Coordinative Chain-Transfer Polymerization of Ethylene with NCN-Ligand Stabilized Complexes of Titanium and Zirconium

Dissertation

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

vorgelegt von

Johannes Obenauf, M.Sc.

geboren am 3. Oktober 1985 in Forchheim

Bayreuth 2015

The following work was carried out from December 2011 to March 2015 at the Chair of Inorganic Chemistry II at the University of Bayreuth, Germany under the supervision of Professor Dr. Rhett Kempe.

This is a full reprint of the dissertation submitted to obtain the academic degree of Doctor of Natural Sciences (Dr. rer. nat.) and approved by the Faculty of Biology, Chemistry and Geosciences of the University of Bayreuth.

Thesis submitted: 18.03.2015
Admission by the executive committee: 26.03.2015
Date of scientific colloquium: 09.07.2015

Faculty director: Prof. Dr. Rhett Kempe

Examination committee:

Prof. Dr. Rhett Kempe	1st reviewer
Prof. Dr. Peter Strohriegl	2nd reviewer
Prof. Dr. Stephan Förster	Chairman
Prof. Dr. Birgit Weber	

Meiner Familie in Dankbarkeit

“Alles ist möglich, vorausgesetzt, dass es genügend unvernünftig ist.“

Niels Bohr (1885–1962)

Abbreviations

Ar	aryl
avg.	average
calcd	calculated
CCTP	coordinative chain-transfer polymerization
CGS	chain-growing state
Cp	cyclopentadienyl
CTA	chain-transfer agent
d	doublet
δ	chemical shift (ppm)
EBI	ethylene-bridged bisindenyl
equiv.	equivalents
HT GPC	high-temperature gel permeation chromatography
Hz	Hertz
J	coupling constant (Hz)
KKTP	Koordinative Kettentransfer Polymerisation
m	multiplet
MAO	methylalumoxane
d-MAO	dry-methylalumoxane
Me	methyl
min	minutes
NMR	nuclear magnetic resonance
PDI	polydispersity index
PE	polyethylene
Ph	phenyl
PP	polypropylene
ppm	parts per million

q	quartet
RE	rare earth
rpm	revolutions per minute
s	singlet
T	temperature
t	time
t	triplet
TEA	triethylaluminium
TM	transition metal
TMA	trimethylaluminium

Table of Contents

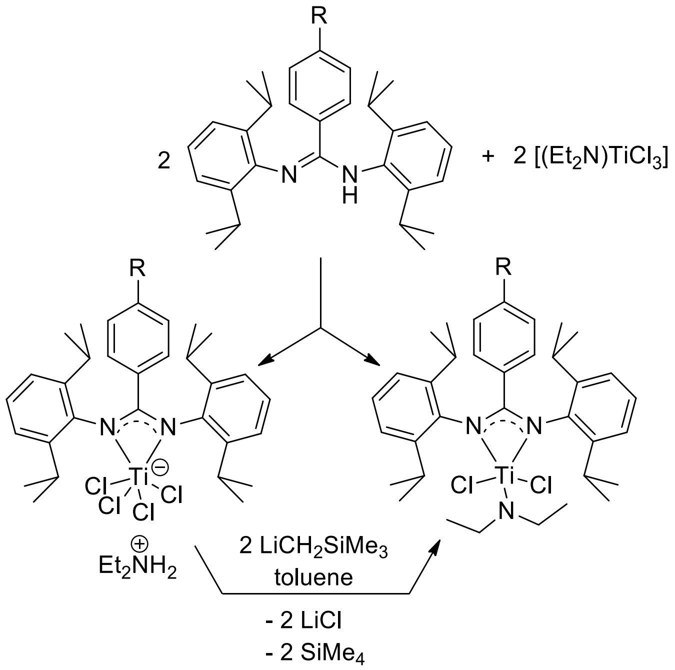
1 Summary/Zusammenfassung

1.1 Summary

Content of the present work is the development of novel group IV transition metal based catalyst systems which are able to polymerize ethylene in a highly controlled and efficient fashion. Besides synthesis and complete characterization of the ligands and complexes, these novel catalyst systems were tested in coordinative chain-transfer polymerization (CCTP) of ethylene. It includes optimization of the reaction conditions, assignment of mechanistic aspects concerning individual polymerization ability and detailed analysis of the resulting poly- or oligomeric products.

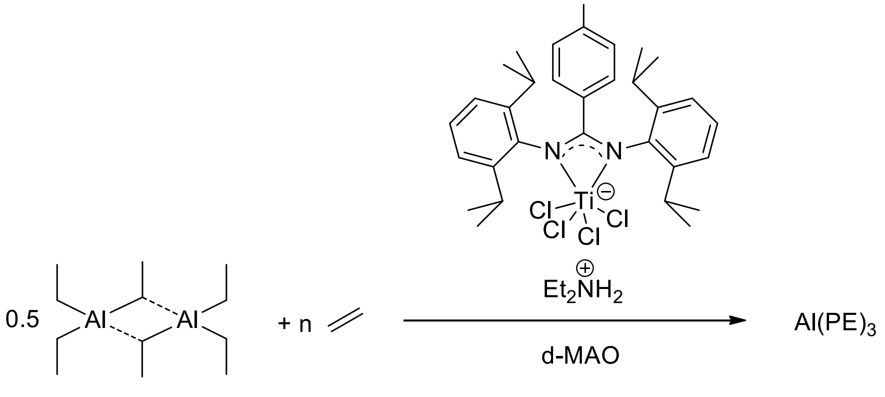
Aminopyridinato (Ap) stabilized rare earth (RE) and transition metal (TM) based catalyst systems can be highly active in coordinative chain-transfer polymerization of ethylene. However, these systems suffered from sensitivity to aluminium alkyls such as ligand transfer to aluminium or supposed blockade of the active site. To sort out this problem, Ap-related ligands were used to stabilize titanium and zirconium based catalyst systems. Amidinato- and guanidinato-ligands can prevent the ligand transfer but may maintain high polymerization activity.

A library of novel mono(amidinato) titanium(IV) complexes was synthesized, fully characterized by NMR spectroscopy, elemental analysis and X-ray single crystal structure analysis. It could be determined that trichloro diethylamido titanium(IV) reacts with a variety of bulky amidines to form a 1:1 mixture of anionic mono(amidinato) tetrachloro titanium(IV) complexes with a diethylammonium counterion and mono(amidinato) dichloro diethylamido titanium(IV) complexes (Scheme 1). The addition of strong bases to the anionic complexes selectively led to the neutral dichloride congeners. In comparison to the non-substituted benzamidinato ligand, X-ray single crystal structure analyses indicated an increased electron-donating ability of these novel ligands. This effect is related to the introduction of electron-donating groups to the backbone of the ligands.



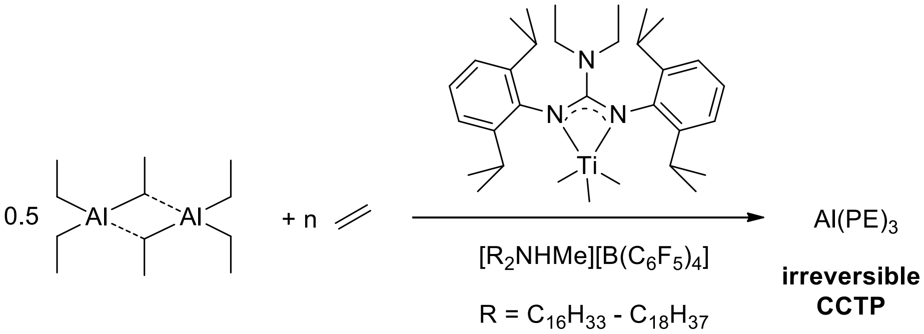
Scheme 1. Synthesis of mono(amidinato) titanium(IV) complexes. R = H, NMe_2, OMe, 2,5-dimethylpyrrole.

These mono(amidinato) titanium(IV) complexes gave rise to highly active polymerization catalysts after activation with d-MAO (activities up to 3500 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$, Scheme 2). High-temperature ^{1}H NMR spectroscopy of the received polymers confirmed Al-terminated polyethylene (PE) due to the absence of olefinic proton resonances after hydrolytic workup. Thus, this reaction can be seen as a metal complex catalyzed version of Ziegler's "Aufbaureaktion". The introduction of electron-donating groups to the backbone of the phenyl groups of the ligands had only marginal influence on the polymerization performance.



Scheme 2. Ethylene polymerization with mono(amidinato) titanium(IV) complexes. R = H, NMe_2, OMe, 2,5-dimethylpyrrole.

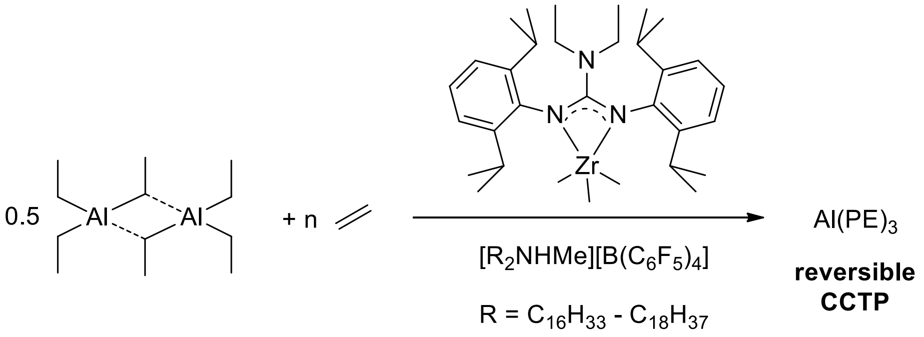
Afterwards, several guanidinato-stabilized titanium(IV) complexes were synthesized and fully characterized. Therefore, several carbodiimides were synthesized, which can be selectively converted into mono(guanidinato) trichloro titanium(IV) complexes by treatment with trichloro diethylamido titanium(IV). Subsequent conversion with methylmagnesium chloride led to the corresponding alkyl complexes (Scheme 3). When sterically demanding guanidinato-ligands are used, this catalyst system is highly active in CCTP of ethylene after activation with *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)-borate. This high activity could also be received in the presence of enormous chain-transfer agent (CTA) amounts, for instance 15400 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ using an Al/Ti ratio of 10000/1. High-temperature ^{1}H NMR experiments could verify no side reactions like β-H elimination/transfer and Al-terminated PE as the only product. The use of alkyl complexes resulted in noticeable reduction of an induction period, which was observed for the corresponding trichlorido complexes. A maximum number of elongated chains of 83.3% could be achieved using a triethylaluminium/catalyst ratio of 1000/1 and an activity of 9900 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$.



Scheme 3. Irreversible coordinative chain-transfer polymerization of ethylene mediated by mono-(guanidinato) titanium(IV) complexes.

Time-dependent polymerization experiments confirmed an irreversible coordinative chain-transfer polymerization, due to no increase of the molecular weight over time but an increase of elongated chains. To overcome this, the steric demand of the ligand was decreased. This resulted in a significant decrease of the polymerization performance. The use of an alkyl group containing and sterically less demanding ligand even resulted in an inactive system.

As the present work and previous studies indicated, the steric demand of the ligand is of particular importance. Another possibility to enhance the chain-growing/chain-transfer-ratio is to replace titanium with its heavier homologue zirconium while keeping the required steric demand of the guanidinato ligand. For this reason the bulky *N*‘,*N*“-bis(2,6-diisopropylphenyl)-*N*,*N*-diethylguanidinato trimethanido zirconium(IV) complex was synthesized and fully characterized. Again, carbodiimide insertion into a metal-amide bond was successful to obtain the required product. In comparison to the titanium analogues, the reaction of trichloro diethylamido zirconium (IV) etherate with *N*,*N*’-bis(2,6-diisopropylphenyl)carbodiimide resulted in a dimeric structure, two mono-(guanidinato) zirconium fragments bridged by two chloro atoms. The corresponding alkyl complex was synthesized by subsequent conversion with methylmagnesium chloride. After initial studies in CCTP of ethylene, followed by optimization of the reaction conditions, a highly active catalyst system was developed (Scheme 4).



Scheme 4. Reversible coordinative chain-transfer polymerization of ethylene with *N*‘,*N*“-bis(2,6-diisopropylphenyl)-*N*,*N*-diethylguanidinato trimethanido zirconium(IV) precatalyst.

After activation of the precatalyst with *N*,*N*,*N*-trialkylammonium tetrakis(pentafluoro–phenyl)-borate, long-term stability of the catalyst was obtained. At CTA/catalyst ratios of more than 10000/1, complete number of elongated chains and narrow molecular weight distributions were obtained. Reversible chain-transfer was found due to increased molecular weight over time. No significant decrease of the activity was observed with increased CTA amounts, in contrast to other reported CCTP catalyst systems, which suffer from an inverse first-order dependency of the reaction in the CTA amount. Therefore, these systems become almost inactive for CTA/catalyst ratios of more than 500/1.

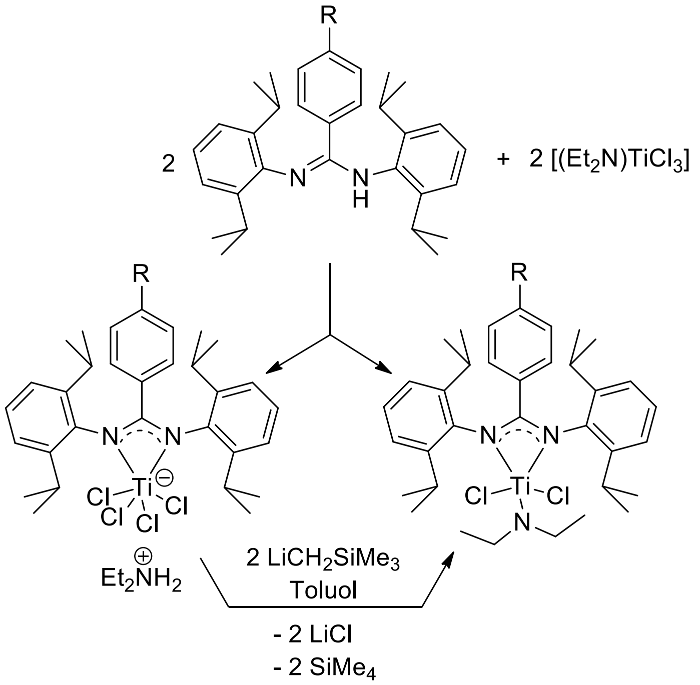
Finally a highly active catalyst system was developed which is able to polymerize ethylene in a highly controlled and efficient fashion. Therefore, it allows the production of tailored oligo- and polyethylenes. In addition to their enormous industrial importance, they can also easily be converted into further products due to their aluminium termination.

