 1H, H), 2.90 (s, 4H, NCH_2), 3.15 (sept, 2H, H), 5.35 (d, 1H, J_{HH} = 9.3 Hz, H), 6.00 (d, 4H, J_{HH} = 8.3 Hz, o-$C_6H_5CH_2$), 6.27 (d, 1H, J_{HH} = 8.0 Hz, H), 6.70 – 7.16 (m, 17H, H, m-$C_6H_5CH_2$, p-$C_6H_5CH_2$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 18.3 (s, 4C, CH_3), 19.0 (s, 2C, CH_3), 21.2 (s, 1C, CH_3), 22.6 (s, 2C, CH_3), 24.5 (s, 2C, CH_3), 26.6 (s, 2C, CH_3), 31.0 (s, 2C, CH), 35.0 (s, 1C, CH), 45.2 (s, 2C, NCH_2), 63.1 (s, 2C, $PhCH_2$), 104.9 (s, 1C, CH), 115.1 (s, 1C, CH), 120.7 (s, 1C, Ph), 121.4 (s, 1C, Ph), 125.7 (s, 1C, C), 127.7 (s, 2C, CH), 128.1 (s, 4C, Ph), 128.4 (s, 4C, Ph), 129.0 (s, 2C, CH), 129.3 (s, 2C, C), 129.4 (s, 1C, CH), 133.3 (s, 1C, C), 134.4 (s, 2C, C), 136.1 (s, 1C, C), 137.9 (s, 6C, C_6H_3), 138.0 (s, 2C, NC), 140.1 (s, 1C, C), 144.6 (s, 1C, C), 145.6 (s, 1C, C), 146.0 (s, 2C, C), 147.2 (s, 2C, C), 149.9 (s, 1C, C), 157.1 (s, 1C, C), 167.7 (s, 1C, CN) ppm.

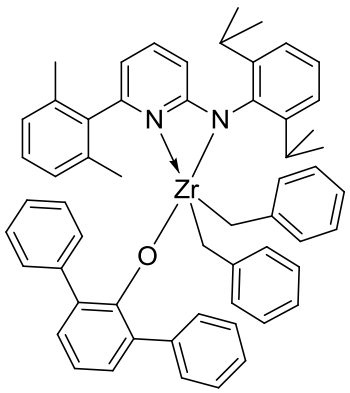
Example 3



Synthesis of [1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imido]-[N-(2,6-diisopropylphenyl)-6-(2,6-dimethylphenyl)pyridin-2-amido]-dibenzylzirconium(IV); $Ap^{+}[1,3\text{-}(2',6'\text{-}Me_2C_6H_3)_2(CH_2N)_2C{=}N]Zr(CH_2Ph)_2$ (Precatalyst **3**).

To a toluene solution (7 mL) containing $Ap^{+}Zr(CH_2Ph)_3$ (202 mg, 0.28 mmol) was added 1,3-bis-(2,6-dimethyl-phenyl)imidazolidin-2-ylideneamine (82 mg, 0.28 mmol) in toluene (7 mL) at room temperature. The reaction mixture was stirred at 50 °C for 12 h. Toluene was evaporated to dryness and the product was washed with hexane (2 mL) to give the yellow product **3**. Suitable crystals for X-ray analysis can be obtained by overlaying a saturated toluene solution with hexane. Yield 241 mg (93%). Elemental analysis for $C_{58}H_{65}N_5Zr$ (923.39): calcd. C 74.44, H 7.10, N 7.58; found C 75.35, H 6,83, N 7.57. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.91 (d, 6H, J_{HH} = 7.4 Hz, H), 1.00 (d, 6H, J_{HH} = 7.4 Hz, H), 2.05 (s, 12H, CH_3), 2.08 (d, 2H, J_{HH} = 10.6 Hz, $C_6H_5CH_2$), 2.21 (d, 2H, J_{HH} = 10.6 Hz, $C_6H_5CH_2$), 2.29 (s, 6H, H), 2.72 (sept, 2H, H), 2.93 (s, 4H, NCH_2), 5.51 (d, 1H, J_{HH} = 9.1 Hz, H), 6.09 (d, 1H, J_{HH} = 8.1 Hz, H), 6.19 (d, 4H, J_{HH} = 8.4 Hz, o-$C_6H_5CH_2$), 6.83 – 7.20 (m, 19H, H, C_6H_3, p-$C_6H_5CH_2$, m-$C_6H_5CH_2$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 18.3 (s, 4C, *C*H_3), 20.7 (s, 2C, *C*H_3), 24.8 (s, 2C, *C*H_3), 25.2 (s, 2C, *C*H_3), 28.3 (s, 2C, *C*H), 45.7 (s, 2C, *C*H_2), 65.9 (s, 2C, *C*H_2), 106.5 (s, 1C, *C*H), 113.3 (s, 1C, *C*H), 120.5 (s, 1C, *C*H), 124.2 (s, 1C, *C*H), 125.5 (s, 1C, *C*), 127.4 (s, 2C, *C*H), 128.1 (s, 3C, *C*H), 128.3 (s, 4C, *C*H), 128.5 (s, 4C, *C*H), 129.0 (s, 2C, *C*H), 129.5 (s, 2C, *C*), 134.8 (s, 1C, *C*), 136.7 (s, 2C, *C*), 137.8 (s, 6C, *C*$_6$H$_3$), 138.2 (s, 2C, N*C*), 140.8 (s, 1C, *C*), 143.0 (s, 1C, *C*), 145.0 (s, 2C, *C*), 146.7 (s, 2C, *C*), 149.8 (s, 1C, *C*), 156.8 (s, 1C, *C*), 172.9 (s, 1C, *C*N) ppm.

Comparative Example 1



Synthesis of [(1,1':3',1"-terphenyl)-2'-oxido]-[N-(2,6-diisopropylphenyl)-6-(2,6-dimethylphenyl)pyridine-2-amido]-dibenzylzirconium(VI); $Ap^{+}(2,6\text{-}Ph_2C_6H_3O)Zr(CH_2Ph)_2$ (Precatalyst **D**).

Toluene (10 mL) was added to $Ap^{+}Zr(CH_2Ph)_3$ (100 mg, 0.138 mmol) and 2,6-diphenylphenol (34 mg, 0.138 mmol) at room temperature. The reaction mixture was stirred at 80 °C for 12 h. Toluene was evaporated to dryness and the product was washed with hexane (5 mL) affording **D** quantitatively as a light yellow spectroscopically pure compound. Suitable crystals for X-ray analysis can be obtained by refluxing a saturated toluene solution for 15 min. and subsequent cooling the solution to room temperature. Yield 114 mg (94%). Elemental analysis for $C_{57}H_{56}N_2OZr$ (876.29): calcd. C 78.13, H 6.44, N 3.20; found C 77.85, H 6.57, N 3.13. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.85 (d, 3H, J_{HH} = 7.5 Hz, H), 1.00 (d, 3H, J_{HH} = 7.6 Hz, H), 1.14 (dd, J_{HH} = 7.5, 7.4 Hz, 6H, H), 1.95 – 2.03 (m, 10H, H, $C_6H_5CH_2$), 3.22 (sept, 1H, H), 3.55 (sept, 1H, H), 5.63 (d, J_{HH} = 8.0 Hz, 1H, H), 6.16 (d, J_{HH} = 8.7 Hz, 1H, H), 6.34 (d, J_{HH} = 10.8 Hz, 4H, o-$C_6H_5CH_2$), 6.67 (t, J_{HH} = 7.3 Hz, 2 H, p-$C_6H_5CH_2$), 6.75 – 7.11 (m, 24H, H, m-$C_6H_5CH_2$, $Ph_2C_6H_3$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 19.9 (s, 2C, CH_3), 23.9 (s, 2C, CH_3), 25.4 (s, 2C, CH_3), 28.9 (s, 2C, CH), 80.1 (s, 2C, CH_2), 105.6 (s, 1C, CH), 114.5 (s, 1C, CH), 121.6 (s, 1C, CH), 122.2 (s, 1C, CH), 124.1 (s, 1C, CH), 124.4 (s, 2C, CH), 124.6 (s, 1C, C), 127.3 (s, 1C, C), 127.7 (s, 3C, CH), 128.1 (s, 4C, CH), 128.2 (s, 2C, CH), 128.4 (s, 4C, CH), 128.8 (s, 2C, CH), 128.9 (s, 4C, CH), 129.8 (s, 4C, CH), 130.2 (s, 2C, CH), 132.7 (s, 2C, C), 135.8 (s, 1C, C), 137.7 (s, 1C, C), 139.8 (s, 2C, C), 142.9 (s, 1C, C), 143.1 (s, 1C, C), 144.7 (s, 1C, C), 147.9 (s, 1C, C), 156.1 (s, 1C, C), 160.4 (s, 1C, C), 172.7 (s, 1C, C) ppm.

Example 4 and Comparative Example 2

Ethylene oligomerization experiments for Runs 1 – 3 (according to the invention) and 4 to 6 (comparative)

The catalytic ethylene oligomerization reactions were performed in a 250 mL glass autoclave (Büchi) in semi-batch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was ethylene flow controlled and equipped with separated toluene, precatalyst and activator injection systems. During a oligomerization run the pressure and the reactor temperature were kept constant while the ethylene flow was monitored continuously. In a typical semi-batch experiment, the autoclave was evacuated and heated for 1 h at 80 °C prior to use. The reactor was then brought to desired temperature, stirred at 1000 rpm and charged with 150 mL of toluene. After pressurizing with ethylene to reach 0.2 MPa (2 bar) total pressure the autoclave was equilibrated for 10 min. Successive co-catalyst solution, activator, and 1 mL of a 0.002 M precatalyst stock solution in toluene was injected, to start the reaction. After 15 min. reaction time the reactor was vented and the residual aluminum alkyls were destroyed by addition of 50 mL of ethanol. Polymeric product was collected, stirred for 30 min. in acidified ethanol and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried on air and subsequently in vacuum at 80 °C.

The results are listed in the following table 1:

Table 1. *Ethylene oligomerization experiments with precatalysts 1 to 3 and D.*

Entry	Precat.	T [°C]	$m_{Pol.}$ [g]	Activity [$kg_{PE} \cdot mol_{cat}^{-1} \cdot h^{-1} \cdot bar^{-1}$]	M_n [$kg \cdot mol^{-1}$]	M_w/M_n
1	**1**	50	1.67	1670	8.4	2.5
2	**2**	50	4.20	4200	6.5	2.5
3	**3**	50	4.50	4500	6.2	3.0
4	**D**	30	traces	n.d.	n.d.	n.d.
5	**D**	50	0.10	98	156525	21.2
6	**D**	70	0.13	128	117274	40.1

Conditions for all runs: precatalyst: 2.0 μmol; activator 2.2 μmol ($[R_2NMeH][B(C_6F_5)_4]$, Zr/B = 1/1.1); toluene: 150 mL; p(ethylene) = 0.2 MPa ; t = 15 min.

Example 5

General description of ethylene oligomerization experiments for Runs 7 – 17

The catalytic ethylene oligomerization reactions were performed in a 250 mL glass autoclave (Büchi) in semi-batch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was ethylene flow controlled and equipped with separated toluene, precatalyst and activator injection systems. During an oligomerization run the pressure and the reactor temperature were kept constant while the ethylene flow was monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 h at 80 °C prior to use. The reactor was then brought to the desired temperature, stirred at 1000 rpm and charged with 150 mL of toluene together with the activator *N*,*N*,*N*-trialkylammonium(tetrapentafluoro-phenyl)borate (220 nmol, 2.45 mg, 11% stock solution in Isopar), the required amount of TIBA (0.1 mL of a 1.0 M solution of TIBA (tri-isobutylaluminum, Zr/Al = 1/500) and 1 g cumene was added as an internal standard, unless mentioned different in the text. After pressurizing with ethylene to reach the desired total pressure, the autoclave was equilibrated for 5 min. Subsequently, 1 mL of a 0.0002 M catalyst stock solution in toluene was injected to start the reaction. During the run, the ethylene pressure was kept constant to within 0.01 MPa of the initial pressure by replenishing the gas flow. After a 15 min. reaction time, the reactor was vented and the solution was then analyzed by GC to determinate the activity and the product distribution.

Example 6

General description of ethylene oligomerization experiments for Runs 18

The catalytic ethylene oligomerization reactions were performed in a 250 mL glass autoclave (Büchi) in semi-batch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was ethylene flow controlled and equipped with separated toluene, precatalyst and activator injection systems. During a oligomerization run the pressure and the reactor temperature were kept constant while the ethylene flow was monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 h at 80 °C prior to use. The reactor was then brought to the desired temperature, stirred at 1000 rpm and charged with 150 mL of toluene together with the activator d-MAO (11.6 mg, 0.2 mmol Zr/Al = 1000). Cumene (1 g) was added as an internal standard. After pressurizing with ethylene to reach a total pressure of 0.2 MPa (2 bar), the autoclave was equilibrated for 5 min. Subsequently, 1 mL of a 0.0002 M catalyst stock solution in toluene was injected to start the reaction. During the run, the ethylene pressure was kept constant to within 0.01 MPa of the initial pressure by replenishing the gas flow. After a 15 min. reaction time, the reactor was vented and the solution was then analyzed by GC to determinate the activity and the product distribution.

Table 2. Ethylene oligomerisation experiments with precatalysts **1** to **3**.

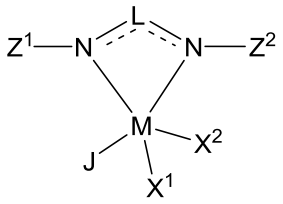
Nr.	Precat.	T °C	Yield [g]	Activity [kg·mol$_{cat}^{-1}$·h^{-1}·bar^{-1}]	C_4 wt.-%	C_6 wt.-%	$>C_6$ wt.-%	purity C_6-fract. [% 1-hexene]
7	**1**	30	2.41	24125	15	20	65 (C_8-C_{24})	> 99
8	**1**	50	2.73	27250	16	20	64 (C_8-C_{24})	> 99
9	**1**	70	3.55	35500	17	18	65 (C_8-C_{30})	> 99
10[b]	**1**	50	0.48	9500	17	21	62 (C_8-C_{22})	> 99
11[c]	**1**	50	2.65	13250	17	22	61 (C_8-C_{26})	> 99
12	**2**	30	1.99	19875	62	27	11 (C_8-C_{12})	> 99

13	**2**	50	2.03	20250	45	31	24 (C_8-C_{18})	> 99
14	**2**	70	0.98	9750	31	30	40 (C_8-C_{14})	> 99
15	**3**	30	4.88	48750	32	29	39 (C_8-C_{22})	> 99
16	**3**	50	3.63	36250	23	27	50 (C_8-C_{24})	> 99
17	**3**	70	1.3	13000	18	24	59 (C_8-C_{14})	> 99
18[d]	**3**	50	0.33	3250	14	17	69 (C_8-$_{20}$)	> 99

Conditions for all runs, deviations are specifically indicated (cf. footnotes [b], [c] and [d]): precatalyst: 0.2 μmol; activator 0.22 μmol ($[R_2NMeH][B(C_6F_5)_4]$, Zr/B = 1/1.1); scavenger: 100 μmol (TIBA); toluene: 150 mL; p(ethylene) = 0,2 MPa ; t = 15 min; yield by ethylen-flow; wt.-% and purity by GC and GCMS-analysis. [b]p(ethylene) = 0.1 MPa. [c]p(ethylene) = 0.4 MPa. [d]activator d-MAO (Zr/Al = 1/1000).

5.12 Claims

1. A complex of formula (I):



(I)

wherein

M is a metal selected from Zr and Hf;

X^1 and X^2 are independently selected from Cl, Br, I, F, H, alkyl, -alkyl-O-alkyl, -alkyl-O-aryl, alkoxy, aryloxy, aralkyl, -alkyl-$SiR^aR^bR^c$, and NR^1R^2, wherein any alkyl group is optionally substituted by one or more substituents selected from OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and $N(C1\text{-}8\ alkyl)_2$, and any aryl group is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, OH, F, Cl, Br, NH_2, NH(C1-8 alkyl) and $N(C1\text{-}8\ alkyl)_2$;

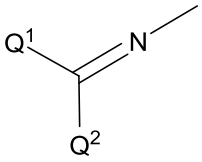
L is selected from CZ^3, N, and PR^3R^4;

Z^1 and Z^2 are independently selected from alkyl, cycloalkyl, heterocycloalkyl, alkenyl, aryl, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl, wherein any alkyl group, alone or as part of another group, and any alkenyl group is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and any aryl group, alone or as part of another group, and any heteroaryl group is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$;

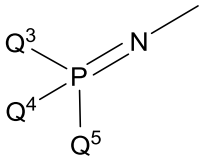
Z^3 is selected from H, alkyl, cycloalkyl, heterocycloalkyl, alkenyl, alkoxy, aryl, aryloxy, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl, F, Cl, Br, NR^1R^2, and PR^3R^4, wherein any alkyl group, alone or as part of another group, and any alkenyl group is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and wherein any aryl group, alone or as part of another group, and any heteroaryl group is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$;

or any suitable groups Z^1 and Z^3 or Z^2 and Z^3 as defined above may be linked to form an optionally substituted five- to seven-membered heterocyclic ring incorporating the nitrogen atom to which Z^1 is attached or the nitrogen atom to which Z^2 is attached;

J is selected from a ligand of the formula (II) or (III):



(II)



(III),

wherein

Q^1 to Q^5 are independently selected from alkyl, cycloalkyl, heterocycloalkyl, alkenyl, alkoxy, aryl, aryloxy, heteroaryl, aralkyl, -alkyl-O-alkyl, -alkyl-O-aryl and NR^5R^6, wherein any alkyl group, alone or as part of another group, and any alkenyl group is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group , alone or as part of another group, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$;

or any suitable groups Q^1 and Q^2 as defined above may be linked to form a five- to seven-membered, carbocyclic or heterocyclic, saturated or unsaturated ring together with the carbon atom to which they are attached, or any suitable groups Q^3 and Q^4 as defined above or Q^4 and Q^5 as defined above may be linked to form a five- to seven-membered, heterocyclic, saturated or unsaturated ring together with the P-atom to which they are attached;

R^a, R^b and R^c are independently selected from alkyl and aryl; and

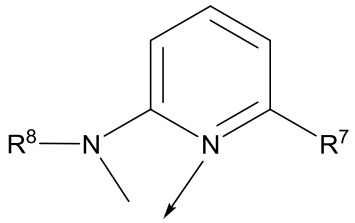
R^1, R^2, R^3, R^4, R^5 and R^6 are independently selected from H, alkyl, cycloalkyl, alkenyl, aryl, and aralkyl, wherein any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$;

or any suitable groups R^1 and R^2 as defined above, R^3 and R^4 as defined above or R^5 and R^6 as defined above may be linked to form an optionally substituted five or six-membered heterocyclic ring including the N or P atom to which they are attached; or, where Q^1 and Q^2, Q^3 and Q^4 or Q^4 and Q^5 are NR^5R^6, two groups R^5 or two groups R^6 as defined above may be linked to form an optionally substituted saturated or unsaturated heterocycle including the two N atoms of the groups NR^5R^6;

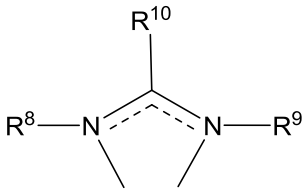
or one of Q^1 to Q^5 as defined above may be linked with one of Z^1 or Z^2 as defined above to form a metallacycle including M.

2. The complex of formula (I) in accordance with claim 1, wherein L is CZ^3.

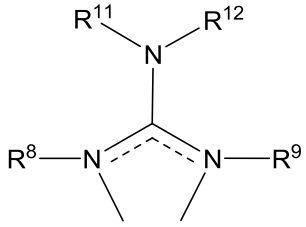
3. The complex of formula (I) in accordance with claim 1, wherein the ligand containing Z^1, L and Z^2 is a ligand is selected from the following formulae (IVa) to (IVc)



(IVa)



(IVb)



(IVc).

wherein

R^7, R^8, and R^9 are independently selected from alkyl, cycloalkyl, aryl, and aralkyl, wherein

any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$;

R^{10} is selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$. Preferably, the aryl group is not substituted or substituted by one or more C1-8 alkyl groups; and

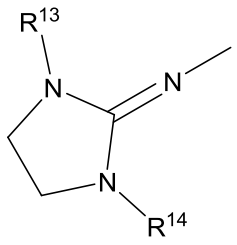
R^{11} and R^{12} are independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein

any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and $N(C1\text{-}8\ alkyl)_2$; or R^{11} and R^{12} as defined above may be linked to form an optionally substituted five or six-membered heterocyclic ring including the N atom to which they are attached.

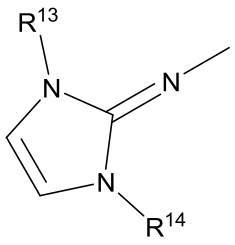
4. The complex of formula (I) in accordance with claim 3, wherein the ligand containing Z^1, L and Z^2 is a ligand of formula (IVa)

5. The complex of formula (I) in accordance with any of claims 1 to 4, wherein J is a ligand of formula (II).

6. The complex of claim 5, wherein J is a ligand of formula (IIa) or (IIb):



(IIa)



(IIb),

wherein

R^{13} and R^{14} are independently selected from H, alkyl, cycloalkyl, aryl, and aralkyl, wherein

any alkyl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from F, Cl, Br and N(C1-8 alkyl)$_2$ and wherein any aryl group, alone or as part of aralkyl, is optionally substituted by one or more substituents selected from C1-8 alkyl, phenyl, C1-8 alkoxy, F, Cl, Br and N(C1-8 alkyl)$_2$.

7. The complex of formula (I) in accordance with any of claims 1 to 4, wherein J is a ligand of formula (III).

8. The complex of formula (I) in accordance with any of claims 1 to 7, wherein X^1 and X^2 are independently selected from Cl, Br, alkyl, -alkyl-$SiR^aR^bR^c$, and aralkyl.

9. A method for the oligomerization of an olefin, which comprises a step of contacting the complex of formula (I) as defined in any of claims 1 to 8, with an olefin.

10. The method of claim 9, wherein the complex of formula (I) is contacted with the olefin in the presence of an activator.

11. The method of claim 9 or 10, wherein the olefin is ethylene.

EP 13158550, **2013**. (Patent Application)

Applicant: Universität Bayreuth

BayPat Ref.: B72249 EP

Vossius & Partner Ref.: W1086 EP

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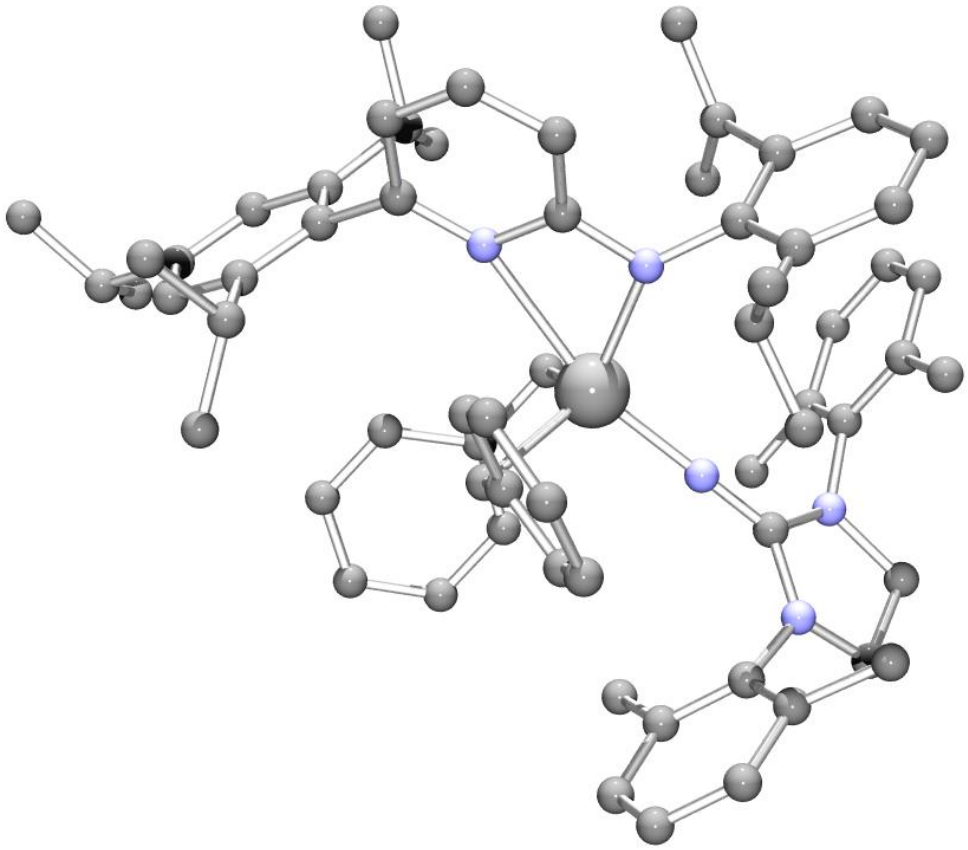

Figure 1

6 A Highly Efficient Titanium Catalyst for the Synthesis of Ultra-High Molecular Weight Polyethylene (UHMWPE)

Isabelle Haas,[a] Christian Hübner,[a] Winfried P. Kretschmer[a] and Rhett Kempe[a]*

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Keywords: Ethylene Polymerization • N ligands • Mixed ligand complexes • Titanium • UHMWPE

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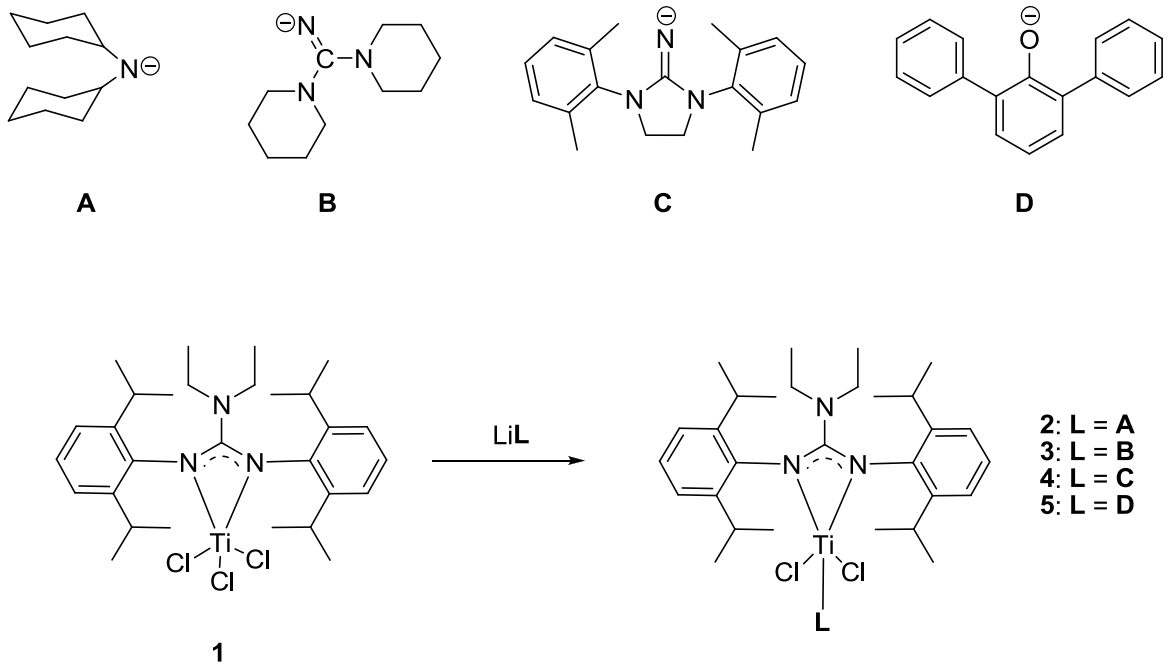
6.1 Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a unique polymer with outstanding physical and mechanical properties. Its molecular weight lies in the range of 2 to 6 million g·mol^{-1}. Most notable are its chemical inertness, lubricity, impact resistance, and abrasion resistance. Therefore UHMWPE has a variety of important commercial uses, including polymer components in knee and hip replacements,[1] pickers for textile machinery, microporous films for battery separators,[2] lining for coal chutes and dump trucks, runners for bottling production lines, as well as bumpers and siding for ships and harbors.[3] We are investigating group 4 metal based polymerization catalysts stabilized by very bulky monoanionic bidentate N-ligands.[4] Recently, our group discovered a guanidinato titanium catalyst system which is able to polymerize ethylene by coordinative chain transfer polymerization.[5] It is highly active in the presence of very high chain transfer agent to catalyst ratios and undergoes polyethylene chain transfer to triethylaluminum. These results encouraged us to develop the new titanium based polymerization catalyst class [GuaTi**L**Cl_2] (Gua = 1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato; **L** = additional monoanionic ligand like, for instance, imidazolidin-2-imide, guanidinate, phenoxide or amide; Scheme 1). Since the bulky guanidinato ligand Gua is monoanionic a second monoanionic ligand can be introduced to alter the properties of the already highly active polymerization catalyst **1** (Scheme 1). Some of the used additional ligands **L**, such as aryloxides[6] and guanidinates[7] or closely related ketimides[8] and phosphoraneimides[9] are already documented in the olefin polymerization chemistry literature, but were never combined with guanidinate ligands. Here we

report on the synthesis and structure of titanium dichloro complexes of the type [GuaTi**L**Cl_2] and their use in ethylene polymerization. One of the introduced catalysts is able to produce UHMWPE with a very high activity.



Scheme 1. Monodentate ancillary ligands (top); synthesis of the complexes **2–5** (bottom).

6.2 Results and Discussion

The titanium precursor complex **1** (Scheme 1) was easily prepared via the reaction of diethylamido titanium trichloride[10] with *N,N'*-bis(2,6-diisopropyl)carbodiimide through methanediimine insertion into the titanium-amide bond.[5] The lithium 1,1,3,3-bis(pentamethylene)guanidinate **LiB** was prepared in situ by reaction of piperidyl lithium with 1-piperidinecarbonitrile,[11] while the sterically protected 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imine **HC** was prepared from the corresponding 1,2-dianilinoethane and cyanogen bromide in toluene according to literature procedures.[12] The two other monoanionic monodentate ligands used are 2,6-diphenylphenoxide **D** and dicyclohexylamide **A** (Scheme 1). Both of them are commercially available, in their protonated form, and were transferred to their corresponding lithium salts via deprotonation of the hydroxide function or amine function, respectively. The guanidinato titanium dichloride complexes **2–5** were prepared by simple salt elimination reactions from the titanium precursor **1** and the Li salts of the ligands (Scheme 1). All complexes were analyzed by NMR spectroscopy, elemental analysis and single crystal structure analysis. Crystals suitable for X-ray analysis were obtained by layering concentrated toluene solutions with hexane or by recrystallization from toluene. The molecular structures of complexes **2–5** are presented

in Figure 1 and Figure 2. Selected bond lengths and angles are listed in Table 1. Crystallographic details are available in the Supporting Information (Table S1).

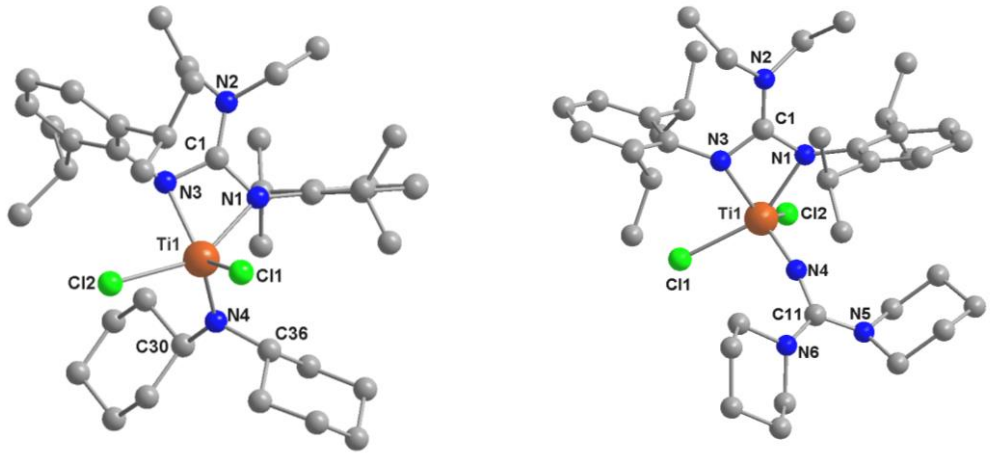


Figure 1. Molecular structures of **2** (left) and **3** (right). Carbon-bonded hydrogen atoms and one toluene molecule in the asymmetric unit of complex **3** are omitted for clarity.

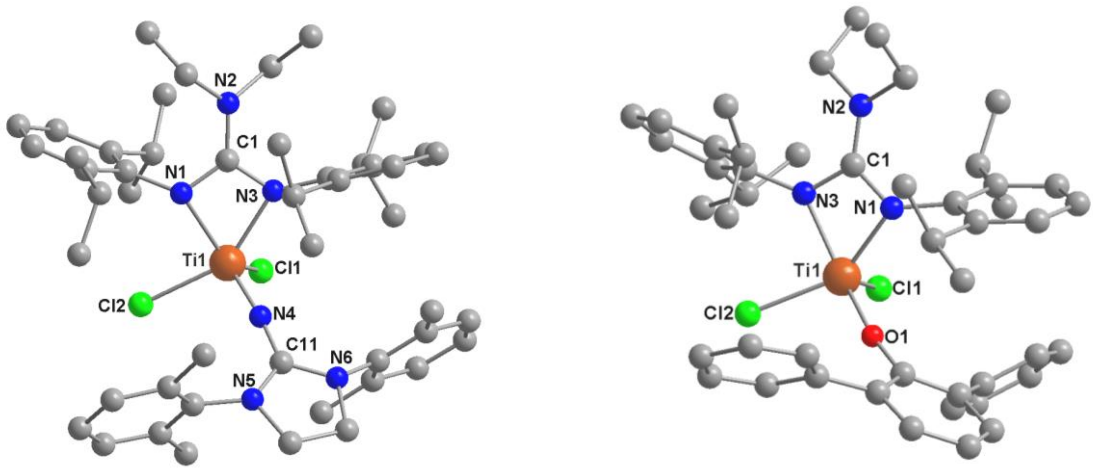


Figure 2. Molecular structures of **4** (left) and **5** (right). Complex **4** crystallized with two independent molecules per asymmetric unit. Carbon-bonded hydrogen atoms are omitted for clarity.

Complexes **2** and **3** crystallize in the monoclinic space group $P2_1/n$, complex **4** in the monoclinic space group C2/c and complex **5** in the monoclinic space group $P2_1$. The titanium center in all four complexes is coordinated in a roughly trigonal bipyramid by the guanidinate ligand, an ancillary ligand and two chloro ligands. The equatorial positions are occupied by Cl1, Cl2 and one of the guanidinate nitrogen donors (N1 in complex **2**, **3** and **5**; N3 in complex **4**). The axial positions are occupied by the second nitrogen donor of the guanidinate ligand and the ancillary ligand's donor atom. The distortion of the trigonal bipyramid results from the very small bite angle of the chelating guanidinate (range 62–

64°), caused by the high steric demand of the 2,6-diisopropyl moieties. The angles around the chelating guanidinate central atom are distorted because of the coordination to the titanium center. The N-C-N angle between the ligating nitrogens is considerably smaller than 120° (range 106–110°) whilst the remaining angles are greater than 120° (range 124–128°). However, the sum of the angles around the central carbon for each chelating guanidinate ligand is 360° indicating no deviation from planarity.[13] Complex **5** shows the same bond length of 1.353(4) Å for all three C-N bonds, they are therefore indistinguishable indicating considerable delocalization of the uncoordinated nitrogen's lone pair into the ligand π-system.[14] This stands in contrast to the crystallographic data of complexes **2**, **3** and **4** in which the C-N bond to the uncoordinated nitrogen atom (range 1.359(2)–1.376(5) Å) is slightly longer than those involving the coordinated nitrogen atoms (range 1.337(5)–1.3533(19) Å).

Table 1. Selected bond lengths [Å] and angles [°].

Complex	2	3	4	5
Ti1-Cl1	2.2851(5)	2.3462(5)	2.2788(13)	2.2185(9)
Ti1-Cl2	2.3232(5)	2.3035(5)	2.3216(14)	2.2824(10)
Ti1-N1	2.0839(13)	2.0787(13)	2.150(3)	2.047(3)
Ti1-N3	2.1011(13)	2.1239(13)	2.097(4)	2.055(2)
Ti1-N4	1.8663(13)	1.7662(14)	1.765(3)	-
Ti1-O1	-	-	-	1.8100(19)
C1-N1	1.3431(19)	1.348(2)	1.337(5)	1.353(4)
C1-N2	1.368(2)	1.359(2)	1.376(5)	1.353(4)
C1-N3	1.3533(19)	1.350(2)	1.336(5)	1.353(4)
C11-N4	-	1.327(2)	1.326(5)	-
C11-N5	-	1.355(2)	1.353(5)	-
C11-N6	-	1.367(2)	1.360(5)	-
N4-C30	1.483(2)	-	-	-
N4-C36	1.493(2)	-	-	-
N1-C1-N3	110.05(13)	109.21(13)	110.2(4)	106.6(3)
N1-Ti1-N3	63.73(5)	63.10(5)	62.15(13)	63.85(10)
Ti1-N4-C11	-	168.05(12)	170.5(3)	-
Cl1-Ti1-Cl2	95.108(18)	95.867(18)	94.86(5)	101.10(4)
∑<(C1)	359.99	359.99	360.0	360.0
∑<(C11)	-	359.99	359.8	-
∑<(N4)	359.98	-	-	-

Closer examination of the ancillary monodentate ligand shows that the sum of the bond angles around C11 is 359.99° (for complex **3**) and 359.8° (for complex **4**), which confirms that the carbon atoms are sp^2–hybridized. An advantage of the monodentate guanidinate ligands is that they can donate more than two electrons to the titanium center due to the presence of lone pairs and C=N double bonds. The additional π-bonds increase the Ti-N bond order and strength, simultaneously decrease the electron deficiency of the titanium center and altogether the stability of the complex is enhanced. Furthermore, as electron donation is maximal when there is a linear Ti-N=C arrangement, consequently the angles in complexes **3** and **4** are found to lie around 170° (170.5° for **4**, 168.1° for **3**). Complex **5** also shows the favorably linear Ti-O-C arrangement with an angle of 170.7(2)°. Moreover, the zwitterionic resonance structures of the two monoanionic guanidinates of complexes **3** and **4** increase the negative charge on the metal-binding nitrogen. The bond lengths of the ancillary ligand and the metal center illustrate this: While the titanium-nitrogen bond lengths are 1.765(3) Å and 1.7662(14) Å in the two guanidinate complexes **4** and **3**, the titanium-oxygen bond length is significantly longer with 1.8100(19) Å in the aryloxide complex **5** and the titanium-amide bond length amounts to 1.8663(13) Å in complex **2**. The N-C bond lengths N4–C30 (1.483(2) Å) and N4–C36 (1.493(2) Å) in the amide complex **2** are significantly longer than $C(sp^3)$–N single bonds,[15] but the sum of the bond angles around N4 is 359.98° and the Ti1-N4 bond length is 1.8663(13) Å short which clearly confirms the sp^2–hybridization of N4.

Table 2. Ethylene homopolymerization with complexes **1–5** (2 μmol Ti complex, 150 mL toluene, 2 bar ethylene, 50 °C, 15 min. run time).

Entry	Cat.	Co-cat.	n(Co-cat.) [μmol]	m(Polymer) [g]	Activity [kg·mol^{-1}·h^{-1}·bar^{-1}]	M_w [g·mol^{-1}][a]	M_w/M_n[a]
1	**1**	MAO	1300	1.67	1670	21000	2.5
2	[b]	MAO	1300	0.18	180	417000	14.5
3	**2**	MAO	1300	-	-	-	-
4	**3**	MAO	1300	0.45	450	19000	2.5
5	**4**	MAO	1300	0.97	970	1259000 (2385000)	93.3
6	**5**	MAO	1300	1.35	1350	188000 (412000)	20.8
7	**1**	d-MAO	1000	1.36	1360	172000	3.3
8	[b]	d-MAO	1000	0.36	360	1465000	123.3
9	**2**	d-MAO	1000	-	-	-	-

10	**3**	d-MAO	1000	2.10	2100	280000	20.9
11	**4**	d-MAO	1000	5.56	5560	1546000	3.8
12	**4**[c]	d-MAO	1000	0.88	8800	2488000	3.4
13	**5**	d-MAO	1000	0.76	760	369000	1.8

[a] Determined by HT-GPC analysis; [b] (*N,N*-Dicyclohexylamido)titanium trichloride; [c] 0.2 µmol Ti complex; numbers in parentheses display the high molecular weight fraction of bimodal distributions.

In order to compare their efficiency in ethylene polymerization, all synthesized complexes were activated with MAO (Table 2, entries 1-6). Complex **1**, without any ancillary ligand, was taken as reference system for the polymerization performances of the new catalyst systems **2**–**5**. The polymerization data of complex **1** activated with MAO showed a high activity of 1670 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$, a polydispersity of 2.5 and a molecular weight of 21000 $g \cdot mol^{-1}$. Complex **2** did not show any polymerization activity after activation with MAO whereas the control test with (*N,N*-dicyclohexylamido)titanium trichloride gave some low polymerization activity. Comparison of the polymerization results of complex **3** and complex **1**, both activated with MAO, showed nearly identical data. Molecular weights of about 20000 $g \cdot mol^{-1}$ and PDIs of 2.5 were obtained (Figure 3).

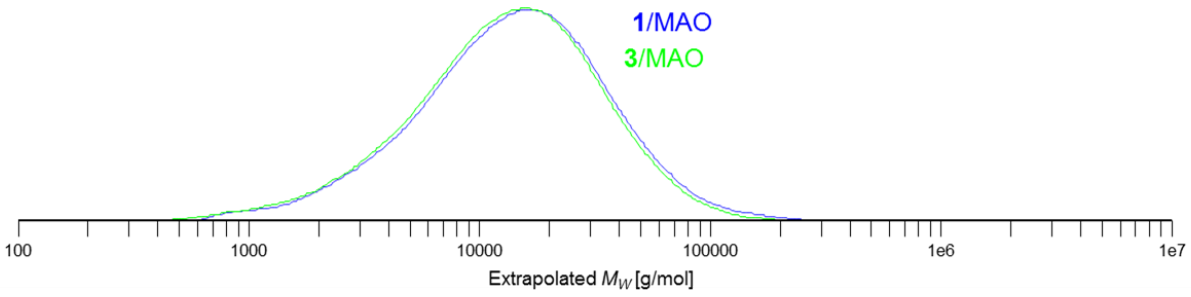


Figure 3. M_W distribution plots of polymers (Table 2, entries 1 and 4).

This concordance indicates an immediate transfer of the ancillary guanidinate ligand of complex **3** to the aluminum alkyl which is usually present in MAO in small amounts. Activation of complex **4** with MAO leads to a clearly bimodal distribution (entry 5). This indicates that two active sites are operating during the polymerization process. The lower molecular weight fraction is identical to the one observed for precatalyst **1**/MAO (entry 1, Figure 4). The very high molecular weight fraction indicates the potential of the catalyst to produce UHMWPE.