1.2 Zusammenfassung

Inhalt der vorliegenden Arbeit ist die Entwicklung neuartiger Übergangsmetallkomplexkatalysatoren der Gruppe 4, welche in der Lage sind, Ethylen sowohl hoch effizient, als auch kontrolliert zu polymerisieren. Neben der Synthese und vollständigen Charakterisierung der Liganden und Komplexe wurden diese neuen Katalysatorsysteme in der Koordinativen Kettentransfer Polymerisation (KKTP) von Ethylen getestet. Dies beinhaltet die Optimierung der Reaktionsbedingungen, die Bestimmung mechanistischer Aspekte sowie die detaillierte Analyse der erhaltenen polymeren und oligomeren Produkte.

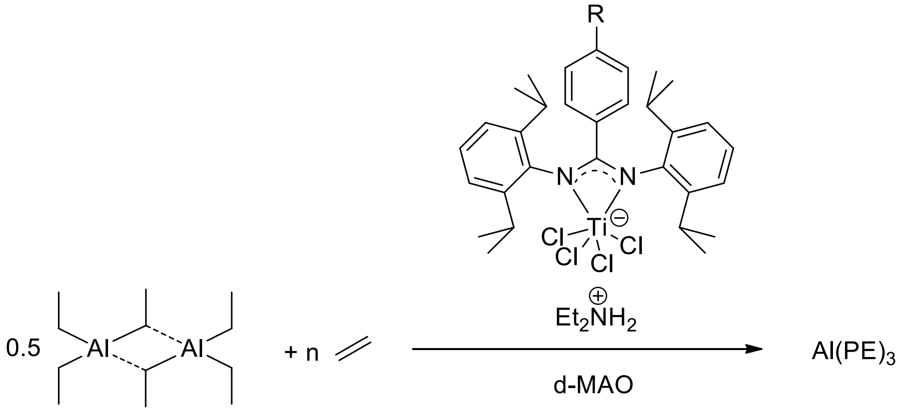
Vorangehende Arbeiten zu Seltenerdmetall- und Übergangsmetallkomplexkatalysatoren stabilisiert durch Aminopyridinato- (Ap) Liganden haben gezeigt, dass diese hoch aktiv in der Koordinativen Kettentransfer Polymerisation von Ethylen sind. Jedoch haben diese Systeme eine hohe Sensibilität gegenüber Aluminiumalkylen, was sich durch Ligandentransfer oder einer möglichen Blockierung des aktiven Zentrums äußert. Um dieses Problem zu lösen wurden übergangsmetallbasierte Systeme entwickelt, welche durch strukturell verwandte Liganden stabilisiert sind. Die Verwendung von Amidinato- oder Guanidinato-Liganden kann einerseits die Ligandenübertragung unterbinden, anderseits aber die Polymerisationsaktivität erhalten.

Hierzu wurde eine Bibliothek neuartiger Mono(amidinato)-Titan(IV)-Komplexe synthetisiert und mittels NMR-Spektroskopie, Elementaranalyse und Röntgeneinkristallstrukturanalyse vollständig charakterisiert. Es wurde gezeigt, dass die Reaktion von Trichlorido(dietylamido)titan(IV) mit einer Reihe von sterisch anspruchsvollen Amidinen in einem 1:1 Gemisch von Mono(amidinato)tetrachloridotitan(IV)-Komplexen mit Diethylammonium-Gegenion und neutralen Mono(amidinato)dichlorido-diethylamidotitan(IV)-Komplexen resultiert (Schema 1). Die Umsetzung der anionischen Komplexe mit starken Basen führte zu den neutralen Mono(amidinato)dichlorido-diethylamidotitan(IV)-Komplexen. Im Vergleich zu dem unsubstituierten Benzamidinato-Liganden zeigen die Röntgeneinkristallstrukturanalysen der substituierten Liganden eine erhöhte Elektronendonorfähigkeit als Resultat der Einführung elektronendonierender funktioneller Gruppen.



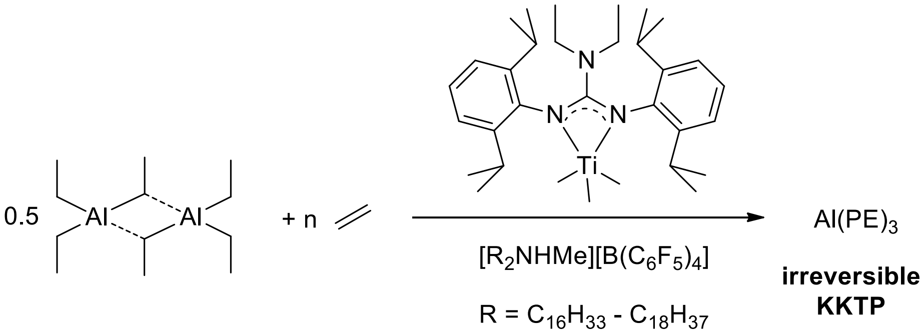
Schema 2. Synthese von Mono(amidinato)-Titan(IV)-Komplexen. R = H, NMe_2, OMe, 2,5-dimethylpyrrol.

Diese Komplexe erwiesen sich nach Aktivierung mit d-MAO als hochaktive Polymerisationskatalysatoren mit Aktivitäten von bis zu 3500 $kg_{PE}mol_{Kat}^{-1}h^{-1}bar^{-1}$ (Schema 2). Die Untersuchung der erhaltenen Polymere mittels hochtemperatur ^1H NMR Spektroskopie bestätigten (durch das Fehlen olefinischer Protonenresonanzen) das Vorliegen von Al-terminierten Polyethylen. Daher kann diese Reaktion als eine metallkomplex-katalysierte Version der Ziegler „Aufbaureaktion“ betrachtet werden. Die Einführung funktionaler Gruppen in das Rückgrat der Phenylreste der Liganden hatte nur geringfügigen Einfluss auf die Polymerisationseigenschaften.



Schema 2. Polymerisation mit Mono(amidinato)-Titan(IV)-Komplexen. R = H, NMe_2, OMe, 2,5-dimethylpyrrol.

Anschließend wurden mehrere Guanidinato-stabilisierte Titan(IV)-Komplexe synthetisiert und vollständig charakterisiert. Hierzu wurden mehrere Carbodiimide synthetisiert, welche durch Umsetzung mit Trichlorido(dietylamido)titan(IV) selektiv durch Methandiimin-Insertion in die Titan-Amid-Bindung zu Mono(guanidinato)trichlorido-titan(IV)-Komplexen reagieren. Eine anschließende Umsetzung dieser Komplexe mit Methylmagnesiumchlorid führte zu den korrespondierenden Alkylkomplexen (Schema 3). Werden sterisch anspruchsvolle Liganden verwendet, erweist sich dieses System nach Aktivierung mit *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)-borat als hochaktiv in der KKTP von Ethylen. Diese Aktivität blieb auch bei sehr hohen Aluminium/Katalysator-Verhältnissen bestehen, beispielsweise 15400 $kg_{PE}mol_{Kat}^{-1}h^{-1}bar^{-1}$ bei einem Triethylaluminium/Katalysator-Verhältnis von 10000/1. Die Verwendung der Alkylkomplexe resultierte in einer deutlichen Reduzierung der Induktionsperiode, welche für die entsprechenden Chlorido-Komplexe beobachtet wurde. Eine maximale Anzahl an verlängerten Ketten von 83,3 % konnte bei einem Triethylaluminium/Katalysator-Verhältnis von 1000/1 erhalten werden.

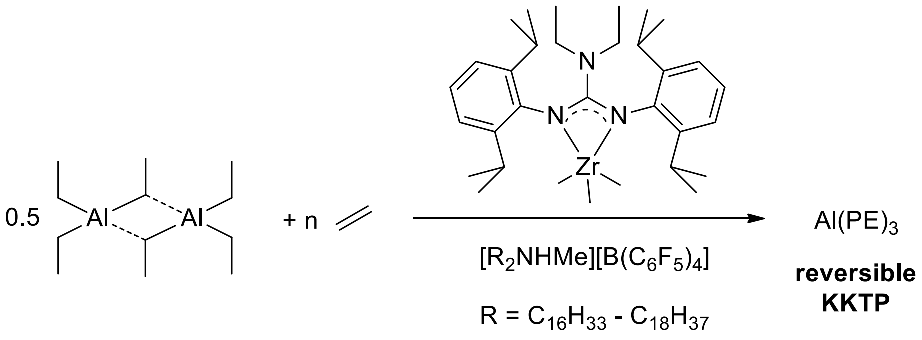


Schema 3. Mono(guanidinato)-Titan(IV)-Komplex vermittelte, irreversible Koordinative Kettentransfer Polymerisation von Ethylen.

Zeitabhängige Experimente belegten eine irreversible Koordinative Kettentransfer Polymerisation. So kommt es zu keiner Zunahme des Molekulargewichts mit der Zeit, sondern lediglich zu einer Zunahme an verlängerten Ketten. Dies deutet auf ein ungünstiges Kettenwachstum/Kettentransfer-Verhältnis hin. Um dieses Verhältnis zu optimieren, wurde ein sterisch weniger anspruchsvoller Ligand verwendet, was jedoch zu einer signifikanten Abnahme der Polymerisationsaktivität führte. Die Verwendung eines Liganden, welcher anstatt eines aromatischen Rests eine Alkylgruppe trägt, resultierte in einem inaktiven System.

Sowohl die vorliegende Arbeit als auch vorangehende Studien verdeutlichen, die erhebliche Bedeutung des sterischen Anspruchs der verwendeten Liganden bei der Polymerisation von Ethylen. Eine Möglichkeit, das Kettenwachstum/Kettentransfer-Verhältnis zu verändern, ist der Austausch von Titan mit dem schwereren Homolog Zirkonium unter Beibehaltung des sterischen Anspruchs des verwendeten Liganden.

Hierzu wurde der entsprechende *N*',*N*"-bis(2,6-diisopropylphenyl)-*N*,*N*-diethylguanidinato trimethanido zirconium(IV) Komplex synthetisiert und vollständig charakterisiert. Es wurde ebenfalls die Synthese durch Carbodiimid-Insertion in die Metall-Amid-Bindung gewählt. Im Gegensatz zum Titan-Analogon führte die Reaktion von Trichlorido-(dietylamido)zirkonium(IV)-etherat mit *N*,*N*'-bis(2,6-diisopropylphenyl)carbodiimid zur Ausbildung einer dimeren, chlorido-verbrückten Spezies. Der entsprechende Alkylkomplex wurde durch Umsetzung mit Methylmagnesiumchlorid synthetisiert. Nach ersten Untersuchungen in der KKTP von Ethylen und anschließender Optimierung der Reaktionsbedingungen erwies sich dieses System als hochaktives Katalysatorsystem (Schema 4).



Schema 4. Reversible Koordinative Kettentransfer Polymerisation von Ethylen mit dem *N*',*N*"-bis(2,6-diisopropylphenyl)-*N*,*N*-diethylguanidinato trimethanido zirkonium(IV) Präkatalysator.

Die Aktivierung dieses Präkatalysators mit *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)-borat führte zu einem sehr langzeitstabilen und hochaktiven Katalysator. So konnte selbst bei Aluminium/Katalysator-Verhältnissen von 10000/1 eine vollständige Anzahl an verlängerten Ketten und enge Molekulargewichtsverteilungen erhalten werden. Eine zeitabhängige Zunahme des Molekulargewichts belegte einen reversiblen Kettentransfer. Viele KKTP Katalysatorsysteme werden bei CTA/Katalysator-Verhältnissen größer 500/1 inaktiv, was auf den inversen Zusammenhang des Kettenwachstums und der CTA-Konzentration nach erster Ordnung zurückzuführen ist. Unter Verwendung des beschriebenen Guanidinato-stabilisierten Zirkonium(IV)-Systems führt die Erhöhung der CTA-Konzentration zu keiner signifikanten Abnahme der Aktivität.

Zusammenfassend wurde ein hochaktives Katalysatorsystem entwickelt, welches in der Lage ist, Ethylen in einer sehr kontrollierten und effizienten Art und Weise zu polymerisieren. Dies ermöglicht daher die Herstellung von maßgeschneiderten Oligo- und Polyethylenen. Neben der enormen industriellen Bedeutung dieser Produkte erlaubt die Aluminiumterminierung zudem eine leichte Darstellung von wertschöpfenden Folgeprodukten.