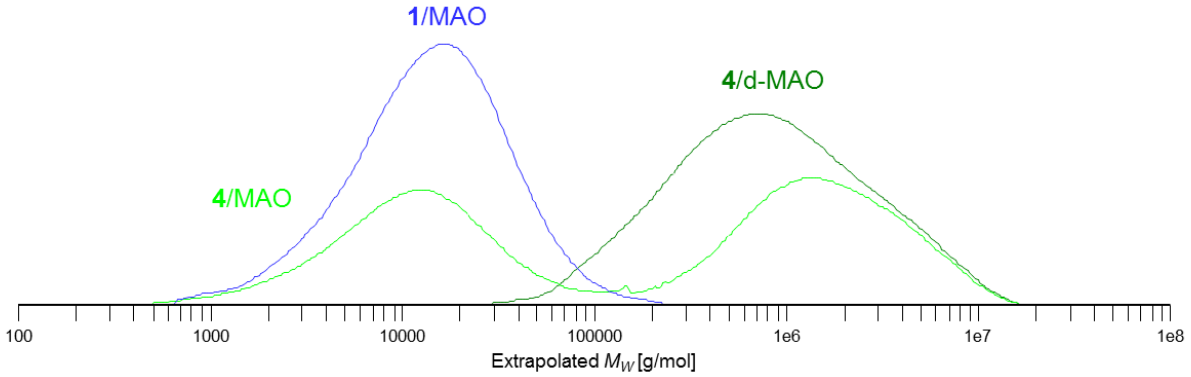


Figure 4. M_W distribution plots of polymers (entries 5, 8 and 11, Table 2).

These GPC data are an explicit evidence for ligand transfer of the imidazolidin-2-imido ligand to the aluminum alkyl. In comparison to the catalyst system **3**/MAO, where immediate ligand transfer is observed, the catalyst system **4**/MAO showed gradual ligand transfer to aluminum alkyls during the 15 min. polymerization runtime. The slower transfer may be due to the higher steric hindrance of the imidazolidin-2-imido ligand compared to the ancillary guanidinate ligand in catalyst system **3**. After activation with MAO catalyst precursor **5** also showed a bimodal distribution of the resulting polymer. The GPC spectra are consistent with the ones obtained by catalyst precursor **4** and indicate that after activation with MAO the obtained low molecular weight fraction is similar to the one obtained with **1**/MAO (entry 1) and the high molecular weight fraction is similar to the one obtained with **5**/d-MAO (entry 13, Figure S1 in the Supporting Information). Even small amounts of free TMA, like in MAO, suffice to transfer the ancillary aryloxide to aluminum. To completely inhibit the ligand transfer described above, all the catalyst precursors were tested with d-MAO as activator, from which free TMA was removed (Table 2, entries 7–13). Under these conditions complex **1** gave a higher molecular weight together with a broader PDI because efficient chain transfer to aluminum was suppressed. Complex **2** did not show any polymerization activity while the control experiment with (*N,N*-dicyclohexylamido)titanium trichloride showed an increase in the molecular weight and an extremely broad polydispersity. The activity of catalyst system **3** significantly increased by the use of d-MAO as activator, as did the molecular weight of the obtained polymer. Complexes **4** and **5** showed monomodal distributions after activation with d-MAO. The GPC spectrum of **5**/d-MAO demonstrated with 1.8 the narrowest PDI of all the tested systems. Furthermore, the activity of catalyst system **4**/d-MAO increased dramatically, as did the molecular weight of the obtained polymer. By lowering the amount of active catalyst from 2 to 0.2 µmol, to avoid diffusion control, activity and molecular weight could be further enhanced, reaching 8800 $kg \cdot mol^{-1} \cdot h^{-1} \cdot bar^{-1}$ and ultra-high molecular weight PE of 2500 $kg \cdot mol^{-1}$.

6.3 Conclusion

In summary, we could show that the reaction of the lithiated amine, guanidine, imidazolidin-2-imine or phenol with [GuaTiCl$_3$] (**1**) selectively led to the desired non-bridged titanium dichlorides. The "addition" of a second anionic ligand alters the polymerization behavior of the originally used precursor complex **1** drastically. Some complexes are absolutely inactive and other show about one order of magnitude higher activity than the already highly active precursor **1**. Furthermore, drastically different polymer products can be obtained - for instance UHMWPE. The many bulky monoanionic non-Cp ligands developed in recent years might be useful candidates to further develop non-bridged mixed ligand group 4 metal complexes combining high polymerization activity and unusual selectivity patterns.

Supporting Information Available

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

Acknowledgements

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6.5 Supporting Information

Table S1. Details of the X-ray crystal structure analyses of complexes **2**–**5**.

Compound	**2**	**3**	**4**	**5**
Formula	$C_{41}H_{66}Cl_2N_4Ti$	$C_{47}H_{72}Cl_2N_6Ti$	$C_{48}H_{66}Cl_2N_6Ti$	$C_{47}H_{57}Cl_2N_3OTi$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1$
a [Å]	10.4350(3)	10.6860(3)	61.2560(10)	10.3710(5)
b [Å]	19.7910(5)	25.4820(6)	10.2690(3)	17.3720(8)
c [Å]	20.2030(5)	17.4500(4)	43.8550(9)	12.5500(6)
α [°]	90	90	90	90
β [°]	104.477(2)	99.011(2)	133.928(2)	109.078(4)
γ [°]	90	90	90	90
V [Å^3]	4039.83(18)	4693.0(2)	19868.1(8)	2136.88(18)
Z	4	4	16	2
Crystal size [mm^3]	0.98×0.73×0.50	0.87×0.74×0.59	0.52×0.16×0.13	0.34×0.20×0.09
$\varrho_{calc.}$ [g·cm^{-3}]	1.206	1.186	1.131	1.241
μ [mm^{-1}] (Mo-Kα)	0.377	0.334	0.316	0.363
T [K]	133(2)	133(2)	133(2)	133(2)
θ range [°]	1.46–25.65	1.43–25.63	1.29–25.38	1.67–26.14
Reflections unique	7617	8835	18735	8048
Refl. Obs. [I > 2σ(I)]	6004	7877	9881	6065
Parameters	443	505	1027	487
wR_2 (all data)	0.0807	0.1061	0.1655	0.0759
R_1 value [I > 2σ(I)]	0.0311	0.0378	0.0674	0.0438
Largest diff. peak and hole [e·Å^{-3}]	0.323/-0.286	0.306/-0.336	0.597/-0.344	0.529/-0.249

CCDC-931074 (for **2**), -931073 (for **3**), -931071 (for **4**) and -931072 (for **5**) 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.

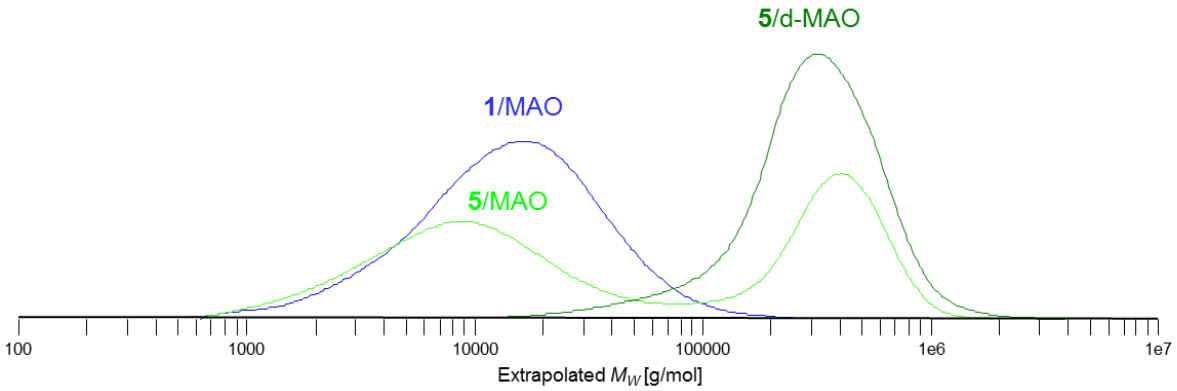


Figure S1. M_W distribution plots of polymers (entries 1, 6 and 13, Table 2).

General Comments: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in a nitrogen or argon filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1 ppm O_2). Deuterated solvents were obtained from Cambridge Isotope Laboratories. Solvents and reagents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy, or sodium ketyl of benzophenone under nitrogen immediately before use.

Toluene for polymerization (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), a 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). MAO (10 wt.-% in toluene, Aldrich) was used as received. D-MAO was prepared by removal of volatiles from PMAO (4.9 wt.-% Al).

Commercial piperidine, 2,6-diphenylphenol, dicyclohexylamine, and titanium(IV) chloride were used as received from Sigma-Aldrich. Piperidine-1-carbonitrile was used as received from Acros Organics. The ligand precursor 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imine[1] and the complex precursors [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato]titanium trichloride[2] and (*N*,*N*-dicyclohexylamido)-titanium trichloride[3] were prepared according to published procedures.

Gel permeation chromatography (GPC): Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories Ltd. PL-GPC 220 high temperature chromatographic unit equipped with DP and RI detectors and two linear mixed bed columns (Olexis, 13 micron particle size). GPC analysis was performed 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 the solutions were run without filtration. The molecular weights of the samples were referenced to polyethylene (M_w = 520–3200000 g·mol^{-1}) and polystyrene (M_w = 580–2800000 g·mol^{-1}) standards. The reported values are the average of at least two independent determinations.

NMR Spectroscopy: NMR spectra were recorded on a Varian INOVA 300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) or INOVA 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 25 °C, were referenced internally using the residual solvent resonances. The chemical shifts (δ) are reported in ppm.

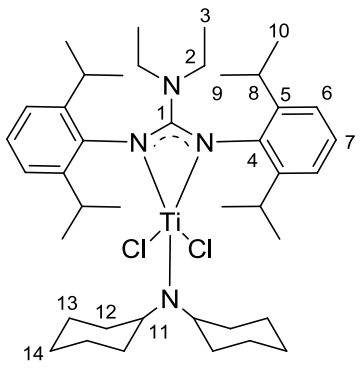
Elemental Analyses (C,H,N): Elemental analyses (C,H,N) were carried out with a Vario elementar EL III instrument.

X-ray Crystallography: X-ray crystal structure analyses were performed with a STOE-IPDS II instrument equipped with an Oxford Cryostream low-temperature unit (λ(MoKα) = 0.71073 Å). Structure solution and refinement were accomplished using SIR97,[4] SHELXL-97[5] and WinGX.[6] Details of the X-ray crystal structure analyses are listed in Table S1.

General Description of Ethylene Polymerization Experiments: The catalytic ethylene polymerization reactions were performed in a 250 mL glass autoclave (Büchi) equipped with a mechanical stirrer in semibatch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature- and pressure-controlled and equipped with separated toluene, catalyst and cocatalyst injection systems. During a polymerization run, the pressure, the ethylene flow, the inner and outer reactor temperature, and the stirrer speed were monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 h at 80 °C prior to use. The reactor was then brought to the desired temperature, stirred at 1000 rpm and charged with 150 mL of toluene together with the activator MAO or d-MAO (dry methylaluminoxane). After pressurizing with ethylene to reach a total pressure of 2 bar, the autoclave was equilibrated for 5 min. Subsequently, 1 mL of a 0.002 M catalyst stock solution in toluene was injected to start the reaction. During the run, the ethylene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing the gas flow. After a 15 min. reaction time, the reactor was vented and acidified ethanol was added. The polymers were filtered and dried at 80 °C.

Synthesis of [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato](dicyclohexylamido)-titanium dichloride (2).

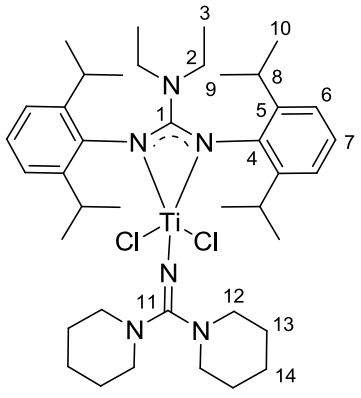
To a solution of dicyclohexylamine (0.54 g, 3 mmol) in thf (10 mL), *n*-BuLi (1.6 M, 1.86 mL, 3 mmol) was added dropwise at -20 °C. The reaction mixture was warmed to room temperature and stirred for 2 h at 50 °C. The lithiated amine was added dropweise to a solution of [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato]titanium trichloride (1.77 g, 3 mmol) in toluene (20 mL). The reaction mixture was stirred for 24 h and LiCl was filtered off. The volume of the filtrate was reduced in vacuum and it



was covered with a layer of hexane. Red crystals were obtained after standing for 2 weeks. Yield 1.83 g (83%). Elemental analysis for $C_{41}H_{66}Cl_2N_4Ti$ (734.77): calcd. C 67.02, H 9.19, N 7.63; found C 64.34, H 9.31, N 7.52. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.36 (t, J_{HH} = 7.0 Hz, 6H, H^3), 0.76 - 0.82 (m, 2H, $H^{12,13,14}$), 0.91 (d, J_{HH} = 6.8 Hz, 12H, $H^{9,10}$), 0.95 – 1.23 (m, 6H, $H^{12,13,14}$), 1.32 (d, J_{HH} = 6.9 Hz, 12H, $H^{9,10}$), 1.38 – 1.68 (m, 12H, $H^{12,13,14}$), 2.41 (q, J_{HH} = 7.2 Hz, 4H, H^2), 3.39 (m, 4H, H^8), 3.82 (m, 2H, H^{11}), 6.84 (m, 6H, $H^{6,7}$) ppm. ^{13}C NMR (100.5 MHz, C_6D_6, 298 K): δ = 12.1 (CH_3, 2C, C^3), 24.5 (CH_3, 4C, $C^{9,10}$), 25.7 (CH_3, 4C, $C^{9,10}$), 28.3 (*C*H, 4C, C^8), 34.1 (CH_2, 8C, $C^{12,13}$), 41.3 (CH_2, 2C, C^2), 61.8 (CH_2, 2C, C^{14}), 124.9 (*C*H, 4C, C^6), 126.7 (*C*H, 2C, C^{11}), 128.2 (*C*H, 2C, C^7), 144.1 (*C*q, 6C, $C^{4,5}$), 170.8 (*C*q, 1C, N*C*^{1}N) ppm.

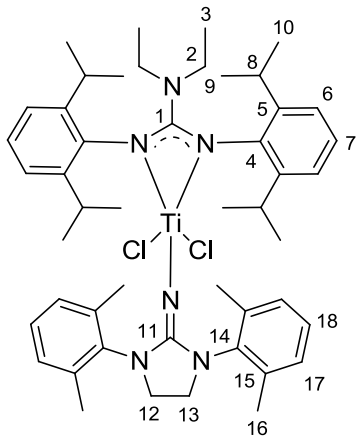
Synthesis of [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato]-[1,1,3,3-bis(pentamethylene)guanidinato]titanium dichloride (3).

To a solution of piperidine (0.14 g, 0.17 mL, 1.7 mmol) in thf (20 mL), *n*-BuLi (1.6 M, 1.07 mL, 1.7 mmol) was added dropwise at -20 °C. The resulting solution was stirred for 1 h at -20 °C. Piperidin-1-carbonitrile (0.19 g, 0.20 mL, 1.7 mmol) was added at -20 °C and the resulting solution was warmed to room temperature and stirred for 2 h. Subsequently a solution of [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato]titanium trichloride (1.00 g, 1.7 mmol) in thf (20 mL) was added dropwise and the resulting reaction mixture was heated for 2 min. to 100 °C. The reaction mixture was stirred for 4 h and filtered. Afterwards all volatiles were removed. The resulting yellow residue was dissolved in toluene (20 mL). Slow evaporation of the solvent over a period of 5 days left yellow crystals. Yield 1.02 g (76%). Elemental analysis for $C_{40}H_{64}Cl_2N_6Ti$ (748.76): calcd. C 64.16, H 8.75, N 11.22; found C 63.92, H 8.39, N 11.21. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.19 (t, J_{HH} = 7.1 Hz, 6H, H^3), 1.09 (s, 12H, $H^{13,14}$), 1.31 (d, J_{HH} = 6.9 Hz, 12H, H^9), 1.52 (d, J_{HH} = 6.6 Hz, 12H, H^{10}), 2.84 (q, J_{HH} = 7.1 Hz, 4H, H^2), 2.87 (s, 8H, H^{12}), 3.89 (m, 4H, H^8), 7.13 (m, 6H, $H^{6,7}$) ppm. ^{13}C NMR (100.5 MHz, C_6D_6, 298 K): δ = 10.6 (CH_3, 2C, C^3), 24.4 (CH_3, 4C, $C^{9,10}$), 25.7 (CH_3, 4C, $C^{9,10}$), 26.0 (CH_2, 8C, $C^{12,13}$), 28.4 (*C*H, 4C, C^8), 40.9 (CH_2, 2C, C^2), 49.5 (CH_2, 2C, C^{14}), 124.2 (*C*H, 4C, C^6), 127.5 (*C*H, 2C, C^7), 144.1 (C_q, 4C, C^5), 145.5 (C_q, 2C, C^4), 153.3 (C_q, 1C, N*C*^{11}N), 170. 5 (C_q, 1C, N*C*^{1}N) ppm.



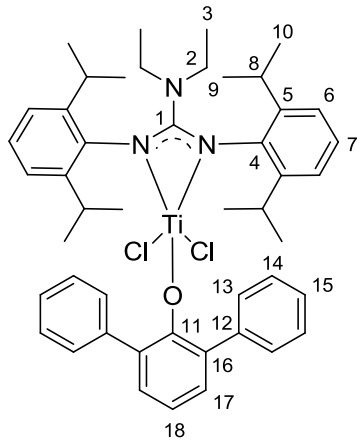
Synthesis of [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato]-[*N',N''*-bis(2,6-dimethylphenyl)imidazolidin-2-iminato]titanium dichloride (4).

To a solution of 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imine (0.5 g, 1.7 mmol) in toluene (20 mL), *n*-BuLi (1.6 M, 1.07 mL, 1.7 mmol) was added dropwise at -20 °C. [1,2-Bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato]titanium trichloride (1.00 g, 1.7 mmol) was dissolved in thf (5 mL) and the lithiated imine was added slowly. The resulting reaction mixture was stirred overnight at room temperature. All volatiles were removed under reduced pressure and the resulting residue was washed twice with hexane to obtain a pure yellow material. Yield 0.45 g (31%). Elemental analysis for $C_{48}H_{66}Cl_2N_6Ti$ (846.86): calcd. C 68.08, H 7.97, N 9.92; found C 67.73, H 8.43, N 9.92. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 0.12 (t, J_{HH} = 7.0 Hz, 6H, H^3), 1.17 (d, J_{HH} = 6.8 Hz, 12H, H^{9,10}), 1.24 (d, J_{HH} = 6.9 Hz, 12H, H^{9,10}), 2.23 (s, 12H, H^{16}), 2.62 (q, J_{HH} = 7.1 Hz, 4H, H^2), 2.77 (s, 4H, H^{12,13}), 3.47 (m, 4H, H^8), 6.71 – 7.12 (m, 12H, H^{6,7,17,18}) ppm. ^{13}C NMR (100.5 MHz, C_6D_6, 298 K): δ = 10.1 (*C*H$_3$, 2C, C^3), 19.0 (*C*H$_3$, 4C, C^{16}), 24.1 (*C*H$_3$, 4C, C^{9,10}), 26.7 (*C*H$_3$, 4C, C^{9,10}), 28.4 (*C*H, 4C, C^8), 40.4 (*C*H$_2$, 2C, C^2), 46.8 (*C*H$_2$, 2C, C^{12,13}), 124.0 (*C*H, 4C, C^6), 129.3 (*C*H, 2C, C^7), 136.4 (*C*q, 2C, C^{14}), 137.4 (*C*H, 6C, C^{17,18}), 143.6 (*C*q, 4C, C^5), 145.0 (*C*q, 2C, C^{14}), 145.4 (*C*q, 2C, C^4), 146.7 (*C*q, 2C, C^{15}), 171.1 (*C*q, 1C, C^1), 172.9 (*C*q, 1C, C^{11}) ppm.



Synthesis of [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato](2,6-diphenylphenoxido)-titanium dichloride (5).

To a solution of 2,6-diphenylphenol (0.42 g, 1.7 mmol) in thf (10 mL), *n*-BuLi (1.6 M, 1.07 mL, 1.7 mmol) was added slowly at -20 °C. The resulting reaction mixture was warmed to room temperature and stirred for 2 h. Subsequently the lithiated phenol was added dropwise to a solution of [1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato]titanium trichloride (1.00 g, 1.7 mmol) in thf (10 mL) and the mixture was stirred for 24 h at room temperature. All volatiles were removed under reduced pressure and the resulting residue was dissolved in toluene. LiCl was filtered off and the volume of the filtrate was reduced in vacuum. The concentrated toluene solution was coverd with a layer of hexane and after 24 h orange crystals were obtained. Yield 0.4 g (40%). Elemental analysis for $C_{47}H_{58}Cl_2N_3OTi$ (799.76): calcd. C 70.58, H 7.31, N 5.25; found C 69.20, H 7.73, N 5.26. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 0.15 (t, J_{HH} = 7.0 Hz, 6H, H^3), 1.04 (d, J_{HH} = 6.9 Hz, 12H, H^9), 1.08 (d, J_{HH} = 6.8 Hz, 12H, H^{10}), 2.48 (q, J_{HH} = 7.3 Hz, 4H, H^2), 3.32 (m, 4H, H^8), 6.70 – 7.19 (m, 16H, H^{6,7,13,14,15}), 7.41 – 7.52 (m, 3H, H^{17,18})



ppm. ^{13}C NMR (100.5 MHz, C_6D_6, 298 K): δ = 11.5 (*C*H$_3$, 2C, C^{3}), 24.4 (*C*H$_3$, 4C, C^{9,10}), 24.5 (*C*H$_3$, 4C, C^{9,10}), 28.6 (*C*H, 4C, C^{8}), 41.2 (*C*H$_2$, 2C, C^{2}), 124.1 (*C*q, 5C, C^{13,14,15}), 124.4 (*C*q, 5C, C^{13,14,15}), 124.6 (*C*H, 4C, C^{6}), 127.7 (*C*H, 3C, C^{17,18}), 128.2 (*C*H, 2C, C^{7}), 132.7 (*C*q, 2C, C^{16}), 135.8 (*C*q, 2C, C^{12}), 143.1 (*C*q, 4C, C^{5}), 145.0 (*C*q, 2C, C^{4}), 163.0 (*C*q, 1C, C^{11}), 168.6 (*C*q, 1C, N*C*^{1}N) ppm.

Synthesis of the Catalyst Stock Solutions: The complexes **2–5** were prepared as described above. For catalytic ethylene conversion the acute red residue was dissolved in toluene (10 mL) and used without further purification.

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7 Aminopyridinate-FI Hybrids, their Hafnium and Titanium Complexes and Living 1-Hexene Polymerization

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7.1 Introduction

One of the most impressive post-metallocene olefin polymerization catalyst systems are the so called FI-catalysts.[1] Based on the principles of "ligand-oriented catalyst design"[2] Fujita and coworkers synthesized group 4 metal complexes stabilized by two phenoxy-imine chelating ligands. Following activation (for example with borates or MAO) the cationic FI-catalyst species is highly active in polymerization of ethylene, α-olefins and copolymerization of ethylene with various comonomers (for example: α-olefins, cyclic olefins or polar functional olefins).[3] Another successful family of ligands which has been used in combination with rare earth and early transition metals in a variety of polymerization protocols[4] are the so-called aminopyridinato ligands (Ap). Ap ligands represent an unsymmetric version of bidentate monoanionic *N,N*-ligands.[5] Herein, we describe a newly designed ligand system, named Ap-FI ligands, which represents a combination of the described FI (phenoxyimine) and Ap ligands (Figure 1, left). Recently, one very successful example for the combination of FI ligands with another ligand system was reported by Kol and coworkers.[6] This ligand hybrid is a combination of one 'half-Salan'[7] and one 'half-Salen' ligand[8] (Salalen, Figure 1, right) linked via an ethylene bridge.[9] Its titanium complexes were used as highly isospecific catalysts for 1-hexene and propylene polymerization.

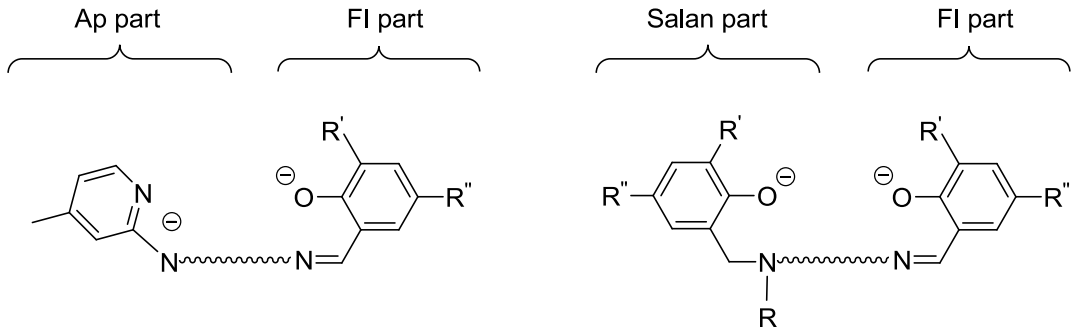
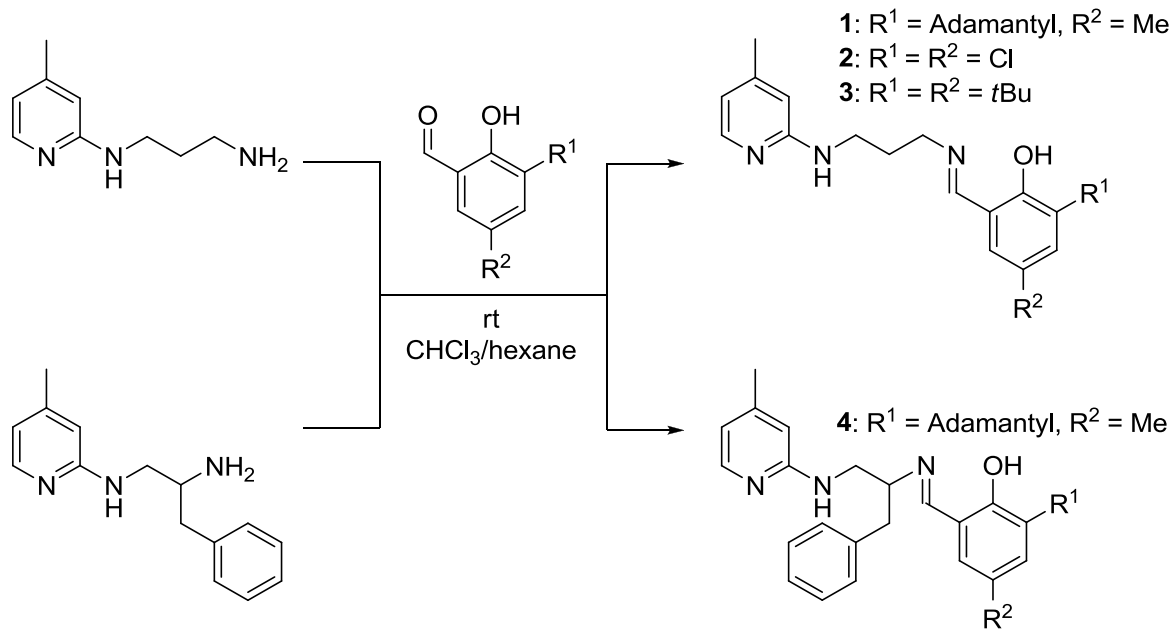


Figure 1. New Ap-FI hybrid ligand system (left) and Salalen ligand system (right).

Furthermore, we report herein on the living 1-hexene polymerization applying Ap-FI hafnium catalysts. Non-terminating polymerization processes address a long-standing scientific challenge: the development of chain-growth polymerization systems that enable consecutive enchainment of monomer units.[10] The advantages of such, so-called living polymerizations,[11] is the high degree of control and access to block copolymers which can undergo micro-phase separation/nanostructuring. Subsequent to the pioneering work of McConville[12] and Schrock[13] about the aspecific living polymerization of 1-hexene, relatively few examples of catalysts that are stereoselective, especially isoselective, and living for olefin polymerization have been reported.[7c,14] The first catalyst to simultaneously achieve the living and isospecific polymerization of 1-hexene was a zirconium amidinate developed by Sita and coworkers in early 2000.[15] After this initial report Kol and coworkers presented an [*O,N,N,O*]-ligand stabilized zirconiumdibenzyl catalyst system[7a] which was found suitable for living isospecific polymerization of 1-hexene.

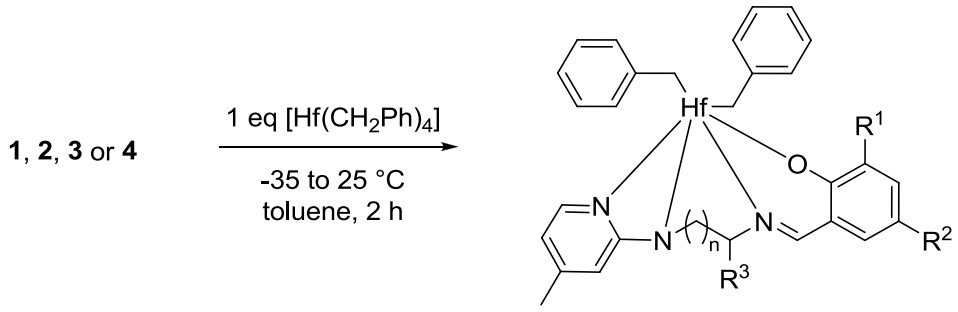
7.2 Results and Discussion

Mono-N-arylated aliphatic diamines, representing the Ap part of the new ligand, were synthesized via Ir-catalyzed alkylation of aromatic amines using unprotected amino alcohols as alkylating agents.[16] This unique protocol allows accessing selectively monoarylated aliphatic diamines. It is the key to the ligand class introduced herein. The substituted salicylaldehydes were either synthesized via ortho-formylation of the corresponding substituted phenol[17] or were commercially available.[18] The subsequent synthesis of the Ap-FI ligands is based on a straightforward condensation of the primary amino function of the mono-N-arylated diamine with one equivalent of the substituted salicylaldehyde (Scheme 1).



Scheme 1. One-step synthesis of the Ap-FI ligands.

With this easy and direct synthesis a wide spectrum of new Ap-FI ligands is accessible. They feature 3-adamantyl-5-methyl, 3,5-di-chloro or 3,5-di-tert-butyl substitution on the phenolate ring of the FI part, a methyl group at 4-position of the Ap part and either a propylene or a substituted ethylene bridge between the two nitrogen donors. All compounds **1–4** were characterized by NMR spectroscopy and elemental analysis. Treatment of one equivalent of $[Hf(CH_2Ph)_4]$ with ligands **1–4** leads to complexes **5–8** of the type $[(Ap\text{-}FI)HfBn_2]$, respectively, due to clean elimination of two toluene molecules (Scheme 2).



5: R^1 = Adamantyl, R^2 = Me, R^3 = H; n = 2
6: R^1 = R^2 = Cl, R^3 = H; n = 2
7: R^1 = R^2 = *t*Bu, R^3 = H; n = 2
8: R^1 = Adamantyl, R^2 = Me, R^3 = Bn; n = 1

Scheme 2. Synthesis of the mononuclear Ap-FI hafnium dibenzyl complexes **5–8**.

The Ap-FI hafnium dibenzyl complexes **5**-**8** were characterized by NMR spectroscopy and elemental analysis and were tested in 1-hexene polymerization studies. Activation of catalyst precursor **5** with 1.5 equiv of $B(C_6F_5)_3$ in neat 1-hexene at room temperature led to an active catalyst (Table 1, entry 1) whereas catalyst precursors **6** and **7** showed moderate activity and catalyst precursor **8** did not show any activity under the same conditions (Table 1, entries 7-9). Very narrow molecular weight distributions (polydispersity indices (PDIs) as low as 1.04) suggested the living nature of the polymerizations. However, the very high polymer molecular weights (M_n = 524000 – 1320000 g·mol^{-1}) relative to the calculated values (M_n^{theo} = 129000 – 308000 g·mol^{-1}) indicate partial precatalyst activation. ^{13}C NMR spectroscopy revealed that the degree of isotacticity in these polymers depends on the substituents in the 2- and 4-positions of the phenoxy ring. Complex **5** showed the most promising characteristics in terms of activity, isospecificity and polymer molecular weight and was chosen for further studies. 1-Hexene polymerizations in solution employing this catalyst (Table 1, entries 2-4) led to ultra-high molecular weight polymer (under ambient conditions) that exhibited elastomeric properties. The degree of isotacticity was found to depend on the polymerization conditions: Polymerization in toluene solution (entry 3) led to a low degree of isotacticity in comparison to the polymerizations in the neat monomer (entry 1), whereas the large volume polymerization of neat 1-hexene (entry 2) gave poly(1-hexene) of similar isotacticity. Polymerization in the non-coordinating solvent heptane led to the highest degree of isotacticity of [*mmmm*] = 92% (entry 4). The latter polymer sample featured an ultra-high molecular weight and a very narrow molecular weight distribution of PDI = 1.02. All four catalyst precursors were inactive in 1-hexene polymerization following activation with 500 equiv MAO. By activation with dimethylanilinium tetrakis(pentafluorophenyl)borate (Table 1, entry 5) or trityl tetrakis(pentafluorophenyl)borate (Table 1, entry 6) precatalyst **5** showed low activity and led to atactic polymers. Namely, of all cocatalysts commonly employed in α-olefin polymerization, only tris(pentafluorophenyl)borane led to catalysts of decent activities, and polymers of desired properties.

Table 1. Comparison of 1-hexene polymerization using catalyst precursors **5**–**8**.[a]

Entry	Prec.	Solvent	Time [h]	Activator	Yield [g]	Activity [g/(mmol·h)]	[*mmmm*] (%)[b]	M_n [g/mol][c]	M_n^{theo}[d] [g/mol]	PDI [c]
1	**5**	-	2	$B(C_6F_5)_3$	3.08	154.0	88	1320000	308000	1.04
2	**5**	50 mL 1-hexene	12	$B(C_6F_5)_3$	5.86	73.9	85	1410000	586000	1.04
3	**5**	8 mL toluene	12	$B(C_6F_5)_3$	0.82	10.3	60	648000[e] 31000	82000	1.22 1.53
4	**5**	8 mL heptane	12	$B(C_6F_5)_3$	0.95	11.9	92	1477000	95000	1.02
5	**5**	-	12	Dmab[f]	0.10	1.3	atactic	443000	10000	1.28

6	**5**	-	12	Tt[g]	0.12	1.5	atactic	630400	12000	1.40
7	**6**	-	5	$B(C_6F_5)_3$	1.29	25.8	87	872000	129000	1.37
8	**7**	-	5	$B(C_6F_5)_3$	1.46	29.2	62	524000	146000	1.30
9	**8**	-	12	$B(C_6F_5)_3$	-	-	-	-	-	-

[a] Conditions: precursor: 10 µmol, neat 1-hexene (3.36 g), activator: 1.5 eq, atmospheric pressure, room temperature. [b] Isotacticity in terms of pentad content. [c] Determined by GPC analysis vs. polystyrene standards. [d] M_n^{theo} is obtained by dividing the amount of polymer obtained by mole of precatalyst employed. [e] Bimodal distribution. [f] Dmab: dimethylanilinium tetrakis(pentafluorophenyl)borate. [g] Tt: trityl tetrakis(pentafluorophenyl)borate.

Because of the divergence in the molecular weight of the obtained poly(1-hexene) compared to the calculated values, our interest was extended to explore possible deactivation reactions of this catalyst system. Some studies, concerning the behavior of an imine function in the backbone of a ligand, have shown them to be noninnocent with possible involvement in a series of transformations such as deprotonation reactions, alkylation,[19] and redox reactions.[20] We found that after storage of catalyst precursor **6** in toluene solution at RT for two months, light yellow crystals were formed whose molecular structure was determined by single crystal X-ray diffraction. Catalyst precursor **6** formed a binuclear species **9** in which the primary non-chiral Ap-FI ligand underwent imine alkylation, thus forming an alkylated (chiral) ligand (Figure 2).

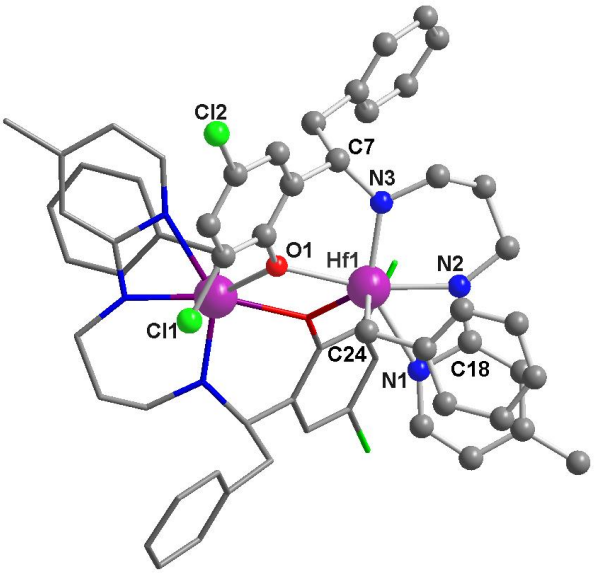
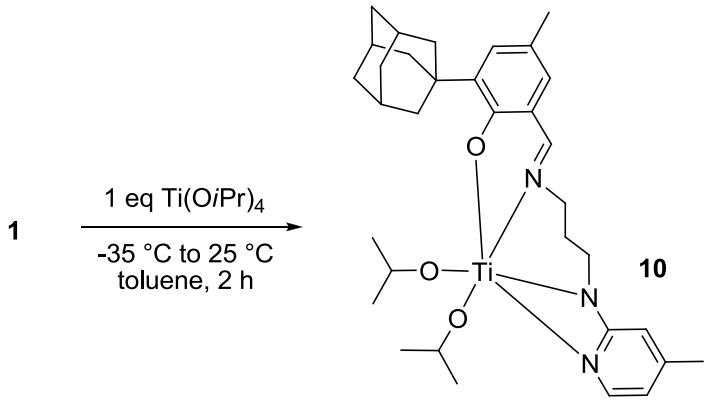


Figure 2. Molecular structure of complex **9**, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: O1-Hf1 2.239(4), O1-Hf1 2.169(4), N1-Hf1 2.352(6), N2-Hf1 2.112(6), N3-Hf1 2.059(6), N1-C18 1.359(9), N2-C18 1.338(9), N3-C7 1.471(9), C24-Hf1 2.255(7), N2-C18-N1 109.4(7), O1-Hf1-C24 83.6(2), N1-Hf1-N2 58.8(2), N3-Hf1-N2 82.9(2), O1-Hf1-N3 82.58(19).

The original Ap-FI ligand **2** is tetradentate-dianionic in complex **6** but converts to tetradentate-trianionic following the imine alkylation to form complex **9**. Both metal centers of the dinuclear species have a slightly distorted octahedral geometry due to the coordination site O1 which binds to both metal centers. Based on this dual coordination the bond length Hf1-O1 is widened (O1-Hf1 2.239(4) Å and 2.169(4) Å). Despite the conversion of ligand precursor **2** to the alkylated species, it wraps diastereospecifically in the *fac-mer* mode of Ap-FI ligands around the metal center. This catalytically inactive dinuclear complex species is one example of a possible deactivation pathway during the polymerization experiments discussed here. Due to the instability of the dialkyl complexes investigations were performed with an isopropoxide complex. The isopropoxide moieties at the metal center are not able to migrate to the imine function and did not show any dynamic behaviour in the proton NMR spectrum. The Ap-FI ligand **1** reacted with $Ti(OiPr)_4$ in a 1:1 ratio in toluene with elimination of two molecules of isopropanol to form the corresponding mono(Ap-FI) titanium diisopropoxide complex **10** (Scheme 3). The corresponding ^1H NMR experiment of the described reaction showed full conversion of the ligand and the titanium precursor to complex **10**, which was characterized by NMR spectroscopy and elemental analysis. Crystals of complex **10** suitable for X-ray structure analysis were grown from a saturated n-hexane solution at room temperature. The molecular structure of complex **10** is presented in Figure 3 and shows a *fac-mer* complex.



Scheme 3. Synthesis of the mono(Ap-FI) titanium diisopropoxide complex **10**.

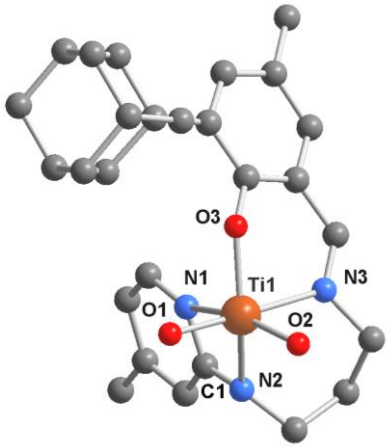


Figure 3. Molecular structure of complex **10**, hydrogen atoms and iPr groups are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: O1-Ti1 1.795(2), N2-Ti1 2.044(3), O2-Ti1 1.821(2), N3-Ti1 2.219(3), O3-Ti1 1.906(2), N1-Ti1 2.273(3), N1-Ti1-O1 90.98(11), O1-Ti1-O2 99.06(11), O2-Ti1-N3 84.94(11), N3-Ti1-N1 85.06(11), N1-C1-N2 108.6(3), N3-Ti1-O3 82.0(1).

The coordination sphere of complex **10** is a slightly distorted octahedron. The bond lengths are typical of the aminopyridinate and phenoxyimine structural motifs. The Ap part coordinates in its amidopyridine form with a short Ti-N_{amido} distance (2.04 Å), and a long Ti-$N_{pyridine}$ distance (2.27 Å).[21] The former bond is slightly longer than in typical cases like in classic aminopyridinato titanium complexes (Ti-$N_{pyridine}$ bond distance: 2.19 Å),[21] which is most likely caused by its trans position to the strongly bonded phenoxy group. The phenoxyimine part shows the typical stronger bonding for the phenoxy group (1.91 Å) compared to the imine group (2.22 Å).[22] The small difference in the bond lengths of the isopropoxide groups (1.80 Å and 1.82 Å, respectively) may indicate a weaker bonding of the trans positioned imine donor compared to the pyridine donor.

7.3 Conclusion

In summary, AP-FI hybrid ligands are introduced here. With the mono-*N*-arylated aliphatic diamines out of an iridium-catalyzed alkylation process, the overall synthesis of the new ligand system is straightforward. ApFI hafnium complexes are highly active in 1-hexene polymerization and produce ultra-high molecular weight poly(1-hexene) with extremely narrow polydispersities in a living fashion. One possible catalyst deactivation pathway proceeds via imine alkylation.

Supporting Information Available

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

Acknowledgements

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7.5 Supporting Information

General Comments: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in a nitrogen or argon filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1 ppm O_2). Deuterated solvents were obtained from Cambridge Isotope Laboratories. Solvents and reagents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy, or sodium ketyl of benzophenone under nitrogen immediately before use. Commercial 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 3,5-dichloro-2-hydroxybenzaldehyde, 2-(1-adamantyl)-4-methylphenol and titanium(IV) isopropoxide were used as received from Sigma-Aldrich. The precursor material 3-adamantyl-2-hydroxy-5-methylbenzaldehyde[1] was prepared according to published procedures. The mono-*N*-arylated aliphatic diamines 3-phenyl-*N'*-pyridin-2-yl-propane-1,2-diamine and *N'*-(4-methyl-pyridin-2-yl)-propane-1,3-diamine were synthesized *via* the published process of Ir-catalyzed amine alkylation of aromatic amines with unprotected amino alcohols.[2]

Table S1. Parameters of the X-ray analysis of **9** and **10**.