2 Introduction

The last century, especially its second half, is often referred to as “the Age of Plastics”.[1] Polymers, or in many cases called plastics, are used in almost every area of life and it is hard to imagine modern lifestyle without those materials. They increasingly substitute highly sophisticated and traditional materials, such as metal or glass, in rapidly growing markets, for instance, consumer electronics, automotive industry or medical technology. In future, this material substitution is playing a decisive role in plastics development by the industry.[2]

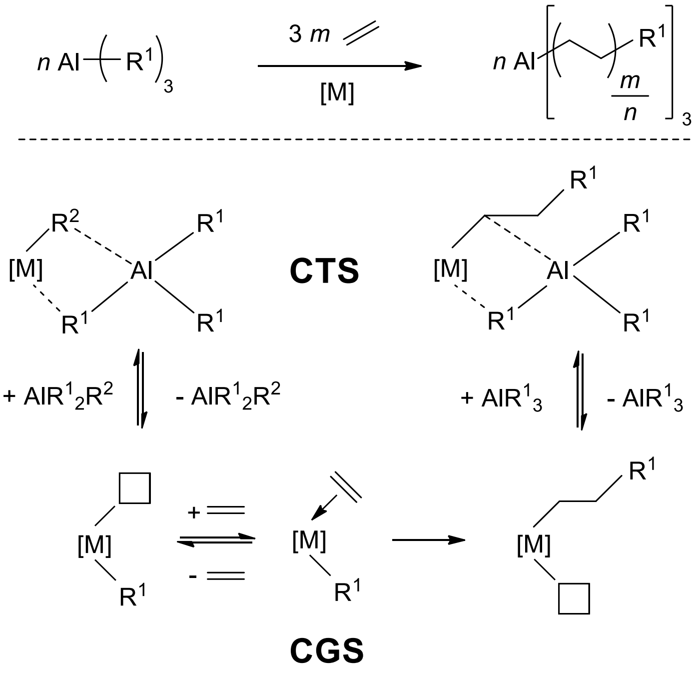
With a worldwide annual production volume of more than 130 million tons, polyolefins are the polymers with the highest production volume and show an unbroken production increase. Polyolefins only consist of carbon and hydrogen atoms, are light in weight and offer a wide variety of properties. Easy available and nontoxic monomers are required for their production and the polymerization itself proceeds with almost no loss or side reactions. These facts legitimate their large-scale production and application as well as ongoing research and development. Facile recycling techniques for polyolefins after their use, such as mechanical procedures to simple articles, pyrolysis to gas and oil or by incineration to energy, can increase their adding value in addition.[3]

It is been almost 80 years when researchers of the Imperial Chemical Industries (ICI) discovered that ethylene can be polymerized at pressures of more than 500 bars and temperatures of 200°C, the so-called ICI high-pressure process.[4,5] In the early fifties, the development of chromium oxide based Phillips catalysts provided a synthetic route to produce polyethylene under milder conditions.[6] Shortly after, a highly active catalyst system based on $TiCl_4/Et_3Al$ was reported by Ziegler and co-workers. Later, this heterogeneous system was used by Natta to produce isotactic polypropylene (PP).[7,8] In 1963, Ziegler and Natta were awarded the Nobel Prize in chemistry for this invention. With the discovery of heterogeneous Ziegler-Natta catalysts a milestone was laid and catalyst research as well as polymer industry was born.[9,10]

One of the central advantages of homogenous catalysts over multisided heterogeneous catalysts are their well-defined active sites, which lead to polymers with specific microstructures and more narrow molecular weight distributions.[11] A few years after

Ziegler's discovery, the first homogenous catalyst system $Cp_2TiCl_2/AlEt_2Cl$ (Cp = cyclopentadienyl) was reported. These titanocene catalysts were useful for model studies and kinetics, but of no commercial interest due to their low activity.[12] But it was only after Kaminsky's and Sinn's initial discovery that partially hydrolyzed trimethylaluminium, in particular methylaluminoxane (MAO), combined with titanium and zirconium metallocenes afford in extremely active polymerization catalysts.[13,14] This led to an explosion of the use of metallocene-based catalyst systems. In addition, the discovery of fluoroaryl-based activators, such as $[R_3NH][B(C_6F_5)_4]$[15] and $[Ph_3C][B(C_6F_5)_4]$[16] led to well-characterizable catalysts with commercially significant activities, requiring only a stoichiometric amount of the co-catalyst.[12] The next step in post-metallocene homogenous catalysts research was the introduction of half-sandwich amide or so-called constrained geometry catalysts.[17] Bercaw and co-workers first employed the preparation of Sc(III) complexes of this type.[18,19] Shortly after, systems based on group IV[20] and their exceptional characteristics in ethylene polymerization and copolymerization of ethylene and higher α-olefins[21,22] were reported.

The intensive research on group IV metallocenes and related catalyst systems at this time entailed the insight into the nature of activated species and possibilities for controlling the properties of the produced polyolefins.[23] Combined with the discovery that MAO co-catalysts[24] afford highly active and long-term stable catalyst systems, these developments have grown out of an increased understanding to stabilize polymerization-active metal centers and to control their activity and selectivity.[25] The enhancement of Ziegler-Natta-, metallocene and post-metallocene catalysts enabled regioselective and stereoselective polymerization processes together with the realization of well-defined branches onto the macromolecular backbone. This control led to great potentialities for fine-tuning of microstructures and architectures of the polymers that determines the physical properties and thus their application area. Generally, this type of polymerization is living, one molecule of initiator/catalyst leads to the growth of one macromolecular chain. With regard to economic aspects, novel polymerization protocols enabling the growth of several macromolecular chains per expensive catalyst molecule are required.[26] To meet these requirements it is necessary to develop new polymerization processes or to optimize existing protocols. Therefore, strategies such as coordinative chain-transfer polymerization (CCTP)[27,28] have been developed. Pioneering work in this field was reported by Samsel *et* *al.*[29,30] and by Mortreux and co-workers.[31–33] Recently, a variety of ethylene/propylene CCTP catalyst systems with rare earth (RE) metals and transition metals (TM) in combination with different chain-transfer agents (CTAs) such as Mg-,[31–35] Zn-[36–48] and Al-alkyls[29,30,49–63] have been documented. Furthermore, enhancements of the CCTP concept such as "chain shuttling"[36,64,65] and "ternary CCTP"[66] have been developed. CCTP consists of a transition metal or rare earth metal-based catalyst and a chain-transfer agent (CTA), usually a main group metal alkyl. The macromolecular chain is transferred from the active catalyst, the chain-growing state (CGS), to the CTA. The CTA is normally considered as the dormant species in the course of the polymerization, via transalkylation (Scheme 1). In contrast to classical living polymerization, CCTP allows the growth of several macromolecular chains per catalyst molecule. End-capped macromolecular chains are obtained, enabling further functionalization reactions based on main group metal chemistry.[27,67–72]



Scheme 1. Net reaction and mechanism of CCTP involving aluminium alkyls. Top: CTS (chain-transfer state); bottom: CGS (chain-growing state). [M] = cationic or neutral transition metal or rare earth metal complex; R^1,R^2 = alkyl moieties; n, m = natural numbers.

The CTS/CGS equilibrium is of essential importance for CCTP ability. Very strong coordination of the CTA leads to almost no chain growth and a very low overall activity is observed. Furthermore, if the equilibrium is shifted extreme to the CGS, the reaction represents more or less a classic polymerization process. In case of rapid exchange compared to chain growth, extreme narrow molecular weight distributions can be obtained. Other termination reactions for instance β-H abstraction are suppressed under the chosen reaction conditions.

The number of polymeric chains produced per catalyst molecule defines the efficiency of CCTP. If all of the alkyl groups of the CTA are involved of the transmetalation the polymer appears to be growing at the main group metal and a metal complex catalyzed version of Ziegler's "Aufbaureaktion" is represented.[27,28] Although known for more than sixty years, the "Aufbaureaktion" is still an important industrial process to produce α-olefins (ALFEN-process) as well as linear aliphatic alcohols together with high purity alumina after oxidation and hydrolytic workup of the aluminium alkyls (ALFOL-process).[73] The direct synthesis of aluminium alkyls from aluminium, hydrogen and olefins, thus converting aluminium alkyls into viable industrial products, is very slow and limited in terms of high molecular weight products. At reaction conditions in which faster insertion could be expected, competitive β-H elimination/transfer processes become dominant. As described above, CCTP can exactly solve this problem. The groups of Bochman[74,75] and Norton[76,77] performed CCTP mechanistic studies and kinetics of chain growth at aluminium catalyzed by $[(EBI)Zr(\mu\text{-}Me)_2AlMe_2][B(C_6F_5)_4]$ (EBI = ethylene-bridged bisindenyl).[77] The reaction is first-order in [olefin] and [catalyst] and of inverse first-order in $[AlR_3]$ (R = PE polymeric chain). This inverse first-order dependence prohibits the use of high CTA/catalyst ratios, resulting in a poor overall polymerization activity and therefore in rather low catalyst economy of the systems reported so far.

The most important plastic worldwide is polyethylene (PE). Because of its low cost and its broad applicability it is essential for our modern lifestyle. The rather apolar nature of PE leads to a limited compatibility with other important polymers or materials. Block co-polymers that consist of a PE-block and a block of other polymers or material could solve this compatibility problem. Furthermore, PE-based block copolymers can be used for nanostructuring by means of microphase separation. This enables the access to several nanostructured PE materials and entails novel applications of such materials.[78] Both approaches rely on an efficient synthesis of PE with an end-group, which allows the easy introduction of further polymer blocks. Because of received end-group functionalized polymers, CCTP seems to be the most promising protocol to polymerize ethylene in a highly controlled and efficient way and to meet the above-mentioned requirements.

[1] V. Busico, *Dalton Trans.* **2009**, 8794–8802.

[2] W. Stefanie, *Kunststoffe* **2010**, *8*, 40–43.

[3] W. Kaminsky, L. Böhm, *Polyolefins: 50 Years after Ziegler and Natta I*, Springer Berlin Heidelberg, Berlin, Heidelberg, **2013**.

[4] D. Oeder, *Chemie unserer Zeit* **1981**, *15*, 98–101.

[5] E. W. Fawcett, R. O. Gibson, P. M. Willcox, J. G. Paton, W. E. George, *GB 471590*, **1936**.

[6] J. P. Hogan, R. L. Banks, *US 2825721*, **1958**.

[7] K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **1955**, *67*, 541–547.

[8] G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, *J. Am. Chem. Soc.* **1955**, *77*, 1708–1710.

[9] H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99–149.

[10] G. Wilke, *Angew. Chem. Int. Ed.* **2003**, *42*, 5000–5008.

[11] W. Kaminsky, A. Laban, *Appl. Catal. A Gen.* **2001**, *222*, 47–61.

[12] G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347–1376.

[13] W. Kaminsky, M. Miri, H. Sinn, R. Woldt, *Die Makromol. Chemie, Rapid Commun.* **1983**, *4*, 417–421.

[14] H. Sinn, W. Kaminsky, H.-J. Vollmer, R. Woldt, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 390–392.

[15] H. W. Turner, G. G. Hlatky, R. R. Eckman, *US5198401*, **1993**.

[16] J. A. Ewen, M. J. Elder, *US5387568*, **1995**.

[17] H. Braunschweig, F. M. Breitling, *Coord. Chem. Rev.* **2006**, *250*, 2691–2720.

[18] P. J. Shapiro, E. Bunel, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867–869.

[19] W. E. Piers, P. J. Shapiro, E. E. Bunel, J. E. Bercaw, *Synlett* **1990**, 74–84.

[20] J. Okuda, *Chem. Ber.* **1990**, *123*, 1649–1651.

[21] J. C. Stevens, F. J. Timmers, D. R. Wilson, G. F. Schmidt, P. N. Nickias, R. Rosen, G. W. Knight, S. Lai, *EP0416815*, **1991**.

[22] J. A. M. Canich, G. G. Hlatky, H. W. Turner, *WO92/00333*, **1992**.

[23] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315.

[24] H. S. Zijlstra, S. Harder, *Eur. J. Inorg. Chem.* **2015**, 19–43.

[25] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447.

[26] P. Zinck, *Polym. Int.* **2012**, *61*, 2–5.

[27] R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764–2773.

[28] A. Valente, A. Mortreux, M. Visseaux, P. Zinck, *Chem. Rev.* **2013**, *113*, 3836–3857.

[29] E. Samsel, *EP0539876*, **1992**.

[30] E. Samsel, D. Eisenberg, *EP0574854*, **1993**.

[31] J.-F. Pelletier, A. Mortreux, X. Olonde, K. Bujadoux, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1854–1856.

[32] J.-F. Pelletier, K. Bujadoux, X. Olonde, E. Adisson, A. Mortreux, T. Chenal, *US 5779942*, **1995**.

[33] T. Chenal, X. Olonde, J.-F. Pelletier, K. Bujadoux, A. Mortreux, *Polymer* **2007**, *48*, 1844–1856.

[34] X. Olonde, A. Mortreux, F. Petit, K. Bujadoux, *J. Mol. Catal.* **1993**, *82*, 75–82.

[35] J.-F. Pelletier, A. Mortreux, F. Petit, X. Olonde, K. Bujadoux, *Catalyst Design for Tailor-Made Polyolefins. Studies in Surface Science and Catalysis. Volume 89. Edited by K. Soga & M. Terano. Kodansha and Elsevier, Tokyo and Amsterdam*, **1994**.

[36] D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* **2006**, *312*, 714–719.

[37] G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, P. J. Maddox, M. van Meurs, *Angew. Chem. Int. Ed.* **2002**, *41*, 489–491.

[38] G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, M. Van Meurs, *J. Am. Chem. Soc.* **2004**, *126*, 10701–10712.

[39] F. Deplace, Z. Wang, N. a. Lynd, A. Hotta, J. M. Rose, P. D. Hustad, J. Tian, H. Ohtaki, G. W. Coates, F. Shimizu, et al., *J. Polym. Sci. Part B Polym. Phys.* **2010**, *48*, 1428–1437.

[40] A. Hotta, E. Cochran, J. Ruokolainen, V. Khanna, G. H. Fredrickson, E. J. Kramer, Y.-W. Shin, F. Shimizu, A. E. Cherian, P. D. Hustad, et al., *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15327–32.

[41] P. D. Hustad, R. L. Kuhlman, E. M. Carnahan, T. T. Wenzel, D. J. Arriola, *Macromolecules* **2008**, *41*, 4081–4089.

[42] P. D. Hustad, R. L. Kuhlman, D. J. Arriola, E. M. Carnahan, T. T. Wenzel, *Macromolecules* **2007**, *40*, 7061–7064.

[43] P. D. Hustad, G. R. Marchand, E. I. Garcia-Meitin, P. L. Roberts, J. D. Weinhold, *Macromolecules* **2009**, *42*, 3788–3794.

[44] H. Kaneyoshi, Y. Inoue, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 5425–5435.

[45] S. Li, R. A. Register, B. G. Landes, P. D. Hustad, J. D. Weinhold, *Macromolecules* **2010**, *43*, 4761–4770.

[46] J. O. Ring, R. Thomann, R. Mülhaupt, J.-M. Raquez, P. Degée, P. Dubois, *Macromol. Chem. Phys.* **2007**, *208*, 896–902.