Compound	**9**	**10**
Formula	$C_{60}H_{56}Cl_4Hf_2N_6O_2$	$C_{33}H_{47}N_3O_3Ti$
Crystal system	orthorhombic	hexagonal
Space group	*Pccn*	$P\bar{3}$
a [Å]	20.0120(8)	23.3440(11)
b [Å]	24.1810(9)	23.3440(11)
c [Å]	11.2450(4)	9.7930(4)
α [°]	90.00	90.00
β [°]	90.00	90.00
γ [°]	90.00	120.00
V [Å^3]	5441.6(4)	4621.6(4)
Z	4	6
Crystal size [mm^3]	0.61×0.2×0.1	0.69×0.15×0.12
$\varrho_{calcd.}$ [g·cm^{-3}]	1.699	1.254
μ [mm^{-1}] (Mo-Kα)	4.059	0.315
T [K]	133(2)	133(2)
θ range [°]	1.32–25.68	1.74–24.68
Reflections unique	5155	5207
Refl. Obs. [I > 2σ (I)]	2796	3357
Parameters	335	365
wR_2 (all data)	0.0658	0.1152
R_1 value [I > 2σ (I)]	0.0359	0.0621
Largest diff. peak and hole [e·Å^{-3}]	0.994/-0.722	0.328/-0.369

CCDC-933517 (for **9**) and -933516 (for **10**) 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.

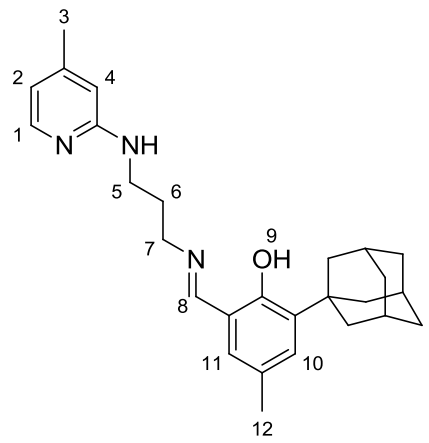
NMR Spectroscopy: NMR spectra were recorded on a Varian INOVA 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75.4 MHz). The ^{1}H and ^{13}C NMR spectra were measured at 25 °C and referenced internally using the residual solvent resonances. All chemical shifts (δ) are reported in ppm.
NMR data for poly(1-hexene) samples were recorded on a Bruker AC-500 spectrometer. $CDCl_3$ was used as solvent for the poly(1-hexene) samples. ^{1}H NMR chemical shift of TMS at δ 0.00, and ^{13}C NMR chemical shift of the solvent at δ 77.16 were used as reference. ^{13}C-NMR was employed to determine stereoregularity ([*mmmm*](%)), and a presence of chain ends of low/high molecular weight polymers at room temperature for the soluble poly(1-hexene).

Gel Permeation Chromatography (GPC): Poly(1-hexene) molecular weights were determined by gel permeation chromatography (GPC) using TSKgel GMHHR-M column on a Jasco instrument equipped with a refractive index detector. Molecular weights relative to polystyrene standards were determined using tetrahydrofuran (HPLC grade, distilled and filtered under vacuum prior to use) as the eluting solvent.

Elemental Analyses (C,H,N): Elemental analyses (C,H,N) were carried out with a Vario elementar EL III instrument.

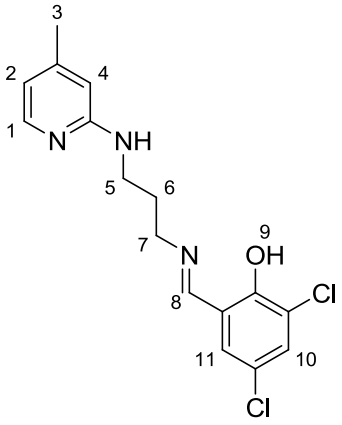
X-ray Crystallography: X-ray crystal structure analyses were performed with a STOE-IPDS II instrument equipped with an Oxford Cryostream low-temperature unit (λ(MoKα) = 0.71073 Å). Structure solution and refinement were accomplished using SIR97,[3] SHELXL-97[4] and WinGX.[5]

Preparation of 1. 3-Adamantyl-2-hydroxy-5-methylbenzaldehyde (1.64 g, 6.07 mmol) and *N'*-(4-methyl-pyridin-2-yl)-propane-1,3-diamine (1.00 g, 6.05 mmol) were dissolved in chloroform (15 mL) and stirred overnight. All volatiles were removed under reduced pressure and the residue was suspended in hexane (15 mL). The suspension was filtered and the resulting residue was evaporated to dryness quantitatively affording **1** as a yellow, spectroscopically pure compound. Elemental analysis for $C_{27}H_{35}N_3O$ (417.59): calcd. C 77.66, H 8.45, N 10.06; found C 77.69, H 8.79, N 9.70. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 14.14 (br s, 1H, H^9), 8.05 (d, *J* = 5.1 Hz, 1H, H^2), 7.81 (s, 1H, H^8), 7.12 (d, *J* = 1.9 Hz, 1H, H^{11}), 6.63 (d, *J* = 1.9 Hz, 1H, H^{10}), 6.22 (d, *J* = 5.1 Hz, 1H, H^1), 5.97 (s, 1H, H^4), 4.97 (br s, 1H, NH), 3.26 – 3.12 (m, 4H, H^5, H^7), 2.37 (s, 6H, H^{adamantyl}), 2.23 (s, 3H, H^3), 2.15 – 2.07 (m, 3H, H^{adamantyl}), 1.94 (s, 3H, H^{12}), 1.85 – 1.76 (m, 6H, H^{adamantyl}), 1.70 – 1.62 (m, 2H, H^6) ppm. ^{13}C

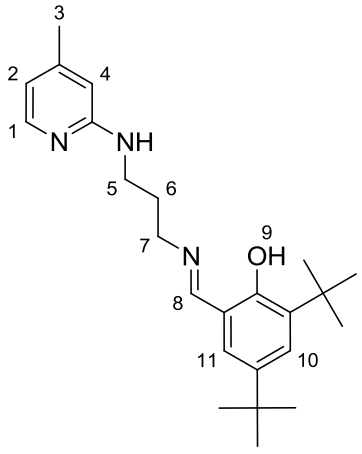


NMR (75.4 MHz, C_6D_6, 298 K): δ = 167.0 (CH), 160.2 (C), 159.7 (C), 148.7 (C), 148.6 (CH), 138.3 (C), 131.3 (CH), 130.4 (CH), 127.2 (C), 119.6 (C), 114.9 (CH), 107.8 (CH), 57.6 (CH_2), 41.3 ($3CH_2$), 40.4 (CH_2), 38.2 ($3CH_2$), 37.9 (C), 31.6 (CH_2), 30.2 (3CH), 21.6 (CH_3), 21.4 (CH_3) ppm.

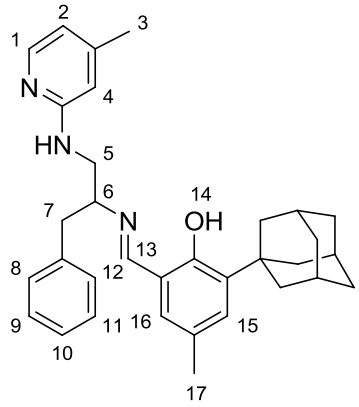
Preparation of 2. 3,5-Dichlorosalicylaldehyde (1.16 g, 6.07 mmol) and *N'*-(4-methyl-pyridin-2-yl)-propane-1,3-diamine (1.00 g, 6.06 mmol) were dissolved in pentane/chloroform (4:1; 20 mL) and stirred overnight. The suspension was filtered and the resulting residue evaporated to dryness, affording **2** quantitatively as a light yellow, spectroscopically pure compound. Elemental analysis for $C_{16}H_{17}Cl_2N_3O$ (337.23): calcd. C 56.82, H 5.07, N 12.42; found C 56.52, H 4.87, N 12.27. ^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 14.22 (br s, 1H, H^9), 8.37 (s, 1H, H^8), 7.82 (d, J = 5.1 Hz, 1H, H^2), 7.43 (d, J = 1.9 Hz, 1H, H^{11}), 7.24 (d, J = 1.9 Hz, 1H, H^{10}), 6.26 (d, J = 5.1 Hz, 1H, H^1), 6.16 (s, 1H, H^4), 3.72 (t, J = 13.0 Hz, 6.7 Hz, 2H, H^7), 3.42 (q, J = 6.4 Hz, 2H, H^5), 2.12 (s, 3H, H^3), 1.99 – 1.96 (m, 2H, H^6) ppm. ^{13}C NMR (75.4 MHz, THF-d_8, 298 K): δ = 165.3 (CH), 160.2 (C), 158.5 (C), 148.3 (CH), 147.6 (C), 132.4 (CH), 129.9 (CH), 123.5 (C), 122.1 (C), 120.5 (C), 113.9 (CH), 108.3 (CH), 56.5 (CH_2), 39.4 (CH_2), 31.7 (CH_2), 20.8 (CH_3) ppm.



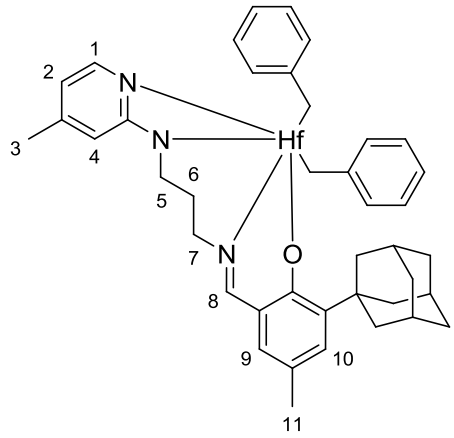
Preparation of 3. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.42 g, 6.06 mmol) and *N'*-(4-methyl-pyridin-2-yl)-propane-1,3-diamine (1.00 g, 6.06 mmol) were dissolved in chloroform (20 mL) and stirred overnight. All volatiles were removed under reduced pressure and the residue was washed with hexane (15 mL). The resulting residue was evaporated to dryness, quantitatively affording **3** as a yellow, spectroscopically pure compound. Elemental analysis for $C_{24}H_{35}N_3O$ (381.55): calcd. C 75.55, H 9.25, N 11.01; found C 75.17, H 9.70, N 10.98. ^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 13.86 (s br, 1H, H^9), 8.43 (s, 1H, H^8), 7.83 (d, J = 5.1 Hz, 1H, H^2), 7.36 (d, J = 1.9 Hz, 1H, H^{11}), 7.14 (d, J = 1.9 Hz, 1H, H^{10}), 6.27 (d, J = 5.1 Hz, 1H, H^1), 6.18 (s, 1H, H^4), 5.65 (br s, 1H, NH), 3.67 (t, J = 13.0 Hz, 6.7 Hz, 2H, H^7), 3.43 (q, J = 6.4 Hz, 2 H, H^5), 2.13 (s, 3H, H^3), 1.99 – 1.96 (m, 2H, H^6), 1.44 (s, 9H, $H^{tert\text{-butyl}}$) 1.30 (s, 9H, $H^{tert\text{-butyl}}$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 167.5 (CH), 160.3 (C), 158.9 (C), 148.4 (CH), 147.5 (C), 140.3 (C), 136.6 (C), 126.9 (CH), 126.7 (CH), 119.1 (C), 113.8 (CH), 108.0 (CH), 57.7 (CH_2), 39.7 (CH_2), 35.5 (C), 34.6 (C), 31.9 (CH_2), 31.7 ($3CH_3$), 29.7 ($3CH_3$), 20.9 (CH_3) ppm.



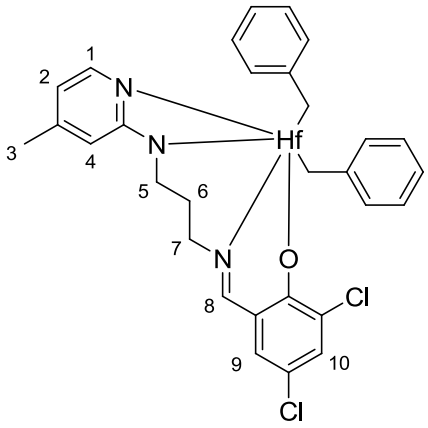
Preparation of 4. 3-Adamantyl-2-hydroxy-5-methylbenzaldehyde (0.97 g, 4.14 mmol) and 3-phenyl-*N'*-(4-methyl-pyridin-2-yl)-propane-1,2-diamine (1.00 g, 4.14 mmol) were dissolved in chloroform (15 mL) and stirred overnight. All volatiles were removed under reduced pressure and the residue was suspended in hexane (15 mL). The suspension was filtered and the resulting residue evaporated to dryness, affording **4** quantitatively as a yellow, spectroscopically pure compound. Elemental analysis for $C_{33}H_{39}N_3O$ (493.68): calcd. C 80.29, H 7.96, N 8.51; found C 79.77, H 8.15, N 8.42. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 14.18 (br s, 1H, H^{14}), 8.10 (d, *J* = 5.1 Hz, 1H, H^2), 7.60 (s, 1H, H^{13}), 7.10 (d, *J* = 1.9 Hz, 1H, H^{16}), 7.04 – 6.95 (m, 5H, $H^{8,9,10,11,12}$), 6.35 (d, *J* = 1.9 Hz, 1H, H^{15}), 6.19 (d, *J* = 5.1 Hz, 1H, H^1), 5.58 (s, 1H, H^4), 4.31 (br s, 1H, NH), 3.91 – 3.83 (m, 1H, H^5), 3.60 – 3.54 (m, 1H, H^6), 3.16 – 3.07 (m, 1H, H^5), 2.85 – 2.79 (m, 1H, H^7), 2.72 – 2.65 (m, 1H, H^7), 2.49 – 2.34 (m, 6H, $H^{adamantyl}$), 2.11 (s, 6H, H^3, H^{17}), 1.92 – 1.78 (m, 9H, $H^{adamantyl}$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 167.0 (CH), 159.4 (C), 159.3 (C), 148.5 (CH), 147.0 (C), 139.2 (C), 137.9 (C), 131.2 (CH), 130.5 (CH), 130.2 (2CH), 128.9 (2CH), 127.1 (C), 126.9 (CH), 119.1 (C), 115.0 (CH), 108.7 (CH), 71.6 (CH), 47.4 (CH_2), 41.2 (C), 41.1 ($3CH_2$), 37.8 ($3CH_2$), 37.5 (CH_2), 30.0 (3CH), 21.2 (CH_3), 21.1 (CH_3) ppm.



Preparation of 5. Ligand **1** (0.052 g, 0.125 mmol) was dissolved in 1 mL of cold toluene and added dropwise to a stirred solution of $HfBn_4$ (0.068 mg, 0.125 mmol) in 1 mL of cold toluene. The reaction mixture was allowed to warm to room temperature. After 2 hours of stirring the solvent was removed under vacuum, yielding an orange solid, which was washed with 1 mL of pentane and dried in vacuo. The final yield was 0.44 g (70%). Elemental analysis for $C_{41}H_{47}HfN_3O$ (776.32): calcd. C 63.43, H 6.10, N 5.41; found C 63.03, H 6.04, N 5.00. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 7.63 (d, J = 5.2 Hz, 1H, H^2), 7.45 – 7.44 (m, 2H, $H^{8,9}$), 7.25 – 6.91 (m, 4H, $H^{10,adamantyl}$), 6.84 – 6.61 (m, 10H, $H^{o-,m-,p-benzyl}$), 6.12 (d, *J* = 5.2 Hz, 1H, H^1), 5.82 (s, 1H, H^4), 2.80 – 2.74 (m, 2H, H^6), 2.64 – 2.60 (m, 4H, $H^{5,7}$), 2.33 (2, 3H, H^3), 2.31 – 2.14 (m, 3H, $H^{adamantyl}$), 2.11 (s, 3H, H^{11}), 2.01 – 1.75 (m, 9H, $H^{adamantyl}$), 1.27 – 1.22 (m, 4H, CH_2^{benzyl}) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ =144.6 (CH), 141.3 (CH), 137.8 (C), 137.0 (C), 136.5 (C), 135.9 (C), 129.0 (CH), 127.7 (CH), 127.2 (2CH), 126.9 (C), 126.5 (C), 126.4 (2CH), 125.3 (4CH), 125.0 (C), 124.1 (C), 123.6 (CH), 121.1 (C), 118.1 (2CH), 110.4 (CH), 74.2 ($2CH_2$), 43.4 ($3CH_2$), 36.4 (CH_2), 33.5 ($3CH_2$), 32.4 (CH_2), 30.1 (CH_2), 28.5 (3CH), 21.1 (CH_3), 19.6 (CH_3) ppm.

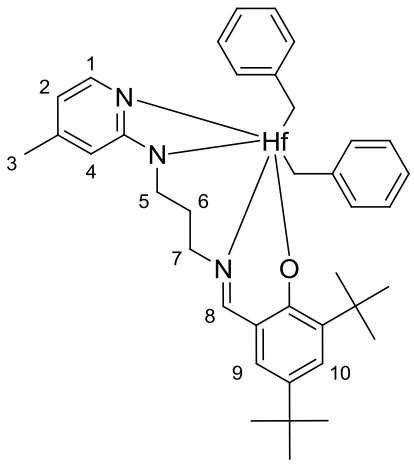


Preparation of 6. Ligand **2** (0.042 g, 0.125 mmol) was dissolved in 1 mL of cold toluene and added dropwise to a stirred solution of $HfBn_4$ (0.068 mg, 0.125 mmol) in 1 mL of cold toluene. The reaction mixture was allowed to warm to room temperature. After 2 hours of stirring the solvent was removed under vacuum, yielding an orange solid, which was washed with 1 mL of pentane and dried in vacuo.



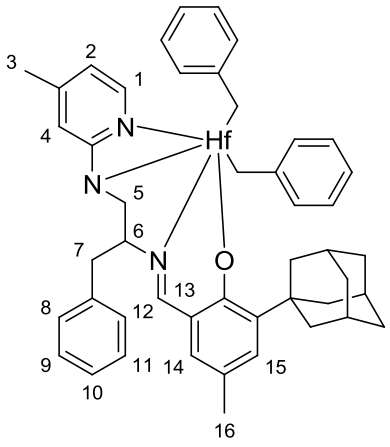
The final yield was 0.15 g (81%). Elemental analysis for $C_{30}H_{29}Cl_2HfN_3O$ (696.97): calcd. C 51.70, H 4.19, N 6.03; found C 51.33, H 4.18, N 5.37. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 7.48 (d, *J* = 5.4 Hz, 1H, H^2), 7.44 (d, *J* = 2.4, 1H, H^9), 7.25 – 6.48 (m, 12H, $H^{8,10,o\text{-},m\text{-},p\text{-benzyl}}$), 5.99 (d, J = 5.4 Hz, 1H, H^1), 5.82 (s, 1H, H^4), 2.71 – 2.65 (m, 2H, H^5), 2.46 – 2.20 (m, 2H, H^6), 1.87 (s, 3H, H^3), 1.81 – 1.56 (m, 2H, H^7), 1.29 – 1.20 (m, 4H, CH_2^{benzyl}), ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 167.0 (CH), 166.1 (C), 159.4 (C), 159.3 (C), 152.7 (C), 145.9 (2C), 143.6 (CH), 135.3 (CH), 132.0 (CH), 128.7 (4CH), 128.1 (4CH), 126.6 (C), 122.9 (C), 121.3 (2CH), 113.4 (CH), 103.6 (CH), 74.1 ($2CH_2$), 63.9 (CH_2), 45.5 (CH_2), 32.3 (CH_3), 23.4 (CH_3) ppm.

Preparation of 7. Ligand **3** (0.048 g, 0.125 mmol) was dissolved in 1 mL of cold toluene and added dropwise to a stirred solution of $HfBn_4$ (0.068 mg, 0.125 mmol) in 1 mL of cold toluene. The reaction mixture was allowed to warm to room temperature. After 2 hours of stirring the solvent was removed under vacuum, yielding an orange solid, which was washed with 1 mL of pentane and dried in vacuo.

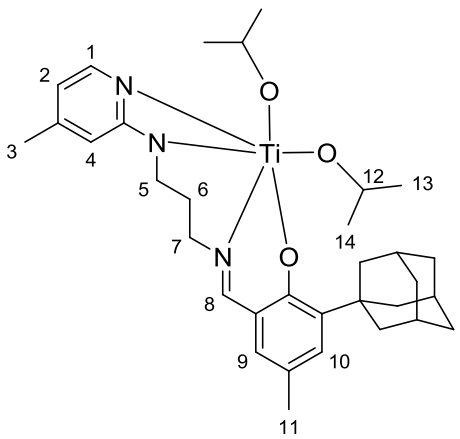


The final yield was 0.29 g (75%). Elemental analysis for $C_{38}H_{47}HfN_3O$ (740,29): calcd. C 61.65, H 6.40, N 5.68; found C 61.62, H 6.81, N 5.25. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 7.86 (s, 1H, H^8), 7.51 (d, *J* = 5.2 Hz, 1H, H^2), 7.48 (d, *J* = 2.5 Hz, 1H, H^9), 6.97 (d, *J* = 2.5 Hz, 1H, H^{10}), 6.77 (t, *J* = 7.2 Hz, 4H, $H^{m\text{-benzyl}}$), 6.58 (d, *J* = 5.2 Hz, 1H, H^1), 6.54 (t, *J* = 7.2 Hz, 2H, $H^{p\text{-benzyl}}$), 6.01 (d, *J* = 7.2 Hz, 4H, $H^{o\text{-benzyl}}$), 5.77 (s, 1H, H^4), 2.75 – 2.72 (m, 2H, H^6), 2.60 – 2.54 (m, 2H, H^7), 1.90 (s, 3H, H^3), 1.82 (s, 9H, $H^{tert\text{-butyl}}$), 1.54 – 1.48 (m, 2H, H^6), 1.35 (s, 9H, $H^{tert\text{-butyl}}$), 1.31 – 1.28 (m, 4H, CH_2^{benzyl}) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 169.2 (CH), 164.5 (C), 158.9 (C), 150.1 (C), 143.2 (CH), 137.8 (C), 136.5 (C), 131.2 (CH), 129.2 (CH), 129.0 (C), 127.6 (6CH), 127.2 (CH), 126.7 (CH), 123.6 (C), 121.1 (C), 120.6 (2CH), 112.4 (CH), 103.2 (CH), 71.3 ($2CH_2$), 63.2 (CH_2), 33.5 (C), 32.4 (C), 45.2 (CH_2), 31.6 ($3CH_3$), 30.7 ($3CH_3$), 29.8 (CH_2), 21.8 (CH_3) ppm.