[47] M. van Meurs, G. J. P. Britovsek, V. C. Gibson, S. A. Cohen, *J. Am. Chem. Soc.* **2005**, *127*, 9913–9923.

[48] W. Zhang, J. Wei, L. R. Sita, *Macromolecules* **2008**, *41*, 7829–7833.

[49] G. C. Bazan, J. S. Rogers, C. C. Fang, *Organometallics* **2001**, *20*, 2059–2064.

[50] C. Boisson, V. Monteil, D. Ribour, R. Spitz, F. Barbotin, *Macromol. Chem. Phys.* **2003**, *204*, 1747–1754.

[51] C. Döring, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2010**, *18*, 2853–2860.

[52] M. Ganesan, F. P. Gabbaï, *J. Organomet. Chem.* **2005**, *690*, 5145–5149.

[53] I. Haas, W. P. Kretschmer, R. Kempe, *Organometallics* **2011**, *30*, 4854–4861.

[54] C. J. Han, M. S. Lee, D.-J. Byun, S. Y. Kim, *Macromolecules* **2002**, *35*, 8923–8925.

[55] W. P. Kretschmer, T. Bauer, B. Hessen, R. Kempe, *Dalt. Trans.* **2010**, *39*, 6847–6852.

[56] W. P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, *Chem. Eur. J.* **2006**, *12*, 8969–8978.

[57] R. L. Kuhlman, T. T. Wenzel, *Macromolecules* **2008**, *41*, 4090–4094.

[58] G. Mani, F. P. Gabbaï, *Angew. Chem.* **2004**, *116*, 2313–2316.

[59] J. Obenauf, W. P. Kretschmer, T. Bauer, R. Kempe, *Eur. J. Inorg. Chem.* **2013**, 537–544.

[60] J. Obenauf, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2014**, 1446–1453.

[61] S. K. T. Pillai, W. P. Kretschmer, M. Trebbin, S. Förster, R. Kempe, *Chem. Eur. J.* **2012**, *18*, 13974–13978.

[62] J. S. Rogers, G. C. Bazan, *Chem. Commun.* **2000**, *2*, 1209–1210.

[63] F. Rouholahnejad, D. Mathis, P. Chen, *Organometallics* **2010**, *29*, 294–302.

[64] V. C. Gibson, *Science* **2006**, *312*, 703–704.

[65] M. Zintl, B. Rieger, *Angew. Chem. Int. Ed.* **2007**, *46*, 333–335.

[66] J. Wei, W. Zhang, L. R. Sita, *Angew. Chem. Int. Ed.* **2010**, *49*, 1768–1772.

[67] L. R. Sita, *Angew. Chem. Int. Ed.* **2009**, *48*, 2464–2472.

[68] S. B. Amin, T. J. Marks, *Angew. Chem. Int. Ed.* **2008**, *47*, 2006–2025.

[69] T. Chung, *Prog. Polym. Sci.* **2002**, *27*, 39–85.

[70] J.-Y. Dong, Y. Hu, *Coord. Chem. Rev.* **2006**, *250*, 47–65.

[71] R. Godoy Lopez, F. D'Agosto, C. Boisson, *Prog. Polym. Sci.* **2007**, *32*, 419–454.

[72] J. Mazzolini, E. Espinosa, F. D'Agosto, C. Boisson, *Polym. Chem.* **2010**, *1*, 793–800.

[73] R. Mülhaupt, *Macromol. Chem. Phys.* **2003**, *204*, 289–327.

[74] M. Bochmann, S. J. Lancaster, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1634–1637.

[75] M. Bochmann, S. J. Lancaster, *J. Organomet. Chem.* **1995**, *497*, 55–59.

[76] R. A. Petros, J. R. Norton, *Organometallics* **2004**, *23*, 5105–5107.

[77] J. M. Camara, R. A. Petros, J. R. Norton, *J. Am. Chem. Soc.* **2011**, *133*, 5263–5273.

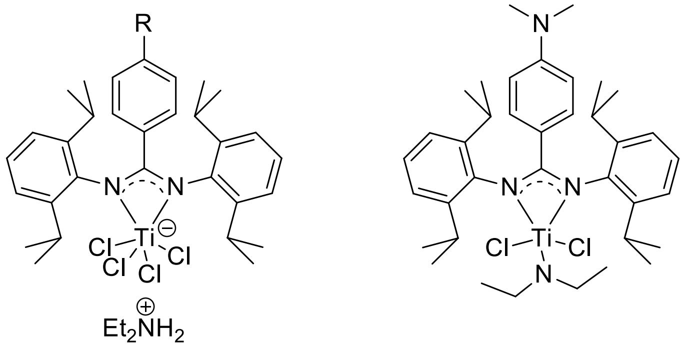
[78] F. S. Bates, M. a Hillmyer, T. P. Lodge, C. M. Bates, K. T. Delaney, G. H. Fredrickson, *Science* **2012**, *336*, 434–440.

3 Overview of Thesis Results

This thesis comprises three publications, which are presented in chapter 4–6. Two of them are published and the third one is in the "to be submitted" stage.

3.1 An Efficient Titanium Amidinate Catalyzed Version of Ziegler's "Aufbaureaktion"

Motivated by previous reported aminopyridinato-, amidinato- and guanidinato-stabilized rare earth and transition metal catalyst systems, which are highly active in coordinative chain-transfer polymerization of ethylene, but suffer from sensitivity towards high aluminium amounts, we became interested in structural related catalyst systems and their coordinative chain-transfer polymerization (CCTP) performance. In consequence, mono(amidinato)-stabilized titanium(IV) complexes were synthesized via amine elimination by the reaction of several amidines with trichloro diethylamido titanium(IV) (Figure 1). Various electron-donating groups were introduced to the backbone of the ligand to increase the stability of the complexes towards high aluminium amounts.



2a-2d

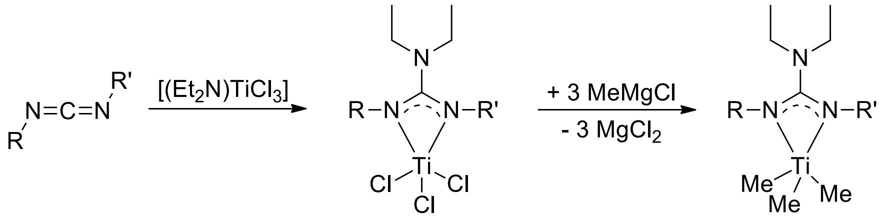
3a

Figure 1. Mono(amidinato) titanium(IV) complexes. R = H, NMe$_2$, OMe, 2,5-dimethyl-pyrrole.

The reaction of trichloro diethylamido titanium(IV) with ArN(H)C(Ar')NAr (Ar = 2,6-diisopropylphenyl; Ar' = Ph, *p*-Me$_2$NC$_6$H$_4$, *p*-MeOC$_6$H$_4$, *p*-(2,5-dimethylpyrrole)C$_6$H$_4$) resulted in ammonium titanates. The addition of (trimethylsilyl)methyl lithium formed mono(amidinato)diethylamido dichlorido titanium(IV) complexes. Polyethylenyl chain-transfer polymerization to aluminium alkyls was observed. After activation of these novel complexes with d-MAO, MAO from which free TMA is removed, ethylene was polymerized with activities of up to 3500 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ and Al-terminated linear polyethylene is the only observed product. The increased electron-donating ability of the ligands had only marginal influence on the polymerization performance.

3.2 Efficient Synthesis of Aluminium-Terminated Polyethylene by Means of Irreversible Coordinative Chain-Transfer Polymerisation Using a Guanidinatotitanium Catalyst

Motivated by a communicated mono(guanidinato) trichloro titanium(IV) complex that represents a highly active ethylene CCTP precatalyst, the performance of such catalyst system was investigated in more detail, especially structural features that enable high catalyst economy and transfer efficiency. A series of structural modified guanidinato-stabilized titanium(IV) complexes were synthesized (Scheme 1) and fully characterized.



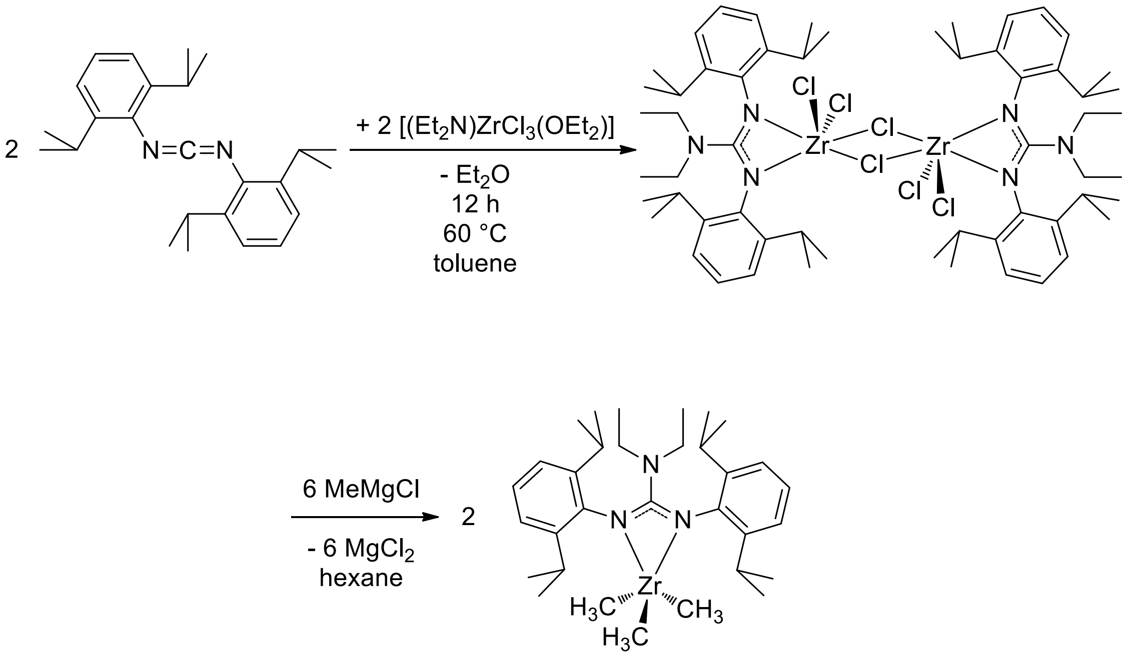
2a R = R' = 2,6-$^iPr_2C_6H_3$ **3a** **4a**
2b R = R' = 2,6-$Me_2C_6H_3$ **3b** **4b**
2c R = 2,6-$Me_2C_6H_3$, R' = ^tBu **3c**

Scheme 1. Synthesis of mono(guanidinato) titanium(IV) complexes.

After activation with *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)-borate this catalyst system showed very high activities in coordinative chain-transfer polymerization of ethylene after a short induction period. In particular, the use of alkyl-complexes resulted in a significant enhancement due to reduced catalyst induction period, which was observed for chlorido-compounds. Initial studies showed high tolerance against high amounts of triethylaluminium as chain-transfer agent. An aluminium/catalyst ratio of up to 25000/1 could be used without influencing the polymerization activity but at low number of elongated chains. To enhance the chain-transfer/chain-growing ratio, the steric bulk of the ligand at the coordinating nitrogen atoms were reduced resulting in significant decrease of the polymerization ability. After optimizing the reaction conditions, especially temperature and ethylene pressure, a maximum number of elongated chains of 83.3% could be achieved. Time-dependent experiments with several amounts of triethylaluminium revealed an irreversible chain-transfer due to no increase of molecular weight over time. Only the number of elongated chains is increased.

3.3 Highly Controlled and Efficient Polymerization of Ethylene

The next aim was to discover a novel group IV based catalyst system that is able to undergo reversible polymeryl chain-transfer. The present work and previous studies verified the enormous importance of the steric demand of the ligand of the CCTP catalysts. The sterically demanding 2,3-bis(2,6-diisopropylphenyl)-1,1-diethylguanidinato ligand was used to synthesize a zirconium based catalyst system (Scheme 2). The reaction of *N*,*N*'-bis(2,6-diisopropylphenyl)carbodiimide with trichloro diethylamido zirconium(IV) etherate resulted in a dimeric di-μ-chlorido-bis[2,3-bis(2,6-diisopropylphenyl)-1,1-diethylguanidinato] tetrachlorido dizirconium(IV) species, which was subsequent converted with methylmagnesium chloride leading to the corresponding monomeric guanidinato trimethanido zirconium(IV) complex. All compounds were fully characterized and their structure revealed by X-ray single crystal structure analyses.



Scheme 2. Synthesis of [2,3-bis(2,6-diisopropylphenyl)-1,1-diethylguanidinato] trimethanido zirconium(IV).

This monomeric precatalyst was tested in CCTP of ethylene. After activation with *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)-borate this system gave rise to an highly active catalyst system in the presence of enormous amounts of triethylaluminium. The reaction conditions were optimized and a long-term stable CCTP catalyst was developed. Complete number of elongated chains was found for an Al/Zr ratio of 10000/1 with an activity of 16900 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ along with narrow polydispersities. High-temperature ^1H NMR experiments could verify Al-termination of the oligomeric products and time-dependent experiments clearly indicated reversible polymeryl chain-transfer due to increased molecular weight over time. Increase of the CTA concentration did not result in a significant decrease of the activity in comparison to the inverse first-order dependency of the reaction in CTA amount reported for other CCTP systems. This catalyst system allows the highly efficient and controlled synthesis of tailor-made oligo- and polyethylenes.

3.4 Individual Contribution to Joint Publications

The results presented in this thesis were obtained in collaboration with others and are published 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 corresponding author.

Chapter 4

This work is published in *Eur. J. Inorg. Chem.* **2013**, *4*, 537–544, with the title

"An Efficient Titanium Amidinate Catalyzed Version of Ziegler's 'Aufbaureaktion'"

Johannes Obenauf, Winfried P. Kretschmer, Tobias Bauer and Rhett Kempe*

I synthesized and characterized all compounds presented in this work and performed the ethylene polymerization experiments. The publication was written by myself. Tobias Bauer performed X-ray single crystal structure analyses. Winfried P. Kretschmer performed the HT GPC analyses. Rhett Kempe supervised this work and was as well as Winfried P. Kretschmer involved in scientific discussions and correction of the manuscript.