Preparation of 8. Ligand **4** (0.062 g, 0.125 mmol) was dissolved in 1 mL of cold toluene and added dropwise to a stirred solution of $HfBn_4$ (0.068 mg, 0.125 mmol) in 1 mL of cold toluene. The reaction mixture was allowed to warm to room temperature. After 2 hours of stirring the solvent was removed under vacuum, yielding an orange solid, which was washed with 1 mL of pentane and dried in vacuo. The final yield was 0.19 g (61%). Elemental analysis for $C_{47}H_{51}HfN_3O$ (852.42): calcd. C 66.22, H 6.03, N 4.93; found C 66.01, H 6.28, N 4.66. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 7.65 (d, *J* = 5.1 Hz, 1H, H^2), 7.63 (s, 1H, H^{13}), 7.43 (s, 1H, H^{14}), 7.13 – 6.90 (m, 5H, $H^{15,m\text{-benzyl}}$), 6.78 – 6.73 (m, 2H, $H^{p\text{-benzyl}}$), 6.61 – 6.41 (m, 12H, $H^{8,9,10,11,12,adamantyl,o\text{-benzyl}}$), 6.06 (d, *J* = 5.1 Hz, 1H, H^1), 5.50 (s, 1H, H^4), 3.45 – 3.37 (m, 2H, H^5), 3.04 – 2.90 (m, 2H, H^7), 2.70 – 2.52 (m, 7H, $H^{6,adamantyl}$), 2.24 – 1.94 (m, 12H, $H^{3,16,adamantyl}$), 1.90 – 1.83 (m, 4H, CH_2^{benzyl}) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 168.4 (CH), 166.0 (C), 161.2 (C), 152.7 (C), 145.5 (C), 145.1 (C), 144.7 (CH), 140.5 (C), 139.1 (C), 135.5 (CH), 132.9 (CH), 130.4 (2CH), 129.1 (4CH), 128.7 (4CH), 127.8 (2CH), 127.3 (CH), 127.1 (C), 123.3 (C), 121.7 (CH), 121.1(CH), 113.8 (CH), 103.6 (CH), 76.9 (CH), 72.7 (CH_2), 72.4 (CH_2), 47.5 (CH_2), 43.1 (CH_2), 41.9 ($3CH_2$), 38.1 (C), 38.0 ($3CH_2$), 30.1 (3CH), 22.2 (CH_3), 21.2 (CH_3) ppm.



Preparation of 10. Titanium(IV) isopropoxide (0.39 mL, 1.31 mmol) was added to a solution of **1** (0.50 g, 1.31 mmol) in toluene (15 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight after which the solvent was removed in vacuum. The residue was suspended in hexane (20 mL) and the overlaying yellow solution was filtered. The filtrate was concentrated under vacuum and allowed to crystallize at room temperature to give colorless crystals (0.41 g, 76%) suitable for X-ray analysis. Elemental analysis for $C_{33}H_{47}N_3O_3Ti$ (581.61): calcd. C 68.15, H 8.15, N 7.22; found C 68.21, H 8.41, N 7.10. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 7.17 (s, 1H, H^8), 7.10 (d, *J* = 5.1 Hz, 1H, H^2), 7.01 (d, *J* = 1.8 Hz, 1H, H^9), 6.28 (d, *J* = 1.8 Hz, 1H, H^{10}), 5.73 (s, 1H, H^4), 5.46 (d, *J* = 5.1 Hz, 1H, H^1), 5.17 (sept, *J* = 6.2 Hz, 1H, H^{12}), 4.74 (sept, *J* = 6.2 Hz, 1H, H^{12}), 4.39 – 4.32 (m, 1H, H^7), 3.92 – 3.88 (m, 1H, H^7), 3.65 – 3.62 (m, 1H, H^5), 2.82 – 2.28 (d, 1H, H^5), 2.50 (d, *J* = 12.1 Hz, 3H, $H^{adamantyl}$), 2.37 (d, *J* = 12.1 Hz, 3H, $H^{adamantyl}$), 2.11 (s, 3H, $H^{adamantyl}$), 2.04 (s, 3H, H^3), 1.94 (d, *J* = 12.1 Hz, 3H, $H^{adamantyl}$), 1.76 (d, *J* = 12.1 Hz, 3H, $H^{adamantyl}$), 1.54 (s, 3H, H^{11}), 1.39 (d, *J* = 6.1 Hz, 3H, $H^{isopropyl\text{-}CH3}$), 1.35 (d, *J* = 6.1 Hz, 3H, $H^{isopropyl\text{-}CH3}$), 1.22 (d, *J* = 6.1 Hz, 3H, $H^{isopropyl\text{-}CH3}$), 1.14 (d, *J* = 6.1 Hz, 3H, $H^{isopropyl\text{-}CH3}$), 1.13 – 1.10 (m, 2H, H^6) ppm. ^{13}C NMR



(125.7 MHz, C_6D_6, 298 K): δ = 167.7 (CH), 163.1 (C), 161.9 (C), 149.8 (CH), 144.0 (C), 138.7 (C), 132.2 (C), 131.5 (CH), 128.4 (CH), 123.3 (C), 110.7 (CH), 105.5 (CH), 78.5 (CH), 76.8 (CH), 63.0 (C), 48.8 (CH_2), 41.0 ($3CH_2$), 37.8 ($3CH_2$), 37.7 (CH_2), 30.7 (CH_2), 30.0 (3CH), 26.9 (CH_3), 26.8 (CH_3), 26.6 (CH_3), 26.3 (CH_3), 21.7 (CH_3), 21.0 (CH_3) ppm.

1-Hexene Polymerization Studies: The activator $B(C_6F_5)_3$ (1.5 equiv) was dissolved in 1 mL of 1-hexene and added to a stirred solution of a dibenzyl hafnium complex of the series **5**–**8** (10 μmol) in 4 mL of 1-hexene. The resulting mixture was stirred until it became viscous. The remaining olefin was removed under vacuum yielding poly(1-hexene) as an orange-yellow gum.

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8 Coordination Chemistry of Ap-FI Hybrids with Titanium and Zirconium and their Ethylene Homopolymerization Performance

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Keywords: Aminopyridinate • Phenoxyimine • Titanium • Zirconium • Ethylene polymerization

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8.1 Abstract

Based on the recently developed Ap-FI hybrid ligand system and the already synthesized mono(Ap-FI) titanium complex [(Ap-FI)Ti(O*i*Pr)$_2$] a new mono(Ap-FI) titanium complex of the type [(Ap-FI)TiCl$_2$] was obtained from the chloro-substituted Ap-FI hybrid ligand. In this complex the Ap-FI hybrid ligand acted as tetradentate dianionic chelate. By changing the steric or electronic properties of the Ap-FI ligands, multi(ApH-FI) complexes of the type [(ApH-FI)$_2$Ti(O*i*Pr)$_2$] or [(ApH-FI)Zr(O*t*Bu)$_3$]$_3$ were synthesized which feature the ligands in their monoanionic form. The new titanium and zirconium complexes were all characterized by elemental analysis, NMR spectroscopy and X-ray crystal structure analysis. The catalyst precursors [(Ap-FI)Ti(O*i*Pr)$_2$] and [(Ap-FI)TiCl$_2$] with the promising *fac-mer* coordination mode of the respective Ap-FI ligand were tested in ethylene polymerization experiments. The results showed that the new catalyst system is able to polymerize ethylene in the presence of MAO and d-MAO, but the noninnocent nature of the Ap-FI ligand inhibits access to narrow polydipersities.

8.2 Introduction

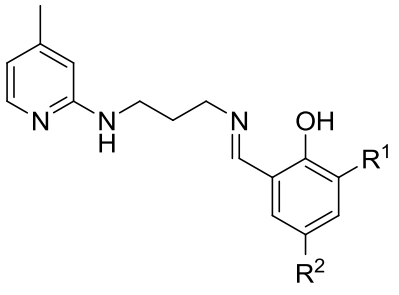
After the discovery of the Ziegler-Natta catalyst[1] in the late 1950s, research and development of the single-site successors metallocenes[2] and constrained-geometry catalysts[3] has made a dramatic impact on polyolefin industry. However, the commercial success of group 4 metallocenes and the aim to control polymer structure while maintaining high polymerization activity by changing the ligand

structure has led to intensive investigations on transition metal complexes as post-metallocene candidates.[4] It turned out that the most promising categories of well-defined catalytic systems for polymerization are cyclopentadienyl-free complexes of group IV metals.[5] This led to a reinforced interest in early-transition-metal complexes of chelating multidentate amine phenolate ligands.[6] These ligands can wrap around oxophilic early transition metals, leading to well-defined geometries at the metal centers and allowing precise control of the complex structure and activity.[7] Recently, our group developed a completely new ligand system, the so-called Ap-FI ligands,[8] which represent a combination of FI (phenoxyimine)[9,6k] and Ap (aminopyridinate)[10,11] ligands. Therefore, Ap-FI ligands also display an example of such multidentate amine phenolate ligands. In this framework, we would like to introduce the variable coordination chemistry of these Ap-FI ligands at titanium and zirconium metal centers. The synthesis of the titianium and zirconium complexes and the resulting different coordination modes were described and discussed. Some of the complexes fulfilled the requirements for promising polymerization catalysts and therefore their preliminary performance in ethylene homopolymerization was tested.

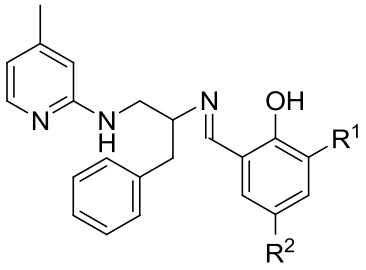
8.3 Results and Discussion

Synthesis and Structure of the Ligands

We recently described the straightforward synthesis of the new Ap-FI ligand hybrids,[8] namely a one-step condensation of the primary amino function of the mono-*N*-arylated diamine[12] with one equivalent of the substituted salicylaldehyde.[13,14] Thus, four different Ap-FI ligands were accessible (Figure 1).



1: R^1 = Adamantyl, R^2 = Me
2: R^1 = R^2 = Cl
3: R^1 = R^2 = *t*Bu



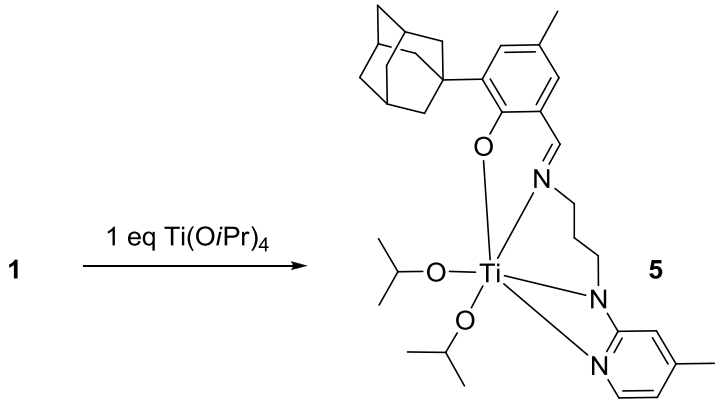
4: R^1 = Adamantyl, R^2 = Me

Figure 1. Ap-FI ligands **1**-**4**.

Because of the Ap-FI hybrid character of the new ligands it is very interesting which subunit dominates the coordination behaviour and adopts the coordination mode of its respective parent ligand. Therefore we studied the coordination chemistry of these ligands with titanium and zirconium.

Synthesis and Structure of the Complexes

The reaction of Ap-FI ligand **1** with Ti(O*i*Pr)$_4$ to obtain the corresponding mono(Ap-FI) titanium diisopropoxide complex **5** (Scheme 1) is already described.[8]



Scheme 1. Synthesis of the mono(Ap-FI) titanium diisopropoxide complex **5**.

The molecular structure of complex **5** is presented in Figure 2 and shows the desired mononuclear *fac-mer* complex.

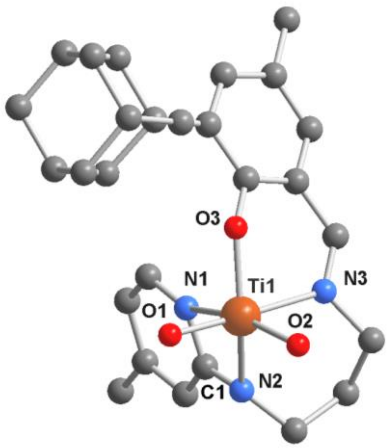
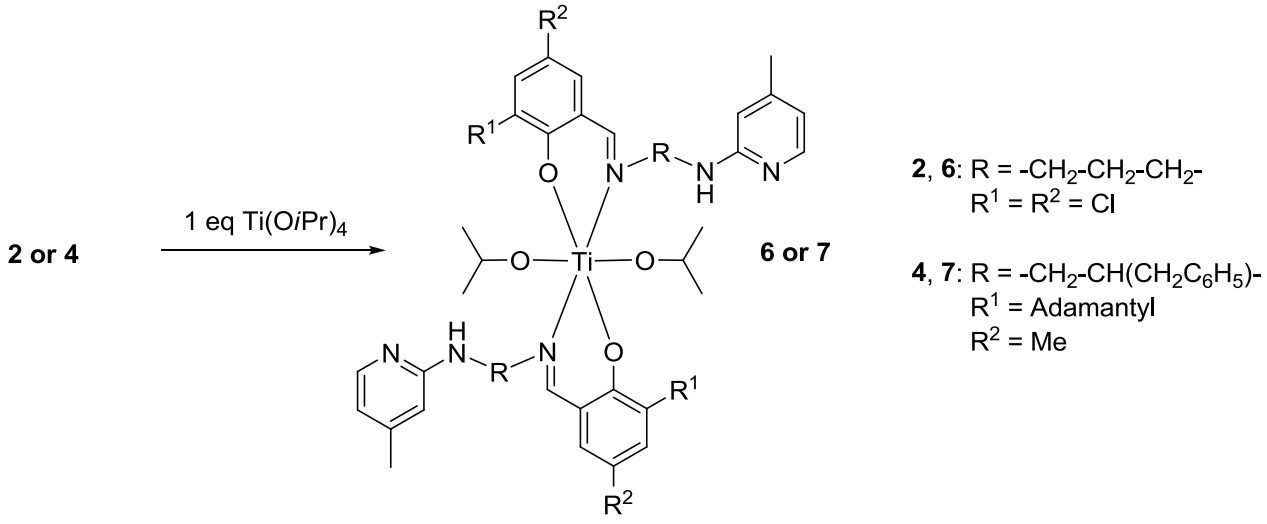


Figure 2. Molecular structure of complex **5**, hydrogen atoms and *i*Pr groups are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: O1-Ti1 1.795(2), N2-Ti1 2.044(3), O2-Ti1 1.821(2), N3-Ti1 2.219(3), O3-Ti1 1.906(2), N1-Ti1 2.273(3), N1-Ti1-O1 90.98(11), O1-Ti1-O2 99.06(11), O2-Ti1-N3 84.94(11), N3-Ti1-N1 85.06(11), N1-C1-N2 108.6(3), N3-Ti1-O3 82.0(1).

The bond lengths of the Ti-$N_{pyridine}$ (2.04 Å) and Ti-N_{amido} bonds (2.27 Å) [11d] as well as the bond lengths of the Ti-$O_{Phenoxy}$ (1.91 Å) and Ti-N_{Imine} bonds (2.22 Å)[15] clearly indicate the adoption of the aminopyridinate and phenoxyimine structural motifs. A detailed analysis of the complex geometry and the binding situation in complex **5** is already described.[8] In summary, the dianionic ligand **1** coordinates in a *fac-mer* mode to the metal center and forms a complex whose crystal structure seems to indicate a promising polymerization catalyst precursor.

In contrast to the above described reaction, ligand **4** reacted in a 2:1 ratio with the metal precursor Ti(O*i*Pr)$_4$ under elimination of two molecules of isopropanol to the bis(ApH-FI) titanium diisopropoxide complex **6** (Scheme 2).



Scheme 2. Syntheses of the bis(ApH-FI) titanium diisopropoxide complexes **6** and **7**.

The corresponding NMR tube reaction showed the exclusive formation of complex **6**. Ligand precursor **2** binds in a bidentate fashion to the metal center and the hydroxyl function is deprotonated while the amine is still protonated. The same reaction with a 1:1 ratio of metal precursor to ligand gave the same signal set of the bis(ApH-FI) titanium diisopropoxide complex and free Ti(O*i*Pr)$_4$. Complex **6** was characterized by NMR spectroscopy and elemental analysis. Suitable crystals of **6** for X-ray analysis (Figure 3) were obtained by slowly cooling a saturated *n*-hexane solution of the complex to -28 °C.

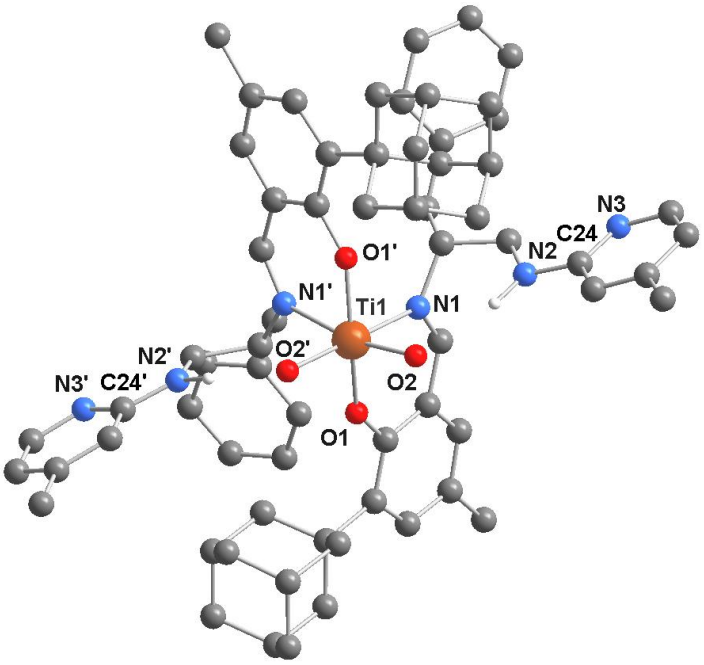


Figure 3. Molecular structure of complex **6**, hydrogen atoms (except NH) and *i*Pr groups are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: O1-Ti1 1.900(2), N1-Ti1 2.269(3), O2-Ti1 1.840(2), N2-C24 1.371(4), C24-N3 1.339(4), O1-Ti1-O2 97.38(10), O2-Ti1-N1 89.77(9), O1-Ti1-N1 81.06(10), N1-Ti1-N1' 80.62(14), O2-Ti1-O2' 100.62(14), N2-C24-N3 116.2(3).

In **6** the coordination sphere around titanium is an octahedron. The Ti-O bond length of the phenoxy group is typical for this structural motif (1.90 Å) but the Ti-N bond length of the imine function is elongated (2.27 Å), maybe because of intramolecular hydrogen bridges towards the free Ap moiety. An elongation of the Ti-O bond length is also shown by the isopropoxide groups. The Ap subunit shows the typical bond length (1.34 – 1.37 Å) and angle (116° instead of 108°) of a non-coordinating aminopyridine.

We considered the shorter carbon bridge and the higher steric pressure through the additional benzyl moiety as likely reasons for the different coordination mode of ligand **4** compared to ligand **1**. Due to this finding we exclusively used the three carbon atom bridge without any further steric hindrance for the following studies.

The conversion of one equivalent of ligand **2** with one equivalent of $Ti(O\textit{i}Pr)_4$ in hexane/ether (1:1) also showed a 2:1 reaction and free metal precursor. The spectroscopically pure bis(ApH-FI) titanium diisopropoxide complex **7** precipitates immediately after elimination of two isopropanol molecules as a white solid (Scheme 2). Complex **7** was characterized by NMR spectroscopy and elemental analysis.

Suitable crystals of **7** for X-ray analysis were obtained by slowly cooling a saturated *n*-hexane solution of the complex to -28 °C (Figure 4).