Chapter 5

This work is published in *Eur. J. Inorg. Chem.* **2014**, *9*, 1446–1453, with the title

"Efficient Synthesis of Aluminium-Terminated Polyethylene by Means of Irreversible Coordinative Chain-Transfer Polymerisation Using a Guanidinatotitanium Catalyst"

Johannes Obenauf, Winfried P. Kretschmer and Rhett Kempe*

I synthesized and characterized all the compounds presented in this publication. I carried out the ethylene polymerization experiments and the X-ray single crystal structure analyses. Winfried P. Kretschmer performed HT GPC analyses. Rhett Kempe and

Winfried P. Kretschmer supervised this work and were involved in scientific discussions and correction of the manuscript.

Chapter 6

This work is *to be submitted*, with the title

“Highly Controlled and Efficient Polymerization of Ethylene”

Johannes Obenauf, Winfried P. Kretschmer and Rhett Kempe*

All compounds presented in this manuscript were synthesized and characterized by myself. I carried out the ethylene polymerization experiments and the X-ray single crystal structure analyses. Winfried P. Kretschmer performed the HT GPC analyses. Rhett Kempe and Winfried P. Kretschmer supervised this work and were involved in scientific discussions and correction of the manuscript.

4 An Efficient Titanium Amidinate Catalyzed Version of Ziegler's "Aufbaureaktion"

Johannes Obenauf,[a] Winfried P. Kretschmer,[a] Tobias Bauer,[a] and Rhett Kempe*[a]

[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany. Fax: +49-921-552-157 E-mail: kempe@uni-bayreuth.de Homepage: http://www.ac2.uni-bayreuth.de

Published in: *Eur. J. Inorg. Chem.* **2013**, *4*, 537–544.

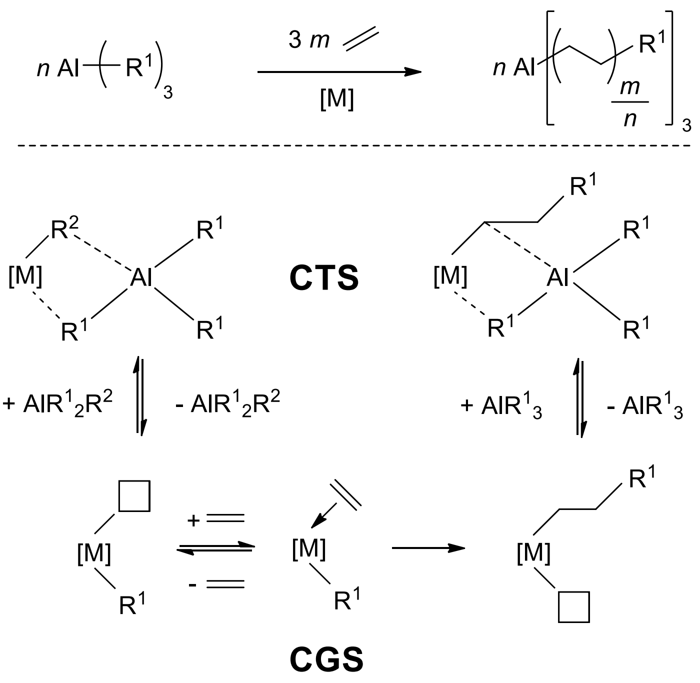
4.1 Abstract

Diethylamidotitanium trichloride reacts with a variety of bulky amidines ArN(H)C(Ar')NAr [Ar = 2,6-diisopropylphenyl; Ar' = Ph, *p*-$Me_2NC_6H_4$, *p*-$MeOC_6H_4$, *p*-(2,5-dimethylpyrrole)C_6H_4] to form ammonium titanates. These new titanium complexes undergo polyethylenyl chain transfer polymerization to aluminium alkyls after activation with d-MAO ("dry methylaluminoxane"). Ethylene is polymerized with an activity of up to 1000 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ in the presence of 1000 equiv. of triethylaluminium. Linear aluminium-terminated polyethylene is the only product observed. This polymerization process can be viewed as an efficient catalytic version of Ziegler's "Aufbaureaktion".

4.2 Introduction

Ziegler's "Aufbaureaktion",[1] the rather slow oligomerization of ethylene mediated by triethylaluminium (TEA), is an important industrial process. Initially, aluminium-terminated linear alkyl chains are produced, which can be oxidized with O_2. After hydrolytic workup aliphatic alcohols are formed with a chain length of (for instance) 6 to 22 carbon atoms and are usually referred to as Ziegler or fatty alcohols. These alcohols have a wide range of applications in personal care, polymer/leather/metal processing, agriculture, cosmetics, flavours, fragrances, plastics (as softeners), paints, coatings, industrial cleaning materials and biocides.[2] Unfortunately, the chain growth in the

"Aufbaureaktion" is very slow and limited in terms of higher molecular weight products. At temperatures at which faster insertion could be expected, competitive β-H elimination/transfer processes become dominant so that OH group terminated polyethylene (PE-OH) cannot be obtained by this method. A polymerization method that produces metal terminated polyethylene is coordinative chain transfer polymerization (CCTP).[3,4] Pioneering work in this field was reported by Samsel et al.[5] as well as by Mortreux and coworkers.[6] Recently, a variety of ethylene/propylene CCTP catalyst systems with rare earth (RE) metals and transition metals in combination with different chain transfer agents (CTAs) such as Mg,[6] Zn[7-9] and Al alkyls[10,11] have been documented. Furthermore, enhancements of the CCTP concept such as "chain shuttling"[9] and "ternary CCTP"[12] have been developed (Scheme 1).



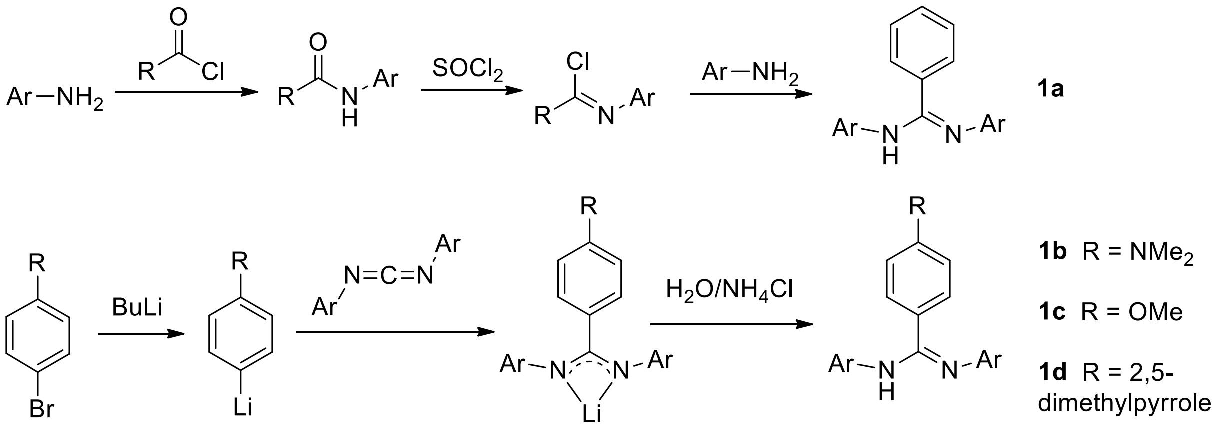
Scheme 1. Net reaction and mechanism of CCTP involving aluminium alkyls; top: CTS (chain transfer state); bottom: CGS (chain growing state). [M] = cationic or neutral transition metal or RE complex; R^1, R^2 = alkyl moiety; *n*, *m* = natural numbers.

In CCTP, the chain growing state (CGS) elongates the polymer chain and the chain transfer state (CTS) exchanges the polymeryl chain between the catalyst and the CTA. In this way, a catalyst can grow more than one "living" chain. Bochmann and Lancaster reported that the exchange of alkyl chains between group 4 metal cations and Al occurs via bimetallic complexes in the CTS.[13] Norton and coworkers described a detailed mechanistic picture of zirconium complex catalyzed chain growth of Al alkyls.[14,15] The kinetics of chain growth have been studied when catalyzed by $[(EBI)Zr(\mu\text{-}Me)_2AlMe_2][B(C_6F_5)_4]$ [EBI = ethylene bridged bis(indenyl)]. This reaction is first order in [olefin] and [catalyst] and inverse first order in $[AlR_3]$.[14] This inverse first order dependence prohibits the use of high CTA/catalyst ratios. High amounts of CTA result in poor overall polymerization activity. As a consequence, most of the described CCTP catalyst systems work with CTA/catalyst ratios < 500 and fail with significantly higher CTA/catalyst ratios. A possible solution to this problem is the design of new catalyst systems that undergo fast chain growth in comparison to chain exchange and still suppress β-H elimination/transfer processes. In such a regime, multiple insertions may compensate efficiency loss caused by high CTA/ catalyst ratios.[16] We recently developed rare earth (RE) based CCTP catalysts[10,17] and varied the nature as well as the steric demand of the monoanionic ligand used to stabilize the organo RE cations. In addition, the size of the RE atom was varied to find a catalyst system that tolerates high CTA/catalyst ratios.[11a–11d,18] Unfortunately, these variations did not lead to CTA/catalyst ratios above 500. Thus, we shifted our attention to group 4 metals, and titanium catalysts in particular. Titanium catalysts stabilized by bulky aminopyridinato (Ap) ligands showed very attractive polymerization activities but suffered from ligand transfer problems.[19] The Ap ligand is transferred to the CTA (alkylaluminium compounds) and the increased electron-donor ability of the ligand increased ligand transfer rates instead of decreasing them.[20] Guanidinates[21,22] and amidinates[23] are chemically related to Ap ligands and were expected to significantly alter ligand transfer rates but to maintain high polymerization activity. Herein, we report a new titanium amidinate based catalyst system that is highly active in the presence of high CTA/catalyst ratios and undergoes polyethylenyl chain transfer to TEA. No β-H elimination/transfer products were observed under the conditions applied here.

4.3 Results and Discussion

Ligand Synthesis

Various synthetic protocols for the synthesis of amidines are known from the literature.[24] For the synthesis of **1a**, the protocol according to Boeré[24b] was slightly modified (Scheme 2, top) by using a simplified workup procedure. 2,6-Diisopropylaniline was treated with one equivalent of benzoyl chloride in an aqueous potassium hydroxide solution. The resulting amide was converted into the corresponding imidoyl chloride, which was treated with a further equivalent of 2,6-diisopropylaniline in the presence of triethylamine to give *N*,*N*'-bis(2,6-diisopropylphenyl)benzamidine (**1a**). Colourless crystals were obtained by crystallization from hot ethanol. Amidines substituted in the *para* position of the phenyl backbone were prepared by insertion reactions of the lithiated arene and *N*,*N*'-bis(2,6-diisopropylphenyl)carbodiimide (Scheme 2, bottom). 4-Bromoanisole, 4-bromo-*N*,*N*-dimethylaniline or 1-(4-bromophenyl)-2,5-dimethyl-1*H*-pyrrole were lithiated with an excess of *n*BuLi and subsequently reacted with *N*,*N*'-bis(2,6-diisopropylphenyl)-carbodiimide to obtain the corresponding lithium amidinates. After hydrolysis with water or saturated ammonium chloride solution and recrystallization from hot ethanol, amidines **1a**–**1d** were obtained in good yields. Owing to the substituent in the *para* position, these ligands are considered to donate more electron density to the metal centre as illustrated in Figure 1.



Scheme 2. Synthesis of *N*,*N*'-bis(2,6-diisopropylphenyl)benzamidines; Ar = 2,6-diisopropylphenyl.

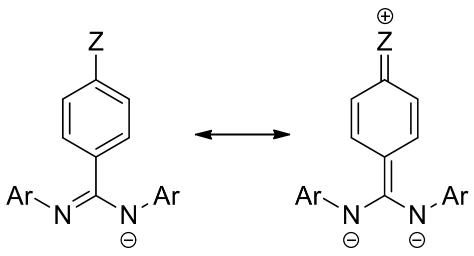
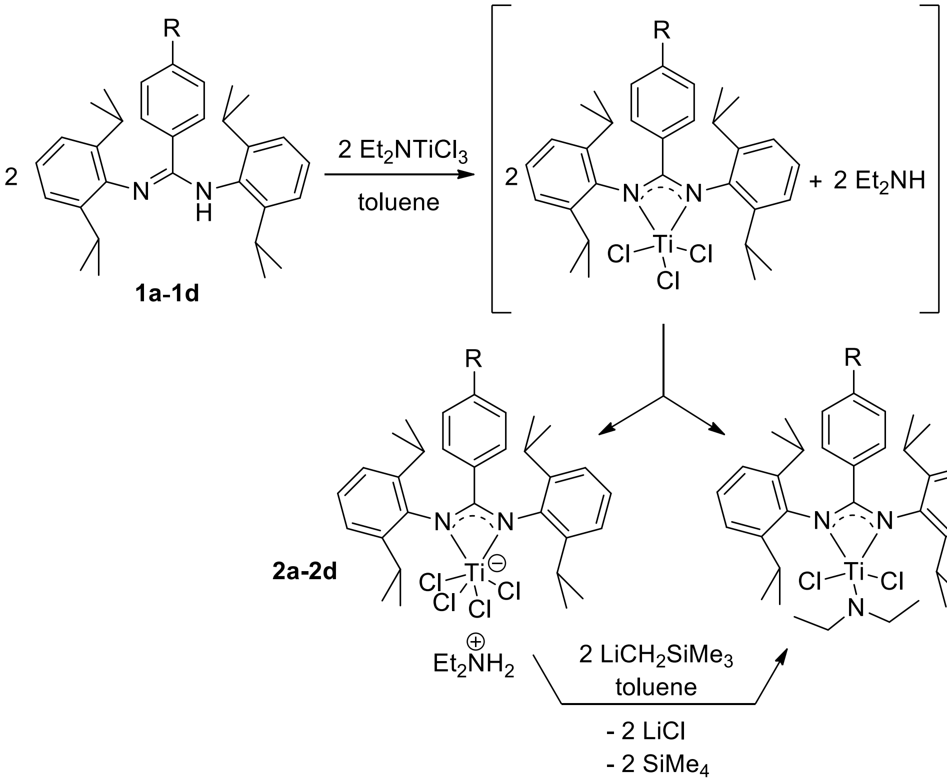


Figure 1. Higher electron-donating ability owing to the introduction of functional groups in the backbone of the ligand.