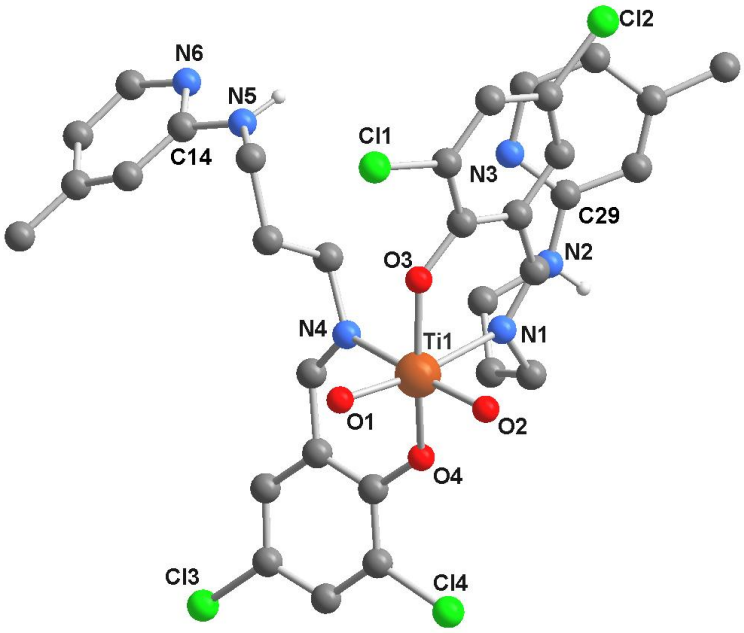
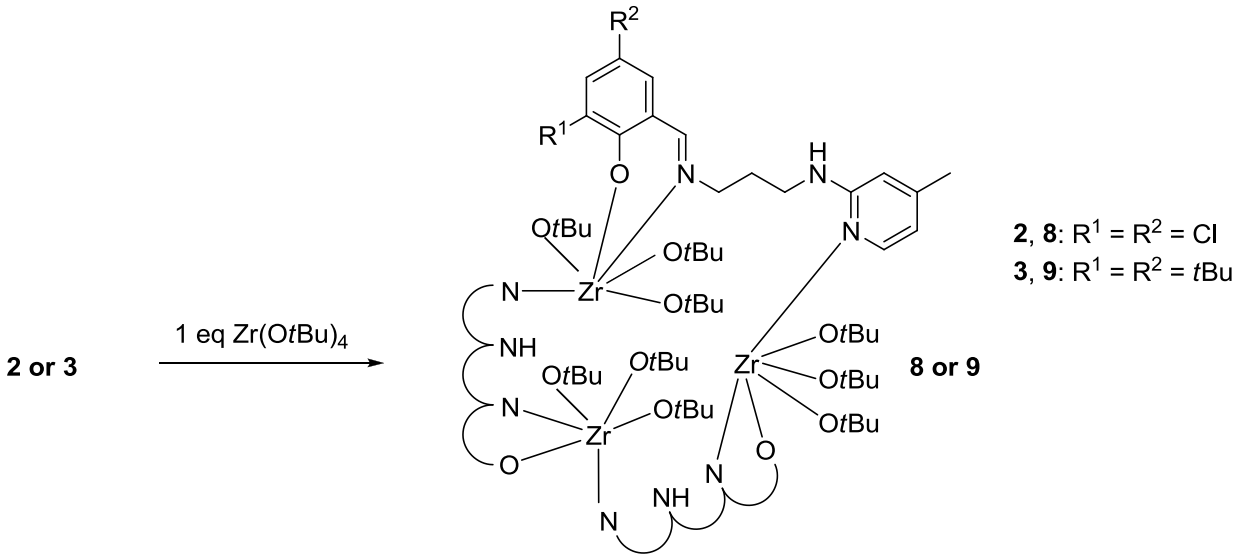


Figure 4. Molecular structure of complex **7**, hydrogen atoms (except NH) and *i*Pr groups are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: O1-Ti1 1.759(8), O2-Ti1 1.738(8), O3-Ti1 1.899(8), O4-Ti1 1.914(8), N1-Ti1 2.224(12), N4-Ti1 2.212(10), N2-C29 1.362(13), N3-C29 1.355(15), N5-C14 1.364(13), N6-C14 1.365(13), O1-Ti1-O2 102.0(4), O2-Ti1-N1 88.5(4), N1-Ti1-N4 81.8(4), O3-Ti1-N1 82.0 (4), O4-Ti1-O1 96.4(4), N2-C29-N3 115.6(14), N5-C14-N6 111.4(12).

The coordination geometry of complex **7** is very similar to that of complex **6**. Typical bond lengths are shown by the phenoxyimine motif and the Ap part also shows the expected bond lengths and angles for its non-coordinating mode. Only the isopropoxide groups stand out with relatively short Ti-O bond lengths of 1.74-1.76 Å which could be due to a weaker bonding of the chloro-substituted ligand **2** compared to **4**.

However, the last two complexes feature only the phenoxyimine part bonded to the metal. Because of that, they contain two free secondary amine functions each and are thus not useful in any polymerization protocol.

Neither does the use of a bigger metal center lead to the desired coordination mode in the case of ligand **2**. A one to one conversion of ligand **2** with zirconium(IV) *tert*-butoxide in diethyl ether/hexane resulted in the elimination of one equivalent of *tert*-butanol and the formation of the cyclic species **8** (Figure 5 and Scheme 3).



Scheme 3. Syntheses of the trinuclear ApH-FI zirconium tri-*tert*-butoxide complexes **8** and **9**.

The hydroxyl function of ligand **2** is deprotonated while the amine function stays protonated. Complex **8** was characterized by NMR spectroscopy and elemental analysis. The corresponding NMR tube reaction showed the quantitative formation of complex **8** so that no other byproducts were observed.

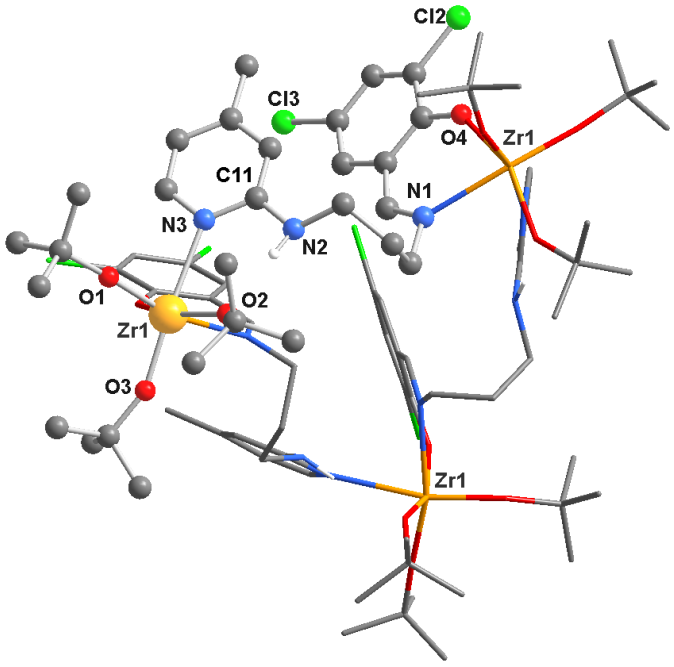
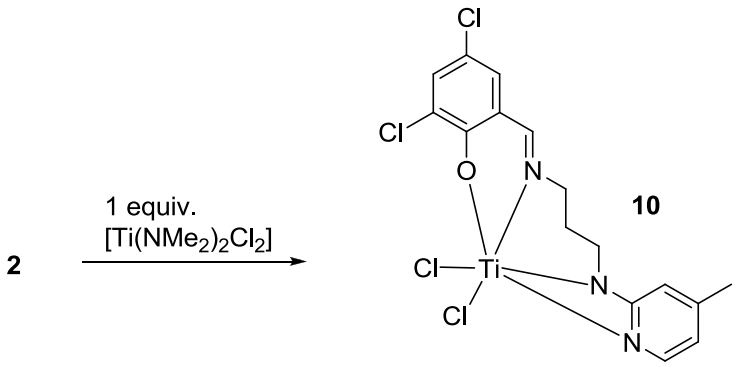


Figure 5. Molecular structure of complex **8**, hydrogen atoms (except NH) are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: O1-Zr1 1.912(4), O2-Zr1 1.999(4), O3-Zr1 1.926(4), O4-Zr1 2.089(4), N3-Zr1 2.507(5), N1-Zr1 2.443(5), N3-C11 1.365(7), N2-C11 1.362(8), O1-Zr1-O2 101.70(17), O2-Zr1-N1 82.68(17), N1-Zr1-O4 75.26(17), O4-Zr1-O1 96.47(17), N3-Zr1-O2 85.66(17), O3-Zr1-O1 102.15(17), N3-C11-N2 116.1(6).

Complex **8** shows an octahedral coordination sphere around the zirconium atom. The coordinating phenoxy group (2.089(4) Å, usually 1.91 Å[15]), the imine group (2.443(5) Å, usually 2.22 Å[15]) as well as the pyridine group (2.507(5) Å, usually 2.154 Å[10d]) all show elongated bonds to the metal compared to their usual structural motifs. This may indicate a high steric pressure in this trinuclear species. Only the *tert*-butoxide groups at O1 and O3 show their typical Ti-O bond lengths of 1.91 – 1.93 Å whereas the *tert*-butoxide group at O2, *trans* to the phenoxy group, features an elongated Ti-O bond of 2.00 Å.

Increasing the steric pressure at the ligand by using ligand **3** also did not lead to the desired mononuclear compound. Ligand **3** reacted with zirconium(IV) *tert*-butoxide clearly in a 1:1 ratio in hexane under elimination of one equivalent of *tert*-butanol to yield complex **9** (Scheme 3). Complex **9** was characterized by NMR spectroscopy and elemental analysis.

After these unexpected results concerning the complexation properties of the new ligand system we tried a different leaving group at the metal center. For this purpose we used for the following studies bis(dimethylamido) titanium(IV) dichloride as precursor material. With this a selective synthesis of the mono(Ap-FI) titanium dichloride complex **10** was possible. One equivalent of ligand **2** reacted readily with one equivalent of bis(dimethylamido) titanium(IV) dichloride in thf/toluene under elimination of two equivalents of dimethylamine (Scheme 4).



Scheme 4. Synthesis of the mononuclear Ap-FI titanium dichloride complex **10**.

In the corresponding NMR tube reaction no other byproducts were observed. Complex **10** was characterized by NMR spectroscopy and elemental analysis as well as XRD analysis (Figure 6).

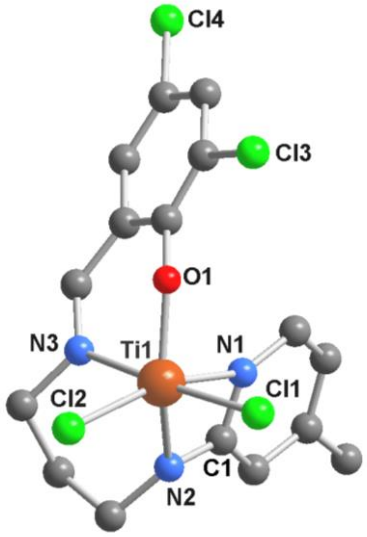


Figure 6. Molecular structure of complex **10**, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Cl1-Ti1 2.323(3), Cl2-Ti1 2.261(4), N1-Ti1 2.173(9), N2-Ti1 1.953(10), N3-Ti1 2.180(9), O1-Ti1 1.868(7), N1-C1 1.336(14), N2-C1 1.345(13), Cl2-Ti1-Cl1 95.59(13), Cl1-Ti1-N1 89.3(2), N1-Ti1-N3 85.2(3), N3-Ti1-Cl2 90.1(3), O1-Ti1-N3 82.8(3), N2-Ti1-Cl2 98.0(3), N2-C1-N1 107.9(10).

The geometry of complex **10** is very similar to the geometry of complex **5** and also shows a slightly distorted octahedron. Like in complex **5** the bond lengths are typical of the aminopyridinate (short Ti-N_{amido} distance of 1.95 Å; long Ti-$N_{pyridine}$ distance of 2.17 Å; N-C-N angle of 108°)[11d] and phenoxyimine (Ti-$O_{phenoxy}$ 1.87 Å; Ti-$N_{pyridine}$ 2.18 Å)[15] structural motifs. The two chloro ligands show different bond lengths (2.32 Å and 2.26 Å, respectively). In summary, the dianionic ligand **2** coordinates in a *fac-mer* mode to the metal center and forms a complex whose crystal structure seems to indicate a promising polymerization catalyst precursor.

After full characterization of the synthesized Ap-FI titanium and zirconium complexes there were two titanium complex species (**5** and **10**) which fulfill the requirements for a promising catalyst precursor. Complexes **5** and **10** clearly show a mononuclear *fac-mer* structure with two remaining isopropoxide or chloro groups, *cis*-located to each other, at the metal center. For this reason the following ethylene polymerization studies were exclusively done with complexes **5** and **10**.

Ethylene Polymerization Studies

For the polymerization studies we chose an amount of 10 µmol catalyst precursor, 150 mL toluene as the solvent, a pressure of 2 bar, a reaction time of 9 h and a temperature of 35 °C as standard conditions.

Despite the well-defined *fac-mer* coordination mode of ligand **1** and **2** in the tested complexes **5** and **10**, they do not show the expected high control during the polymerization process.

When complex **5** is activated with commercial MAO only poor activities but high molecular weights can be observed. The activity slightly increases with the amount of MAO but the broad PDIs (PDI = polydispersity) of 2 to 3 nearly stay the same (Table 1, entry 1 – 3; Figure 7).

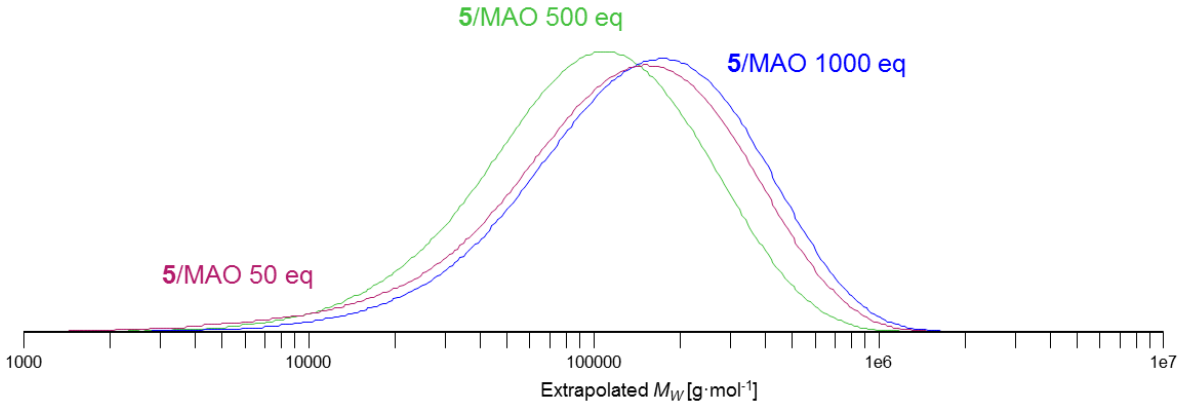


Figure 7. Molecular weight distribution (GPC) of the polymerization experiments listed in Table 1, entry 1-3.

Complex **10** even shows bimodal distributions when activated with commercial MAO (Table 1, entry 4 and 5; Figure 8). Compared to complex **5**, complex **10** gives higher activities and higher molecular weights but broader PDIs.

Table 1. Comparison of the ethylene polymerization with catalyst precursors **5** and **10** when activated with commercial MAO.[a]

Entry	Precursor	Activator MAO [eq (mmol)]	Yield [g]	Activity [g_{PE}·mol^{-1}·h^{-1}·bar^{-1}]	M_w [kg·mol^{-1}][b]	PDI[b]
1	**5**	50 (0.5)	0.03	167	180.2	3.0
2	**5**	500 (5)	0.08	444	136.7	2.3
3	**5**	1000 (10)	0.13	722	205.7	2.4
4	**10**	50 (0.5)	0.77	4272	654.0	88.0
				peak 1	754.0	9.8
				peak 2	1.7	1.5
5	**10**	500 (5)	1.04	5750	612.9	73.2

					peak 1	651.5	18.3
					peak 2	0.9	1.4
6	**10**	1000 (10)	1.01	5589		602.9	46.0

[a] Conditions: Precursor (**5** or **10**): 10 µmol, toluene 150 mL, pressure: 2 bar, time: 9 h, temperature: 35 °C. [b] Determined by HT-GPC analysis vs. polyethylene standards.

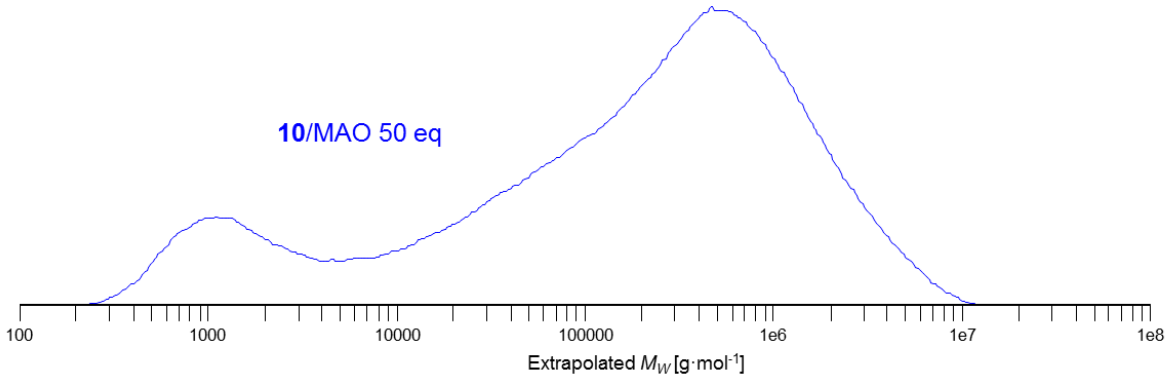


Figure 8. Bimodal molecular weight distribution (GPC) of the polymerization experiment 4 listed in Table 1.

By switching the co-catalyst to dry methylaluminoxane (d-MAO; all volatiles, especially free trimethylaluminum (TMA), are removed from the commercially bought MAO) both of the catalysts show higher activities and high molecular weights of up to 1,751 kg/mol for the resulting polymeric product but the PDIs remain broad (Table 2). This increase in activity by the use of d-MAO probably indicates that the new titanium complexes are sensitive to TMA.

Table 2. Comparison of the ethylene polymerization of catalyst precursors **5** and **10** when activated with d-MAO.[a]

Entry	Precursor	Activator d-MAO [eq (mmol)]	Yield [g]	Activity [g_{PE}·mol^{-1}·h^{-1}·bar^{-1}]	M_w [kg·mol^{-1}][b]	PDI[b]
1	**5**	500 (5)	0.55	3056	1,411.4	4.3
2	**10**	500 (5)	1.18	6556	1,751.0	15.3

[a] Conditions: Precursor (**5** or **10**): 10 µmol, toluene 150 mL, pressure: 2 bar, time: 9 h, temperature: 35 °C. [b] Determined by HT-GPC analysis vs. polyethylene standards.

Because of the poor ethylene polymerization activities and the partially bimodal molecular weight distributions we assume that the ligand and especially the imine function of the ligand is involved in some transformations during the polymerization process. Bimodal distributions are often caused by the *in situ* formation of a second catalyst species. Maybe the *fac-mer* coordination mode is not stable under polymerization conditions or the imine function is alkylated so that a different catalyst species appears during the polymerization process.

8.4 Conclusion

Depending on the electronic and steric properties of the new Ap-FI ligand hybrids as well as on the eliminated function (alcohol or amine elimination) two different mono(Ap-FI) and bis(ApH-FI) titanium complexes and two different trinuclear ApH-FI zirconium complexes were selectively synthesized. In the first case the Ap-FI ligands acted as tetradentate dianionic ligands. In the second case they acted as bidentate monoanionic ligands and in the third case they acted as bridging tridentate monoanionic ligands. All different coordination modes were characterized by X-ray structure analysis and therefore the bond lengths and angles were discussed in detail. The structures of the mono(Ap-FI) complexes show the desired *fac-mer* coordination mode of the ligand. X-ray structures of the bis(ApH-FI) titanium and the trinuclear ApH-FI zirconium complexes show free Ap coordination sites and therefore were not useful for any polymerization protocol. The two mono(Ap-FI) titanium complexes described herein are active in ethylene polymerization and produce high molecular weight PE. Better activities can be achieved with the use of d-MAO as co-catalyst instead of commercial MAO. This indicates a sensitivity of the catalyst precursors towards TMA.

8.5 Experimental Section

General Comments: All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in a nitrogen or argon filled glove box (mBraun 120-G) with a high-capacity recirculator (< 0.1 ppm O_2). Deuterated solvents were obtained from Cambridge Isotope Laboratories. Solvents and reagents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy, or sodium ketyl of benzophenone under nitrogen immediately before use.

Toluene for polymerization (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu catalyst, and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu catalyst and molecular sieves (Aldrich, 4 Å). d-MAO was prepared by removal of volatiles from MAO (4.9 wt.-% Al).

Commercial 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 3,5-dichloro-2-hydroxybenzaldehyde, 2-(1-adamantyl)-4-methylphenol, titanium(IV) isopropoxide and zirconium(IV) *tert*-butoxide were used as received from Sigma-Aldrich. The precursor materials bis(dimethylamido) titanium(IV) dichloride[16] and 3-adamantyl-2-hydroxy-5-methylbenzaldehyde[14] were prepared according to published procedures. The mono-*N*-arylated aliphatic diamines 3-phenyl-*N'*-pyridin-2-yl-propane-1,2-diamine and *N'*-(4-methyl-pyridin-2-yl)-propane-1,3-diamine were synthesized *via* the published process of Ir-catalyzed amine alkylation of aromatic amines with unprotected amino alcohols.[12] The Ap-FI ligands **1**-**4** and the mono(Ap-FI) titanium complex **5** were synthesized according to published procedures.[8]

NMR spectroscopy: NMR spectra were recorded on a Varian INOVA 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75.4 MHz). The ^{1}H and ^{13}C NMR spectra were measured at 25 °C and referenced internally using the residual solvent resonances. All chemical shifts (δ) are reported in ppm.

Gel permeation chromatography (GPC): Gel permeation chromatography (GPC) analysis for polyethylene was carried out on a Polymer Laboratories Ltd. PL-GPC 220 high temperature chromatographic unit equipped with DP and RI detectors and two linear mixed bed columns (Olexis, 13 micron particle size). GPC analysis were performed at 150 °C 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 the solutions were run without filtration. The molecular weights of the samples were referenced to polyethylene (M_w = 520–3200000 g·mol^{-1}) and polystyrene (M_w = 580–2800000 g·mol^{-1}) standards. The reported values are the average of at least two independent determinations.

Elemental analyses (C,H,N): Elemental analyses (C,H,N) were carried out with a Vario elementar EL III instrument.

X-ray Crystallography: X-ray crystal structure analyses were performed with a STOE-IPDS II instrument equipped with an Oxford Cryostream low-temperature unit (λ(MoKα) = 0.71073 Å). Structure solution and refinement were accomplished using SIR97,[17] SHELXL-97[18] and WinGX.[19] Details of the X-ray crystal structure analyses are listed in Table 3 and Table 4.