Complex Synthesis

Amidines **1a–1d** were treated with one equivalent of diethylamidotitanium trichloride [$(Et_2N)TiCl_3$] in toluene at room temperature to form the corresponding amidinatotitanium trichloride complexes by amine elimination. However, NMR experiments and X-ray crystal structure analysis showed that the reactions of **1a–1d** with [$(Et_2N)TiCl_3$] lead to the amidinatotitanium trichloride only as an intermediate product, along with one equivalent of diethylamine (Scheme 3). The released amine reacts with the amidinatotitanium trichloride to form equal amounts of an amidinatodiethylamidotitanium dichloride and diethylammonium chloride. The latter reacts with the remaining amidinatotitanium trichloride to form a diethylammonium amidinatotetrachlorotitanate. Treatment of these anionic complexes **2a–2d** with (trimethylsilyl)methyllithium or butyllithium selectively leads to the neutral amidinato diethylamidotitanium dichloride complexes (Scheme 3).



Scheme 3. Synthesis of the complexes **2a–2d** and **3b**.

All complexes were analyzed by NMR spectroscopy and elemental analysis. Single crystal structure analyses were carried out for selected complexes. Crystals suitable for X-ray analysis were obtained by layering concentrated toluene solutions with hexane or by recrystallization from hot hexane. The molecular structures of complexes **2a**, **2b**, **2d** and **3b** are presented in Figures 2, 3 and 4. Selected bond lengths and angles are listed in Table 1. Crystallographic details are available in the Supporting Information (Table S1).

These new diethylammonium amidinato-tetrachlorotitanates form dimeric structures. Two complex anions are bridged by the diethylammonium counterions through NH···Cl hydrogen bonds (illustrated for **2b** in Figure 2).

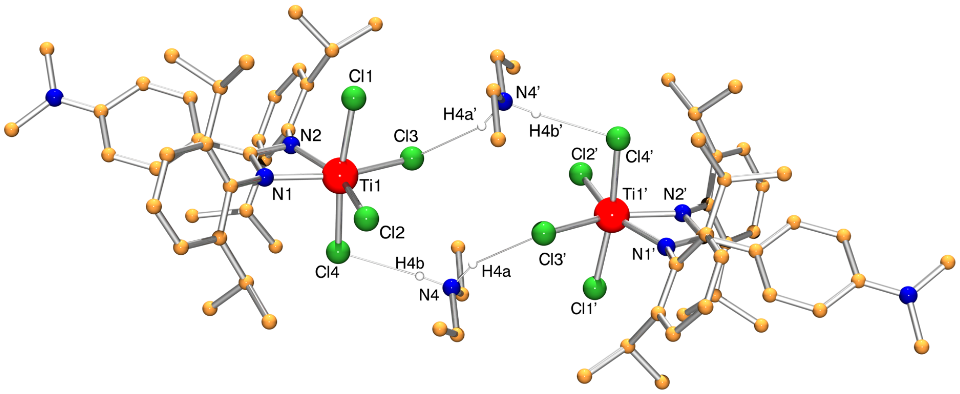


Figure 2. Dimeric structure of **2b**. Carbon-bonded hydrogen atoms are omitted for clarity.

In complexes **2a**–**2d**, the titanium centres are pseudo-octahedrally coordinated by four chloro and two nitrogen atoms to yield an anion accompanied by the diethylammonium counterion. The two Ti–N bond lengths are in the range found for benzamidinato-titanium complexes.[25] The N1–C1, N2–C1 and C5–N3 bond lengths are significantly shorter than C(sp2)–N single bonds and slightly longer than C–N double bonds. The sums of the bond angles around N3 are 360.1 (**2b**), 359.4 (**2d**) and 359.9° (**3b**), which confirms that the nitrogen atoms are sp^2 hybridized. Furthermore, the introduction of electron-donating groups leads to a quinoid π-electron system, which results in significantly shorter C3–C4 bond lengths than the C2–C3 and C4–C5 bond lengths, as suggested in Figure 1. This clearly indicates that the lone pair of the introduced substituents participates in the ligand π system and can increase the electron density at the titanium centre, which results in closer bonding to the ligand. The N1–Ti1–N2 bond angle is smaller than that in [$\{PhC(NSiMe_3)_2\}TiCl_3$], which indicates the higher steric demand of the 2,6-diisopropylphenyl moieties.

Compound **3b** crystallizes in the monoclinic space group $P2_1/n$. The metal centre is coordinated by the amidinate ligand, a diethylamido ligand and two chloro ligands to form a neutral complex (Figure 3). The N1–Ti1–N2 bond angle [62.4(3)°] is slightly smaller than those in **2a**–**2d**.

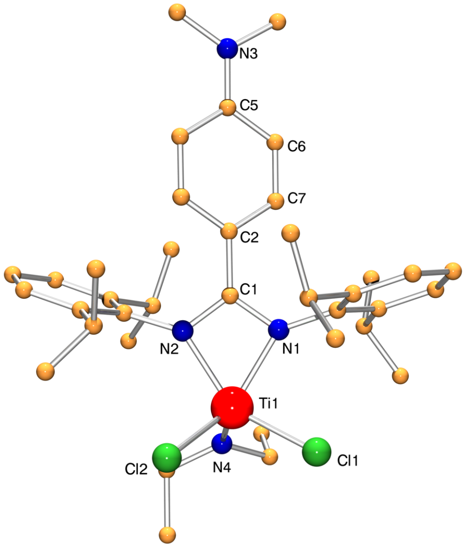


Figure 3. Molecular structure of **3b**. Carbon-bonded hydrogen atoms are omitted for clarity.

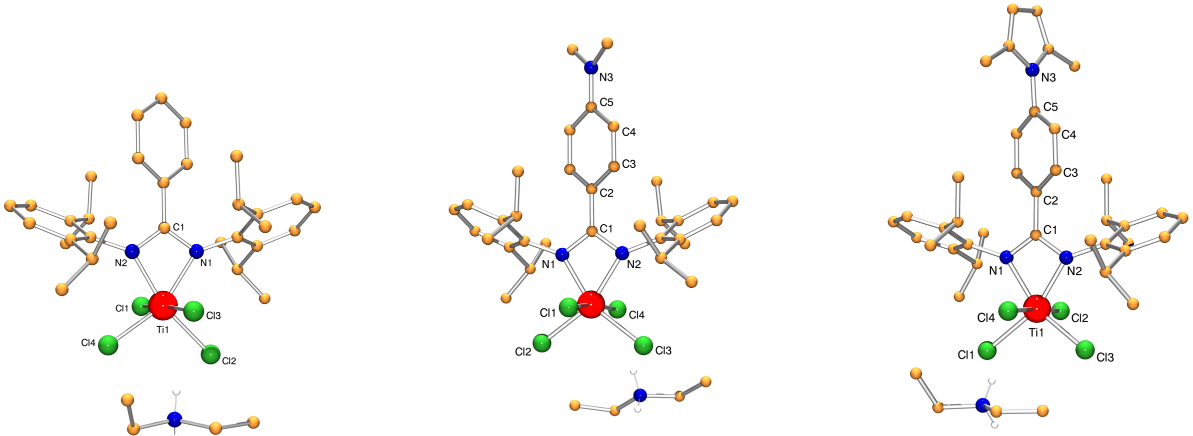


Figure 4. Molecular structures of **2a**, **2b** and **2d** (from left to right). Carbon-bonded hydrogen atoms are omitted for clarity.

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

	2a	**2b**	**2d**	**3b**
Ti1–N1	2.1032(16)	2.040(2)	2.093(3)	2.0758(19)
Ti1–N2	2.0540(16)	2.088(2)	2.053(3)	2.0730(18)
T1–Cl1	2.3287(6)	2.3381(8)	2.3541(13)	2.272(3)
T1–Cl2	2.3418(6)	2.2686(9)	2.3253(12)	2.272(3)
T1–Cl3	2.3601(6)	2.3711(8)	2.2677(13)	–
T1–Cl4	2.2774(6)	2.3917(8)	2.3545(11)	–
C1–N1	1.335(2)	1.352(3)	1.328(5)	1.351(3)
C1–N2	1.337(3)	1.338(3)	1.355(5)	1.343(3)
C1–C2	1.483(6)	1.468(4)	1.488(6)	1.472(3)
C2–C3	–	1.396(4)	1.386(6)	1.392(3)
C3–C4	–	1.372(4)	1.399(6)	1.377(3)
C4–C5	–	1.402(4)	1.376(6)	1.409(4)
C5–N3	–	1.361(3)	1.438(6)	1.365(3)
N1–C1–N2	109.66(16)	108.3(2)	109.2(4)	108.19(19)
N1–Ti1–N2	63.37(6)	63.72(8)	63.66(13)	63.47(7)
∑<(C1)	359.99	359.8	359.9	359.99
∑<(N3)	–	360.1	359.4	359.9

Polymerization Studies

The activation of the precatalysts **2a–c** and **3b** with methylaluminoxane (MAO) leads to active polymerization catalysts at 50 °C with activities of up to 900 $kg_{PE}mol^{-1}h^{-1}bar^{-1}$ and polyethylene with molecular weights between 23 and 90 $kgmol^{-1}$ (Table 2). We suppose that the diethylammonium ion is deprotonated and ends up at the aluminium species. The temperature influences the polymerization rather strongly (Table 2, Entries 2–4). At 50 °C, **2b** produces polyethylene with a molecular weight of 29 $kgmol^{-1}$ with an activity of 900 $kg_{PE}mol^{-1}h^{-1}bar^{-1}$ (Table 2, Entry 2). A decrease of the temperature to 30 °C resulted in no significant difference in activity, but a nearly sevenfold increase in molecular weight accompanied by a broadening of the polydispersity was obtained (Table 2, Entry 3). Increasing the temperature to 80 °C led to a significant decrease in the polymerization ability (Table 2, Entry 4). The low activity at 80 °C could result from catalyst decomposition at this temperature. As a consequence, further studies were conducted at 50 °C. To rule out ligand transfer from Ti to trimethylaluminium (TMA),[18,26] further experiments were also done with d-MAO, MAO from which free TMA was removed. Alteration of the ligand backbone did not give greatly different polymerization results at this stage. Polymerization with **3b** leads to a clearly bimodal distribution. This indicates that two active sites are operating if **3b** is used as a precatalyst. One of the distributions is identical to the one observed for precatalyst **2b** under identical conditions (Figure 5). One of these active sites could be identical to the single site catalyst that is generated by MAO activation of **2b**. The other one could result from a diethylamido-containing species. The activity of the complexes increases if activated with d-MAO (Table 3) instead of MAO. Higher molecular weight polyethylene, roughly one order of magnitude higher than for the MAO runs, was observed for all catalysts, which indicates that a polymeryl chain transfer to TMA occurs if MAO is used as an activator. The addition of defined amounts of TEA to the d-MAO runs supports this hypothesis. The variation of the TEA-to-Ti ratio from 500 to 1000 to 2000 to 10000 resulted in a decrease of the molecular weight, activity and polydispersity. The activation of **3b** with d-MAO leads to a monomodal but broad distribution and shows evidence of a bimodal distribution; the distribution is clearly bimodal with MAO. The influence of functional groups in the backbone of the ligands was also examined. NMR investigations of the polymers obtained showed that all polymer chains are fully saturated as there are no olefinic resonances (Figure S1 in the Supporting Information). This can only be explained by the exclusive presence of metal-terminated polymer before hydrolysis with acidified ethanol.

Table 2. Ethylene polymerization using MAO.[a]

Entry	Precat.[a]	m_{PE} [g]	Activity [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]	M_w [$kgmol^{-1}$]	M_w/M_n
1	**2a**	0.90	900	24.2	2.8
2	**2b**	0.90	900	28.6	6.0
3	**2b**[b]	0.80	800	197.8	16.8
4	**2b**[c]	0.13	130	6.3	2.3
5	**2c**	0.60	600	49.4	6.0
6	**2d**	0.70	700	22.3	4.8
7	**3b**	0.80	800	91.6	11.4

[a] Conditions: precatalyst 2.0 μmol; MAO 1.3 mmol, toluene 150 mL; p = 2 bar; t = 15 min; T = 50 °C. [b] T = 30 °C. [c] T = 80 °C.

Table 3. Ethylene polymerization using d-MAO.[a]

Entry	Precat.[a]	TEA (equiv.)	m_{PE} [g]	Activity [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]	M_w [$kgmol^{-1}$]	M_w/M_n
8	**2a**	0	1.40	1400	232.9	8.9
9	**2a**	500	0.80	800	8.0	2.1
10	**2b**	0	1.60	1600	228.4	4.5
12	**2b**	500	1.20	1200	7.4	4.1
13	**2b**	1000	1.00	1000	3.5	2.3
14	**2b**	2000	0.7	700	1.9	1.7
15	**2b**	10000	0.35	350	1.0	1.3
16	**2c**	0	0.80	800	310.3	2.2
17	**2c**	500	0.30	300	8.4	2.3
18	**2d**	0	1.30	1300	86.2	10.0
19	**2d**	500	0.80	800	6.9	3.0
20	**3b**	0	3.50	3500	384.4	4.9

[a] Conditions: precatalyst 2.0 μmol; d-MAO 1.0 mmol; toluene 150mL; p = 2bar; t = 15min; T = 50°C.

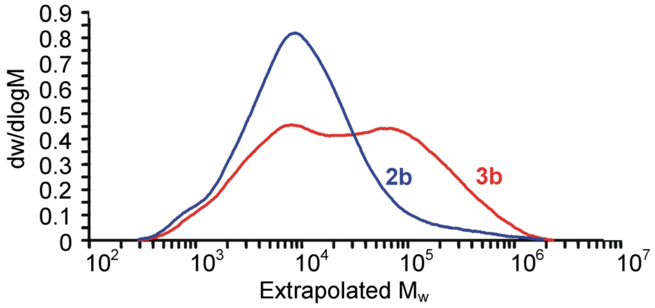


Figure 5. M_w distribution plots of polymers (Table 2, Entries 2 and 7).

4.4 Conclusion

Several conclusions can be drawn from the present study. Mono(amidinato) titanium complexes can be synthesized by amine elimination. The treatment of amidines with diethylamidotitanium trichloride leads to anionic mono(amidinato) titanium tetrachloride complexes with diethylammonium counterions and mono(amidinato) diethylamidotitanium dichloride complexes. The titanates can also be converted selectively into neutral dichloride complexes by addition of strong bases. The introduction of electron-donating groups to the backbone of the ligands gives rise to increased electron-donating ability of these ligands. Only marginal influences of that electron donor ability towards the polymerization performance were observed. These mono(amidinato) titanium complexes gave rise to highly active polymerization catalysts after activation with d-MAO. The polymerization can be viewed as a catalyzed version of Ziegler's "Aufbaureaktion".

4.5 Experimental Section

General Comments: All manipulations and reactions were carried out under dry argon by using standard Schlenk and glovebox techniques. Solvents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy or sodium ketyl of benzophenone under argon immediately before use. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). $[(Et_2N)TiCl_3]$ was prepared according to literature procedures.[27] Commercial *n*BuLi (2.5 M in hexane) and all other chemicals were used as received. Elemental analyses were carried out with a Vario elementar EL III apparatus.

NMR Spectroscopy: NMR spectra were obtained with a Varian INOVA 400, Varian INOVA 300 or Bruker ARX250 spectrometer. Chemical shifts are reported in ppm relative to the residual proton signals of the deuterated solvent. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use.

Gel Permeation Chromatography (GPC): Gel permeation chromatography (GPC) analysis was carried out with a PL-GPC 220 (Agilent, Polymer Laboratories) high-temperature chromatographic unit equipped with differential pressure (DP) and refractive index (RI) detectors and two linear mixed bed columns (Olexis, 13-micron particle size). GPC analysis were performed at 150 °C and with 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.05 wt.-%, c = 1 mgmL^{-1}) in the mobile phase solvent in an external oven, and the solutions were run without filtration. The molecular weights of the samples were referenced to PE (M_w = 520–3200000 gmol^{-1}) and PS (M_w = 580–2800000 gmol^{-1}) 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 [λ(Mo-K_α) = 0.71073 Å] equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished with SIR97,[28] SHELXL-97[29] and WinGX.[30] Selected details of the X-ray crystal structure analyses are listed in Table 1.

CCDC-902396 (for **2a**), -903295 (for **2b**), -902394 (for **2d**) and -903293 (for **3b**) 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.

Ethylene Polymerization: The polymerizations were carried out in a 300 mL Büchi glass autoclave with an ethylene flow display equipped with external heating (water bath) at 2 bar ethylene pressure. The autoclave was evacuated and purged with ethylene. Toluene (150 mL) was added into the autoclave and saturated with ethylene. The stock solutions of catalyst and cocatalyst were prepared in a glovebox. After addition of the cocatalyst and complete saturation with ethylene, the catalyst was added. After 15 min of reaction time, the reactor was vented and acidified ethanol was added. The polymers were filtered and dried at 80 °C.

Ligand Synthesis

***N*,*N*'-Bis(2,6-diisopropylphenyl)benzamidine (1a):** To a solution of 2,6-diisopropylaniline (10 mL, 9.4 g, 53 mmol) in potassium hydroxide solution (100 mL, 10% in water), benzoyl chloride (6.7 mL, 8.19 g, 58 mmol) was added with vigorous stirring. The purple precipitated solid was collected by filtration and washed with water and hexane. The resulting *N*-2,6-diisopropylphenylbenzamide (10.00 g, 50.7 mmol) was heated at reflux for one hour in thionyl chloride (20 mL). The excess thionyl chloride was removed under reduced pressure, and *N*-(2,6-diisopropylphenyl)benzimidoyl chloride was obtained as a yellow oily residue. To a solution of this intermediate (5 g, 16.7 mmol) and triethylamine (2.3 mL, 1.7 g, 16.7 mmol) in toluene (50 mL), 2,6-diisopropylaniline (3.1 mL, 3.8 g, 16.7 mmol) was added. The mixture was heated to reflux for two hours. Subsequently, the reaction mixture was poured into water. The organic phase was separated, washed twice with water and dried with anhydrous sodium sulfate. After removal of the solvent, the residue was recrystallized from hot ethanol (5.4 g, 69% with respect to the imidoyl chloride). ^{1}H NMR (250 MHz, C_6D_6): δ = 0.95 [d, J = 6.4 Hz, 6 H, CH(CH_3)$_2$], 1.02 [d, J = 6.2 Hz, 6 H, CH(CH_3)$_2$], 1.37 [d, J = 6.6 Hz, 6 H, CH(CH_3)$_2$], 1.49 [d, J = 6.7 Hz, 6 H, CH(CH_3)$_2$], 3.35 [m, 2 H, CH(CH$_3$)$_2$], 3.52 [m, 2 H, CH(CH$_3$)$_2$], 5.70 (s, 1 H, NH), 6.50–7.63 (m, 11 H, ArH) ppm.

***N*,*N*'-Bis(2,6-diisopropylphenyl)-4-dimethylaminobenzamidine (1b):** *n*BuLi (2.5 M in hexane, 4.0 mL, 10 mmol) was slowly added to a solution of 4-bromo-*N*,*N*-dimethylaniline (2.01 g, 10 mmol) in THF (40 mL) at −78 °C. After stirring for 3 h, a solution of *N*,*N*'-bis(2,6-diisopropylphenyl)carbodiimide (3.31 g, 8.6 mmol) in THF (20 mL) was added dropwise. The solution was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue was dissolved in ether. To this solution, a saturated ammonium chloride solution (5 mL) was added, and the mixture was stirred for 1 h. The aqueous phase was separated and washed twice with ether. The organic phases were combined and dried with anhydrous sodium sulfate. After filtration and removal of the solvent, the residue was recrystallized from hot ethanol. The obtained colourless crystals were isolated, washed with cold ethanol and dried under vacuum (3.9 g, 74 %). ^{1}H NMR (250 MHz, C_6D_6): δ = 0.81 [d, *J* = 6.7 Hz, 6 H, $CH(CH_3)_2$], 0.90 [d, *J* = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.14 [d, *J* = 6.7 Hz, 6 H, $CH(CH_3)_2$], 1.24 [d, *J* = 6.9 Hz, 6 H, $CH(CH_3)_2$], 2.81 [s, 6 H, $N(CH_3)_2$], 3.08 [m, 2 H, $CH(CH_3)_2$], 3.37 [m, 2 H, $CH(CH_3)_2$], 5.51 (s, 1 H, N*H*), 6.38–7.20 (m, 10 H, Ar*H*) ppm.

***N*,*N*'-Bis(2,6-diisopropylphenyl)-4-methoxybenzamidine (1c):** To a solution of 4-bromoanisole (2.0 mL, 16 mmol) in hexane (40 mL), *n*BuLi (6.4 mL, 16 mmol) was added dropwise at room temperature. Stirring of the solution for 4 h produced a white precipitate. The supernatant solution was decanted, and the residue was washed twice with hexane, dried under vacuum and subsequently dissolved in ether. A solution of *N*,*N*'-bis(2,6-diisopropylphenyl)carbodiimide (3.55 g, 13.8 mmol) in ether was added dropwise, and the mixture was stirred overnight. To this solution, a saturated ammonium chloride solution (5 mL) was added, and the mixture was stirred for 1 h. The aqueous phase was separated and washed twice with ether. The combined organic phases were dried with anhydrous sodium sulfate and filtered. The solvent was removed in vacuo. Recrystallization of the residue from hot ethanol led to pale yellow crystals (1.3 g, 65 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.91 [d, *J* = 6.4 Hz, 6 H, $CH(CH_3)_2$], 0.92 [d, *J* = 6.2 Hz, 6 H, $CH(CH_3)_2$], 1.38 [d, *J* = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.39 [d, *J* = 6.7 Hz, 6 H, $CH(CH_3)_2$], 3.08 (s, 3 H, OCH_3), 3.31 [m, 2 H, $CH(CH_3)_2$], 3.49 [m, 2 H, $CH(CH_3)_2$], 5.88 (s, 1 H, N*H*), 6.51–7.65 (m, 10 H, Ar*H*) ppm.

***N*,*N*'-Bis(2,6-diisopropylphenyl)-4-(2,5-dimethylpyrrole-1-yl)benzamidine (1d):** To a solution of 1-(4-bromophenyl)-2,5-dimethylpyrrole[31] (2.00 g, 8.0 mmol) in hexane (30 mL), *n*BuLi (3.4 mL, 8.5 mmol) was added dropwise at −78 °C. Stirring of the mixture for four hours at room temperature resulted in a white solid. The supernatant solution was decanted, and the solid was washed twice with hexane. After removal of the supernatant solution, the solid was dried in vacuo. To the obtained [4-(2,5-dimethyl-1*H*-pyrrole-1-

yl)phenyl]lithium (1.00 g, 5.64 mmol) in diethyl ether (30 mL) a solution of *N*,*N*'-bis(2,6-diisopropylphenyl)carbodiimide (1.84 g, 5.08 mmol) in diethyl ether (15 mL) was added dropwise at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. Saturated ammonium chloride solution (3 mL) was added and stirred vigorously for 1 h. The organic phase was separated, and the aqueous phase was extracted several times with ether. The combined organic phases were dried with anhydrous sodium sulfate, filtered and the solvent was removed under reduced pressure. Recrystallization from hot ethanol led to orange crystals (1.08 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 [d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$], 0.92 [d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$], 1.18 [d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$], 1.29 [d, J = 7.0 Hz, 6 H, $CH(CH_3)_2$], 1.87 (s, 6 H, CH_3-pyrrole), 3.13 [m, 4 H, $CH(CH_3)_2$], 5.68 (s, 1 H, N*H*), 5.78 (s, 2 H, C*H*-pyrrole), 6.89–7.40 (m, 10 H, Ar*H*) ppm.

Complex Synthesis

Diethylammonium [*N*,*N*'-Bis(2,6-diisopropylphenyl)benzamidinato-tetrachlorotitanate] (2a): Diethylamidotitanium trichloride (0.350 g, 1.55 mmol) and **1a** (0.60 g, 1.35 mmol) were dissolved in toluene (20 mL), and the solution was stirred for 24 h at room temperature. The solvent was removed under reduced pressure, and the dark brown residue was dissolved in toluene and filtered. Dark red crystals were obtained by layering the filtrate with hexane (0.41 g, 43%). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.03 [d, J = 6.8Hz, 12 H, $CH(CH_3)_2$], 1.49 [t, J = 6.8 Hz, 6 H, $H_2N(CH_2CH_3)_2$], 1.74 [d, J = 6.5 Hz, 12 H, $CH(CH_3)_2$], 2.69 [q, J = 7.2 Hz, 4 H, $H_2N(CH_2CH_3)_2$], 3.87 [m, 4 H, $CH(CH_3)_2$], 6.63–7.30 (m, 11 H, Ar*H*), 7.73 [s, 2 H, $H_2N(CH_2CH_3)_2$] ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 13.2 [$H_2N(CH_2CH_3)_2$], 23.8 [$CH(CH_3)_2$], 24.0 [$CH(CH_3)_2$], 28.8 [$CH(CH_3)_2$], 49.2 [$H_2N(CH_2CH_3)_2$], 124.57, 131.5, 130.9, 131.0, 143.0, (ArC), 177.7 (NCN) ppm. $C_{35}H_{51}Cl_4N_3Ti$ (703.49): calcd. C 59.76, H 7.31, N 5.97; found C 58.97, H 7.45, N 5.82.

Diethylammonium [*N*,*N*'-Bis(2,6-diisopropylphenyl)-4-dimethylamidobenzamidinato-tetrachlorotitanate] (2b): Compound **1b** (0.214 g, 0.44 mmol) and diethylamidotitanium trichloride (0.10 g, 0.44 mmol) were dissolved in toluene (20 mL), and the solution was stirred for one hour at room temperature. Dark red crystals were obtained by layering with hexane (0.150 g, 48 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.94 [t, *J* = 6.9 Hz, 6 H, $H_2N(CH_2CH_3)_2$], 1.49 [d, *J* = 6.6 Hz, 12 H, $CH(CH_3)_2$], 1.60 [d, *J* = 6.4 Hz, 12 H, $CH(CH_3)_2$], 1.96 [s, 6 H, $N(CH_3)_2$], 3.80 [m, 4 H, $CH(CH_3)_2$], 4.09 [q, *J* = 6.9 Hz, 4 H, $H_2N(CH_2CH_3)_2$], 7.09–7.25 (m, 10 H, Ar*H*), 7.41 [s, 2 H, $H_2N(CH_2CH_3)_2$] ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 13.1 [$H_2N(CH_2CH_3)_2$], 24.3 [$CH(CH_3)_2$], 25.6 [$CH(CH_3)_2$], 29.1 [$CH(CH_3)_2$], 38.7 [$N(CH_3)_2$], 48.8 [$H_2N(CH_2CH_3)_2$], 110.2, 124.8, 126.8, 133.5, 143.4, 144.4, 145.7, 157.3 (ArC), 182.6 (NCN) ppm. $C_{37}H_{56}Cl_4N_4Ti$ (746.55): calcd. C 59.53, H 7.56, N 7.50; found C 59.40, H 7.64, N 7.61.