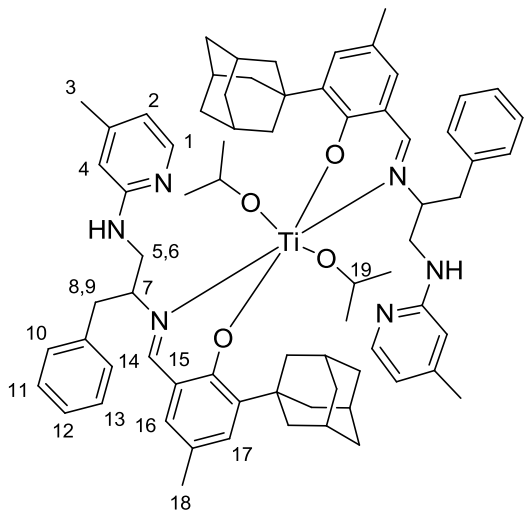
Table 3. Parameters of the X-ray analysis of **5**, **6** and **7**.

Compound	**5**	**6**	**7**
Formula	$C_{33}H_{47}N_3O_3Ti$	$C_{72}H_{90}N_6O_4Ti$	$C_{38}H_{46}Cl_4N_6O_4Ti$
Crystal system	hexagonal	tetragonal	triclinic
Space group	$P\bar{3}$	$I4_1/a$	$P\bar{1}$
a [Å]	23.3440(11)	17.972(3)	10.1130(12)
b [Å]	23.3440(11)	17.972(3)	13.3870(18)
c [Å]	9.7930(4)	44.4760(11)	16.856(2)
α [°]	90.00	90.00	102.353(5)
β [°]	90.00	90.00	104.054(5)
γ [°]	120.00	90.00	92.543(5)
V [Å^3]	4621.6(4)	14365(4)	2151.3(5)
Z	6	8	2
Crystal size [mm^3]	0.69×0.15×0.12	0.75×0.52×0.41	0.34×0.09×0.07
$\varrho_{calcd.}$ [g·cm^{-3}]	1.254	1.065	1.298
μ [mm^{-1}] (Mo-K$_\alpha$)	0.315	0.167	0.491
T [K]	133(2)	133(2)	133(2)
θ range [°]	1.74–24.68	1.22–24.68	1.28–24.64
Reflections unique	5207	6050	7232
Refl. Obs. [I > 2σ(I)]	3357	2091	928
Parameters	365	467	484
wR_2 (all data)	0.1152	0.0925	0.1602
R_1 value [I > 2σ(I)]	0.0621	0.0425	0.0573
Largest diff. peak and hole [e·Å^{-3}]	0.328/-0.369	0.188/-0.190	0.245/-0.262

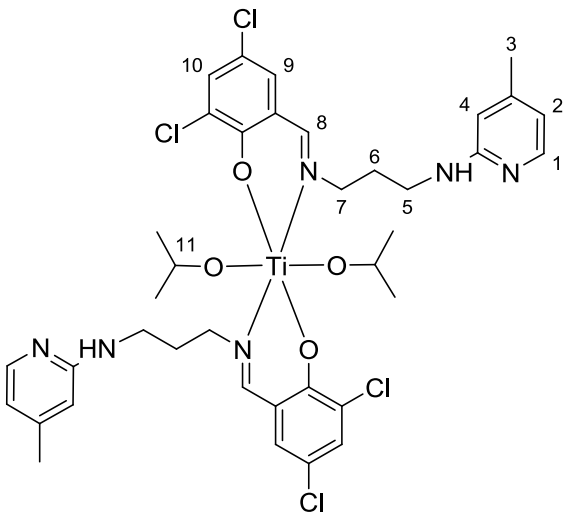
Table 4. Parameters of the X-ray analysis of **8** and **10**.

Compound	**8**	**10**
Formula	$C_{84}H_{129}Cl_6N_9O_{12}Zr_3$	$C_{16}H_{15}Cl_4N_3OTi$
Crystal system	trigonal	monoclinic
Space group	$R\bar{3}$	$P2_1/c$
a [Å]	25.4530(9)	8.2070(7)
b [Å]	25.4530(9)	8.7960(8)
c [Å]	26.8070(10)	26.098(3)
α [°]	90.00	90.00
β [°]	90.00	96.125(5)
γ [°]	120.00	90.00
V [Å^3]	15040.3(9)	1873.2(3)
Z	6	4
Crystal size [mm^3]	0.20×0.13×0.08	0.46×0.14×0.10
$\varrho_{calcd.}$ [g·cm^{-3}]	1.287	1.613
μ [mm^{-1}] (Mo-K$_\alpha$)	0.522	1.037
T [K]	133(2)	133(2)
θ range [°]	1.20–24.58	1.57–24.63
Reflections unique	5614	3149
Refl. Obs. [I > 2σ(I)]	2679	1325
Parameters	388	226
wR_2 (all data)	0.0948	0.2179
R_1 value [I > 2σ(I)]	0.0624	0.0777
Largest diff. peak and hole [e·Å^{-3}]	0.344/-0.660	0.484/-0.407

Preparation of 6. Titanium(IV) isopropoxide (0.30 mL, 1.00 mmol) was added to a solution of **4** (0.50 g, 1.00 mmol) in toluene (15 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h after which the solvent was removed in vacuum. The residue was suspended in hexane (20 mL) and the overlaying yellow solution was filtered. The filtrate was concentrated under vacuum and allowed to crystallize at low temperature (-28 °C) to give yellow crystals (0.37 g, 64%) suitable for X-ray analysis. Elemental analysis for $C_{72}H_{90}N_6O_4Ti$ (1150.65): calcd. C 75.11, H 7.88, N 7.30; found C 75.30, H 7.89, N 7.80. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 8.23 (s, 2H, H^{15}), 8.08 (d, *J* = 5.1 Hz, 2H, H^2), 7.42 (d, *J* = 1.9 Hz, 2H, H^{16}), 7.02 – 6.95 (m, 6H, $H^{11,12,13}$), 6.70 (d, *J* = 1.9 Hz, 2H, H^{17}), 6.52 – 6.43 (m, 4H, $H^{10,14}$), 6.26 (s, 2H, H^4), 6.16 (d, *J* = 5.1 Hz, 2H, H^1), 5.61 (br s, 2H, NH), 5.50 (sept, *J* = 6.2 Hz, 2H, H^{19}), 5.34 – 5.20 (m, 2H, H^7), 3.80 – 3.69 (m, 4H, $H^{5,6}$), 2.70 – 2.59 (m, 2H, H^8), 2.48 (s, 12H, $H^{adamantyl}$), 2.46 - 2.34 (m, 2H, H^9), 2.28 (s, 6H, H^{18}), 2.05 (s, 6H, $H^{adamantyl}$), 1.98 – 1.89 (m, 6H, $H^{adamantyl}$), 1.86 (s, 6H, H^3), 1.78 – 1.66 (m, 6H, $H^{adamantyl}$), 1.55 (d, *J* = 6.2 Hz, 6H, $H^{isopropyl-CH3}$), 1.34 (d, *J* = 6.2 Hz, 6H, $H^{isopropyl-CH3}$) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, 298 K): δ = 166.7 (CH), 165.6 (CH), 162.0 (C), 162.9 (C), 157.8 (C), 157.0 (C), 148.4 (CH), 148.1 (CH), 148.0 (C), 147.2 (C), 141.1 (C) 139.4 (C), 137.4 (C), 136.6 (C), 133.7 (CH), 133.5 (CH), 131.4 (CH), 130.8 (CH), 129.8 (2CH), 129.5 (2CH), 128.5 (2CH), 128.2 (2CH), 127.4 (CH), 127.1 (C), 127.0 (C), 126.4 (CH), 120.1 (C), 119.6 (C), 114.6 (CH), 114.1 (CH), 108.2 (CH), 107.4 (CH), 78.5 (CH), 71.1 (CH), 62.8 (CH), 62.0 (CH), 46.8 (CH_2), 45.8 (CH_2), 41.2 (C), 41.0 ($3CH_2$), 40.7 (C), 40.6 ($3CH_2$), 37.7 (CH_2), 37.6 (CH_2), 37.4 ($3CH_2$), 37.3 ($3CH_2$), 29.5 (3CH), 29.4 (3CH), 26.5 (CH_3), 26.3 (CH_3), 26.0 (CH_3), 25.8 (CH_3), 20.7 ($2CH_3$), 20.6 ($2CH_3$) ppm.

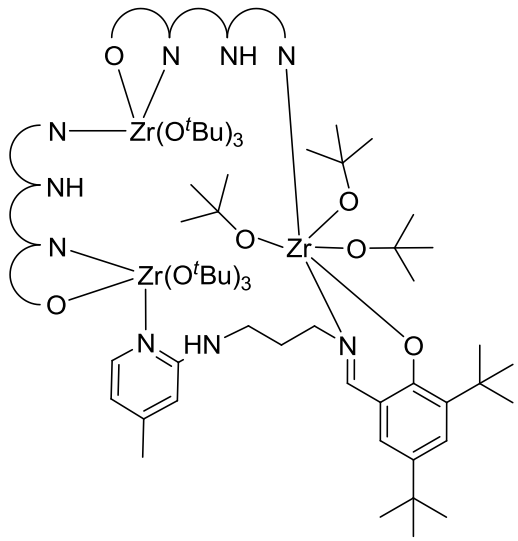


Preparation of 7. Titanium(IV) isopropoxide (0.44 mL, 1.49 mmol) was added to a solution of **2** (0.50 g, 1.48 mmol) in hexane/ether (1:1; 28 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. The yellow overlaying solution was filtered off and the white precipitate was evaporated to dryness affording **7** as a white spectroscopically pure compound (0.39 g, 31%). Suitable crystals for X-ray analysis were grown from a saturated hexane solution at low temperature (-28 °C). Elemental analysis for



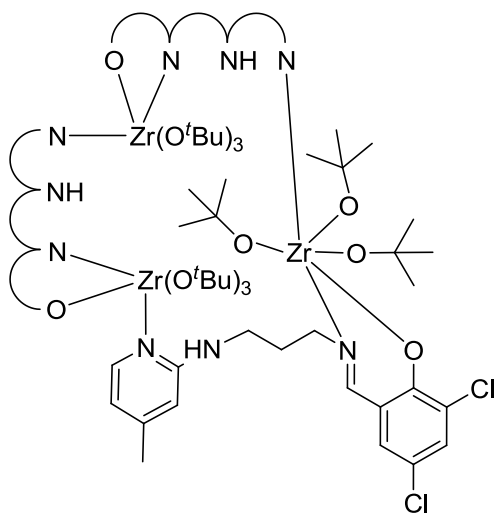
$C_{38}H_{46}Cl_4N_6O_4Ti$ (840.49): calcd. C 54.30, H 5.52, N 10.00; found C 54.05, H 5.39, N 9.98. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 8.10 (d, *J* = 5.2 Hz, 2H, H^2), 7.37 (d, *J* = 1.9 Hz, 2H, H^9), 7.32 (s, 2H, H^8), 6.67 (d, *J* = 1.9 Hz, 2H, H^{10}), 6.22 (d, *J* = 5.2 Hz, 2H, H^1), 5.80 (s, 2H, H^4), 4.87 (sept, *J* = 6.2 Hz, 2H, H^{11}), 4.17 (s br, 2H, NH), 3.48 – 3.06 (m, 8H, $H^{5,7}$), 1.94 (s, 6H, H^3), 1.90 –1.76 (m, 4H, H^6), 1.23 (d, *J* = 5.9 Hz, 6H, $H^{isopropyl\text{-}CH3}$), 1.16 (d, *J* = 5.9 Hz, 6H, $H^{isopropyl\text{-}CH3}$) ppm. ^{13}C NMR (75.4 MHz, THF-d_8, 298 K): δ = 164.3 (2CH), 159.3 (2C), 158.6 (2C), 148.2 (2CH), 147.5 (2C), 133.5 (2CH), 131.4 (2CH), 124.5 (2C), 123.3 (2C), 120.7 (2C), 114.3 (2CH), 108.0 (2CH), 80.1 (2CH), 60.1 ($2CH_2$), 39.3 ($2CH_2$), 31.4 ($2CH_2$), 25.6 ($2CH_3$), 25.4 ($2CH_3$), 20.8 ($2CH_3$) ppm.

Preparation of 8. Ligand **2** (0.51 g, 1.50 mmol) was dissolved in diethyl ether/hexane (28 mL, 5:2) and cooled to 0 °C. Zirconium(IV) *tert*-butoxide (0.58 g, 1.50 mmol) was added dropwise to the solution and the resulting mixture was warmed to room temperature and stirred overnight. The orange overlaying solution was filtered off and the yellow precipitate was evaporated to dryness affording **8** as a spectroscopically pure compound (0.64 g, 66%). Elemental analysis for $C_{84}H_{129}Cl_6N_9O_{12}Zr_3$ (1943.37):



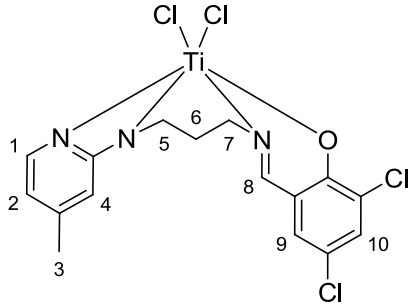
calcd. C 51.92, H 6.69, N 6.49; found C 51.91, H 6.56, N 6.70. ^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 8.16 (s, 3H, CH^{imine}), 7.84 (d, *J* = 5.1 Hz, 3H, $ArH^{pyridine}$), 7.39 (d, *J* = 2.3 Hz, 3H, $ArH^{phenoxyimine}$), 7.13 (d, *J* = 2.3 Hz, 3H, $ArH^{phenoxyimine}$), 6.29 (d, *J* = 5.1 Hz, 3H, $ArH^{pyridine}$), 6.18 (s, 3H, $ArH^{pyridine}$), 5.61 (br s, 3H, NH), 4.00 (t, *J* = 14.0 Hz, *J* = 7.2 Hz, 6H, CH_2), 3.36 (q, *J* = 6.4 Hz, 6H, CH_2), 2.14 (s, 9H, $CH_3^{pyridine}$), 2.10 (m, 6H, CH_2), 1.25 (s, 81H, $CH_3^{tert\text{-}butoxide}$) ppm. ^{13}C NMR (75.4 MHz, THF-d_8, 298 K): δ = 168.2 (3CH), 160.3 (3C), 159.8 (3C), 148.4 (3CH), 147.7 (3C), 133.3 (3CH), 132.4 (3CH), 126.3 (3C), 123.7 (3C), 117.5 (3C), 114.0 (3CH), 108.2 (3CH), 74.7 (9C), 60.5 ($3CH_2$), 39.1 ($3CH_2$), 32.9 (27 CH_3), 32.1 ($3CH_2$), 20.8 ($3CH_3$) ppm.

Preparation of 9. Ligand **3** (0.50 g, 1.31 mmol) was dissolved in hexane (10 mL) and cooled to 0 °C. Zirconium(IV) *tert*-butoxide (0.5 mL, 1.31 mmol) was added dropwise to the solution and the resulting mixture was warmed to room temperature and stirred overnight. The orange solution was evaporated to dryness affording **9** as a spectroscopically pure compound (0.87 g, 96%). Elemental analysis for $C_{108}H_{183}N_9O_{12}Zr_3$ (2073.33): calcd. C 62.56, H 8.90, N 6.08; found C 63.26, H 9.37, N 5.73. ^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 8.21 (s, 3H, CH^{imine}), 7.85 (d, *J* = 5.1 Hz, 3H, $ArH^{pyridine}$), 7.41 (d, *J* = 2.3 Hz, 3H, $ArH^{phenoxyimine}$), 7.04 (d, *J* = 2.3 Hz, 3H, $ArH^{phenoxyimine}$), 6.28 (d, *J* = 5.1 Hz, 3H, $ArH^{pyridine}$),



6.20 (s, 3H, ArH^{pyridine}), 5.59 (br s, 3H, NH), 4.00 (t, J = 14.0 Hz, J = 7.2 Hz, 6H, CH_2), 3.38 (q, J = 6.4 Hz, 6H, CH_2), 2.16 (s, 9H, $CH_3^{pyridine}$), 2.08 (m, 6H, CH_2), 1.51 (s, 54H, $CH_3^{tert\text{-butoxide}}$), 1.28 (s, 81H, $CH_3^{tert\text{-butoxide}}$) ppm. ^{13}C NMR (75.4 MHz, THF-d_8, 298 K): δ = 171.0 (3CH), 162.7 (3C), 160.3 (3C), 148.4 (3CH), 147.5 (3C), 138.7 (3C), 136.7 (3C), 129.4 (3CH), 129.1 (3CH), 122.3 (3C), 113.8 (3CH), 108.1 (3CH), 60.4 ($3CH_2$), 39.4 ($3CH_2$), 35.9 ($9CH_3$), 34.3 (9C), 33.4 ($27CH_3$), 33.0 (3C), 32.8 (3C), 31.7 ($3CH_2$), 30.4 ($9CH_3$), 20.9 ($3CH_3$) ppm.

Preparation of 10. A solution of ligand **2** (0.25 g, 0.74 mmol) in thf (10 mL) was added dropwise to a solution of bis(dimethylamido)titanium(IV) dichloride (0.18 g, 0.87 mmol) in toluene (5 mL) and the mixture was stirred for 2 h. The resulting red solution was concentrated under vacuum and filtered. Layering the filtrate with hexane yielded brown crystals of the product **10** (0.31 g, 92%). Elemental analysis for $C_{16}H_{15}Cl_4N_3OTi$ (454.99): calcd. C 42.24, H 3.32, N 9.24; found C 42.17, H 3.76, N 9.61. ^{1}H



NMR (300 MHz, THF-d_8, 298 K): δ = 8.01 (s, 1H, H^8), 7.64 (d, J = 1.9 Hz, 1H, H^9), 7.31 (d, J = 1.9 Hz, 1H, H^{10}), 7.24 (d, J = 5.1 Hz, 1H, H^2), 6.24 (s, 1H, H^4), 6.02 (d, J = 5.1 Hz, 1H, H^1), 4.95 – 4.81 (m, 2H, H^7), 4.51 – 4.35 (m, 2H, H^5), 2.11 (s, 3H, H^3), 2.54 – 2.28 (m, 2H, H^6) ppm. ^{13}C NMR (75.4 MHz, THF-d_8, 298 K): δ = 166.5 (C), 163.0 (CH), 158.0 (C), 151.3 (C), 142.8 (CH), 133.2 (CH), 132.4 (CH), 126.1 (C), 123.9 (C), 123.5 (C), 112.3 (CH), 107.2 (CH), 63.1 (CH_2), 49.2 (CH_2), 30.6 (CH_2), 21.6 (CH_3) ppm.

Synthesis of the Catalyst Stock Solutions: The complexes **5** and **10** were prepared as described above. For catalytic ethylene conversion the respective yellow or brown residue was dissolved in toluene (10 mL) and used without further purification.

Ethylene Polymerization Studies: The catalytic ethylene polymerization reactions were performed in a 250 mL glass autoclave (Büchi) equipped with a mechanical stirrer in semibatch mode (ethylene was added by replenishing the flow to keep the pressure constant). The reactor was temperature- and pressure-controlled and equipped with separate toluene and catalyst/co-catalyst injection systems. During a polymerization run the pressure, the ethylene flow, the inner and the outer reactor temperature and the stirrer speed were monitored continuously. In a typical semibatch experiment, the

autoclave was evacuated and heated for 1 h at 80 °C prior to use. The reactor was then brought to the desired temperature, stirred at 1000 rpm and charged with 150 mL of toluene together with the required amount of MAO (1.508 M in toluene) or d-MAO (270 mg, 5 mmol). After pressurizing with ethylene to reach a total pressure of 2 bar, the autoclave was equilibrated for 5 min. Subsequently, the catalyst stock solution in toluene (0.01 M, 1 mL) was injected into the autoclave to start the reaction. During the run the ethylene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing the gas flow. After 15 min. of reaction time the reactor was vented and the residual aluminum alkyls were destroyed by addition of 50 mL ethanol to the reactor. The polymeric product was collected, stirred for 30 min. in acidified ethanol and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and then in vacuo at 80 °C to a constant weight.

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8.6 References

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9 List of Publications

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

1) M. Dötterl, I. Haas, H. G. Alt, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1502–1506.
"Solubility Behaviour of $TiCl_4$, $ZrCl_4$, and $HfCl_4$ in Chloroaluminate Ionic Liquids"

2) I. Haas, W. P. Kretschmer, R. Kempe, *Organometallics* **2011**, *30*, 4854–4861.
"Synthesis of Aluminum-Terminated Linear PE with a Hafnium Aminopyridinate Catalyst"

3) I. Haas, W. P. Kretschmer, R. Kempe; *to be submitted.*
"Flipping the Switch from Polymerization to Oligomerization with a Monoanionic η^1-Imidazolidiniminate as Ancillary π-Donor Ligand"

4) I. Haas, W. P. Kretschmer, R. Kempe, *EP* 13158550, **2013**. (Patent Application)
"Complexes for the Catalytic Oligomerization of Olefins"

5) I. Haas, C. Hübner, W. P. Kretschmer, R. Kempe, *Chem. Eur. J.,* doi: 10.1002/chem.201301176.
"A Highly Efficient Titanium Catalyst for the Synthesis of Ultra-High Molecular Weight Polyethylene (UHMWPE)"

6) I. Haas, T. Dietel, K. Press, M. Kol, R. Kempe; *submitted to Chem. Eur. J.*
"Aminopyridinate-FI hybrids, their hafnium and titanium complexes and living 1-hexene polymerization"

7) I. Haas, T. Dietel, R. Kempe; *to be submitted.*
"Coordination chemistry of Ap-FI hybrids with titanium and zirconium and their ethylene homopolymerization performance"

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11 Declaration/Erklärung

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

This work has so far neither been submitted to the Bayreuth Graduate School of Mathematical and Natural Sciences nor to any other scientific institution for the purpose of a doctoral thesis.

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

Diese Arbeit wurde bisher weder an der Bayreuther Graduiertenschule für Mathematik und Naturwissenschaften noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht.

Bayreuth, den _____

Isabelle Haas