Diethylammonium [*N*,*N*'-Bis(2,6-diisopropylphenyl)-4-methoxybenzamidinato-tetrachlorotitanate] (2c): Compound **2c** was prepared according to the procedure for **2b** by using the following amounts: **1c** (0.208 g, 0.44 mmol) and diethylamidotitanium trichloride (0.10 g, 0.44 mmol), yield 0.141 g, 46 %. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.21 [t, *J* = 6.6 Hz, 6 H, $H_2N(CH_2CH_3)_2$], 1.31 [d, *J* = 6.5Hz, 12 H, $CH(CH_3)_2$], 1.45 [d, *J* = 6.4Hz, 12 H, $CH(CH_3)_2$], 2.49 [q, *J* = 7.0Hz, 4 H, $H_2N(CH_2CH_3)_2$], 2.92 (s, 3 H, OCH_3), 3.55 [sept, *J* = 6.6 Hz, 4 H, $CH(CH_3)_2$], 7.18–7.30 (m, 10 H, Ar–*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 13.2 [$H_2N(CH_2CH_3)_2$], 24.2 [$CH(CH_3)_2$], 25.7 [$CH(CH_3)_2$], 29.0 [$CH(CH_3)_2$], 49.1 [$H_2N(CH_2CH_3)_2$], 54.6 (OCH_3), 113.3, 120.9, 124.7, 127.0, 133.3, 143.5, 144.9, 162.2, 162. 7 (ArC), 177.3 (NCN) ppm. $C_{36}H_{53}Cl_4N_3OTi + C_7H_8$ (825.64): calcd. C 62.55, H 7.45, N 5.09; found C 61.07, H 7.79, N 5.37.

Diethylammonium [*N*,*N*'-Bis(2,6-diisopropylphenyl)-4-(2,5-dimethylpyrrole-1-yl)benzamidinatotetrachlorotitanate] (2d): Compound **2d** was prepared according to the procedure for **2b** by using the following amounts: **1d** (0.400 g, 0.70 mmol) and diethylamidotitanium trichloride (0.169 g, 0.70 mmol). Dark red crystals were obtained by layering with hexane (0.270 g, 47 %). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.75 [d, *J* = 6.7 Hz, 12 H, $CH(CH_3)_2$], 1.13 [d, *J* = 6.6Hz, 12 H, $CH(CH_3)_2$], 1.25 [m, 6 H, $H_2N(CH_2CH_3)_2$], 3.17 [q, *J* = 7.3Hz, 4 H, $H_2N(CH_2CH_3)_2$], 3.75 [m, 4 H, $CH(CH_3)_2$], 5.74 (s, 6 H, CH_3-pyrrole), 6.81–7.87 (m, 12 H, Ar*H*), 7.59 [s, 2 H, $H_2N(CH_2CH_3)_2$] ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 11.4 (CH_3-pyrrole), 13.1 [$N(CH_2CH_3)_2$], 24.0 [$CH(CH_3)_2$], 25.9 [$CH(CH_3)_2$], 29.1 [$CH(CH_3)_2$], 43.1 [$N(CH_2CH_3)_2$], 107.2, 125.2, 125.8, 128.2, 128.6, 128.7, 129.5, 132.3, 136.6, 138.5, 143.5, 144.0 (ArC) ppm. $C_{103}H_{140}Cl_8N_8Ti_2$ (1869.63): calcd. C 66.17, H 7.55, N 5.99; found C 65.97, H 7.81, N 5.81.

[*N*,*N'*-Bis(2,6-diisopropylphenyl)-4-dimethylamino-benzamidinato]-dichlorodiethylamidotitanium(IV) (3b): Compound **1b** (0.30 g, 0.62 mmol) and diethylamidotitanium trichloride (0.14 g, 0.62 mmol) were dissolved in toluene (20 mL), and the solution was stirred for 1 h at room temperature. (Trimethylsilyl)methyllithium (0.058 g, 0.62 mmol) was added, and the mixture was stirred overnight, which brightened the dark red solution. The solution was filtered, and the residue was extracted twice with toluene. The solvent was removed under reduced pressure. Recrystallization from hot hexane led to bright red crystals (0.40 g, 80 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.08 [t, J = 6.9 Hz, 6 H, $N(CH_2CH_3)_2$], 1.20 [d, J = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.64 [d, J = 6.7 Hz, 12 H, $CH(CH_3)_2$], 2.04 [s, 6 H, $N(CH_3)_2$], 3.95 [sept, J = 6.7 Hz, 4 H, $CH(CH_3)_2$], 4.23 [q, J = 7.0 Hz, 4 H, $N(CH_2CH_3)_2$], 7.00–7.52 (m, 10 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 13.2 [$N(CH_2CH_3)_2$], 24.3 [$CH(CH_3)_2$], 25.6 [$CH(CH_3)_2$], 28.9 [$CH(CH_3)_2$], 38.7 [$N(CH_3)_2$], 48.9 [$N(CH_2CH_3)_2$], 110.0, 114.8, 124.6, 126.8, 133.3, 143.4, 151.7 (ArC), 177.8 (NCN) ppm. $C_{37}H_{54}Cl_2N_4Ti$ + 0.5 C_6H_{14} (716.71): calcd. C 67.03, H 8.58, N 7.82; found C 65.08, H 8.78, N 7.40.

Supporting Information (see footnote on the first page of this article): Crystallographic details and high-temperature ^{1}H NMR spectrum of the obtained PE.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (DFG) SFB 840 and from SASOL Germany GmbH is gratefully acknowledged.

4.6 References

[1] a) K. Ziegler, H. G. Gellert, H. Kühlhorn, H. Martin, K. Meyer, K. Nagel, H. Sauer, K. Zosel, *Angew. Chem.* **1952**, *64*, 323; b) K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **1955**, *67*, 541–547.

[2] *Sasol Olefins & Surfactants*, Annual review **2010**.

[3] R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764–2773.

[4] L. R. Sita, *Angew. Chem.* **2009**, *121*, 2500; *Angew. Chem. Int. Ed.* **2009**, *48*, 2464–2472.

[5] a) E. G. Samsel, EP 0539876, **1993**; b) E. G. Samsel, D. C. Eisenberg, EP 0574854, **1993**.

[6] a) J.-F. Pelletier, A. Mortreux, X. Olonde, K. Bujadoux, *Angew. Chem.* **1996**, *108*, 1980–1982; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1854–1856; b) J.-F. Pelletier, K. Bujadoux, X. Olonde, E. Adisson, A. Mortreux, T. Chenal, US 5779942, **1998**; c) T. Chenal, X. Olonde, J.-F. Pelletier, K. Bujadoux, A. Mortreux, *Polymer* **2007**, *48*, 1844–1856.

[7] a) G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, P. J. Maddox, M. van Meurs, *Angew. Chem.* **2002**, *114*, 507–509; *Angew. Chem. Int. Ed.* **2002**, *41*, 489–491; b) G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, M. van Meurs, *J. Am. Chem. Soc.* **2004**, *126*, 10701–10712; c) M. van Meurs, G. J. P. Britovsek, V. C. Gibson, S. A. Cohen, *J. Am. Chem. Soc.* **2005**, *127*, 9913–9923; d) H. Kaneyoshi, Y. Inoue, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 5425–5435; e) J. O. Ring, R. Thomann, R. Mülhaupt, J.-M. Raquez, P. Degee, P. Dubois, *Macromol. Chem. Phys.* **2007**, *208*, 896–902.

[8] a) W. Zhang, L. R. Sita, *J. Am. Chem. Soc.* **2008**, *130*, 442–443; b) W. Zhang, J. Wei, L. R. Sita, *Macromolecules* **2008**, *41*, 7829–7833; c) J. Wei, W. Zhang, R. Wickham, L. R. Sita, *Angew. Chem.* **2010**, *122*, 9326–9330; *Angew. Chem. Int. Ed.* **2010**, *49*, 9140–9144; d) C. Giller, G. Gururajan, L. Wie, W. Zhang, W. Hwang, D. B. Chase, J. F. Rabolt, L. R. Sita, *Macromolecules* **2011**, *44*, 471–482.

[9] a) D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T.Wenzel, *Science* **2006**, *312*, 714–719; b) P. D. Hustad, R. L. Kuhlman, D. J. Arriola, E. M. Carnahan, T. T. Wenzel, *Macromolecules* **2007**, *40*, 7061–7064; c) P. D. Hustad, R. L. Kuhlman, E. M. Carnahan, T. T. Wenzel, D. J. Arriola, *Macromolecules* **2008**, *41*, 4081–4089; d) R. L. Kuhlman, T. T. Wenzel, *Macromolecules* **2008**, *41*, 4090–4094; e) A. Hotta, E. Cochran, J. Ruokolainen, V. Khanna, G. H. Fredrickson, E. J. Kramer, Y.-W. Shin, F. Shimizu, A. E. Cherian, P. D. Hustad, J. M. Rose, G. W. Coates, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15327–15332; f) T. T. Wenzel, D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, *Metal Catalysts in Olefin Polymerization* (Ed.: Z. Guan), in: *Topics in Organometallic Chemistry*, Springer, Berlin, Heidelberg, **2009**, vol. 26, p. 65–104; g) S. Li, R. A. Register, B. G. Landes, P. D.

Hustad, J. D. Weinhold, *Macromolecules* **2010**, *43*, 4761–4770; h) P. D. Hustad, G. R. Marchand, E. I. Garcia-Meitin, P. L. Roberts, J. D. Weinhold, *Macromolecules* **2009**, *42*, 3788–3794; i) F. Deplace, Z. Wang, N. A. Lynd, A. Hotta, J. M. Rose, P. D. Hustad, J. Tian, H. Ohtaki, G. W. Coats, F. Shimizu, K. Hirokane, F. Yamada, Y.-W. Shin, L. Rong, S. Toki, B. S. Hsiao, G. H. Fredrickson, E. J. Kramer, *J. Polym. Sci., Part B* **2010**, *48*, 1428–1437.

[10] W. P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, *Chem. Eur. J.* **2006**, *12*, 8969–8978.

[11] a) J. S. Rogers, G. C. Bazan, *Chem. Commun.* **2000**, 1209–1210; b) G. C. Bazan, J. S. Rogers, C. C. Fang, *Organometallics* **2001**, *20*, 2059–2064; c) C. J. Han, M. S. Lee, D.-J. Byun, S. Y. Kim, *Macromolecules* **2002**, *35*, 8923–8925; d) G. Mani, F. P. Gabbaï, *Angew. Chem.* **2004**, *116*, 2313–2316; *Angew. Chem. Int. Ed.* **2004**, *43*, 2263–2266; e) G. Mani, F. P. Gabbaï, *J. Organomet. Chem.* **2005**, *690*, 5145–5149; f) C. Döring, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2010**, *18*, 2853–2860; g) W. P. Kretschmer, T. Bauer, B. Hessen, R. Kempe, *Dalton Trans.* **2010**, *39*, 6847–6852.

[12] J. Wei, W. Zhang, L. R. Sita, *Angew. Chem.* **2010**, *122*, 1812–1816; *Angew. Chem. Int. Ed.* **2010**, *49*, 1768–1772. [13] a) M. Bochmann, S. J. Lancaster, *J. Organomet. Chem.* **1995**, *497*, 55–59; b) M. Bochmann, S. J. Lancaster, *Angew. Chem.* **1994**, *106*, 1715–1718; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1634–1637. [14] R. A. Petros, J. R. Norton, *Organometallics* **2004**, *23*, 5105–5107. [15] J. M. Camara, R. A. Petros, J. R. Norton, *J. Am. Chem. Soc.* **2011**, *133*, 5263–5273. [16] a) I. Haas, W. P. Kretschmer, R. Kempe, *Organometallics* **2011**, *30*, 4854–4861; b) K. Michiue, R. F. Jordan, *Organometallics* **2004**, *23*, 460–670; c) S. Murtuza, O. L. Casagrande Jr., R. F. Jordan, *Organometallics* **2002**, *21*, 1882–1890.

[13] a) M. Bochmann, S. J. Lancaster, *J. Organomet. Chem.* **1995**, *497*, 55–59; b) M. Bochmann, S. J. Lancaster, *Angew. Chem.* **1994**, *106*, 1715–1718; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1634–1637.

[14] R. A. Petros, J. R. Norton, *Organometallics* **2004**, *23*, 5105– 5107.

[15] J. M. Camara, R. A. Petros, J. R. Norton, *J. Am. Chem. Soc.* **2011**, *133*, 5263–5273.

[16] a) I. Haas, W. P. Kretschmer, R. Kempe, *Organometallics* **2011**, *30*, 4854–4861; b) K. Michiue, R. F. Jordan, *Organometallics* **2004**, *23*, 460–670; c) S. Murtuza, O. L. Casagrande Jr., R. F. Jordan, *Organometallics* **2002**, *21*, 1882–1890.

[17] For a review please see: R. Kempe, *Z. Anorg. Allg. Chem.* **2010**, *636*, 2135–2147.

[18] C. Döring, R. Kempe, *Eur. J. Inorg. Chem.* **2009**, *3*, 412–418.

[19] A. Noor, W. P. Kretschmer, G. Glatz, R. Kempe, *Inorg. Chem.* **2011**, *50*, 4598–4606.

[20] H. Muhammad, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2011**, *36*, 5512–5522.

[21] S. K. T. Pillai, W. P. Kretschmer, M. Trebbin, S. Förster, R. Kempe, *Chem. Eur. J.* **2012**, *18*, 13974–13978.

[22] C. Jones, *Coord. Chem. Rev.* **2010**, *254*, 1273–1289.

[23] a) J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219–300; b) F. T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403–481; c) N. Nagashima, H. Kondo, T. Hayashida, Y. Yamaguchi, M. Gondo, S. Masuda, K. Miyazaki, K. Matsubara, K. Kirchner, *Coord. Chem. Rev.* **2003**, *245*, 177–190.

[24] a) J.-A. Gautier, M. Miocque, C. C. Farnoux, *The synthesis of amidinates*, in: *The Chemistry of the amidines and imidates*, John Wiley & Sons, Hoboken, **1975**; b) R. T. Boeré, V. Klassen, G. Wolmerhäuser, *J. Chem. Soc., Dalton Trans.* **1998**, 4147–4154; c) D. Liguori, F. Grisi, I. Sessa, A. Zambelli, *Macromol. Chem. Phys.* **2003**, *204*, 164–170; d) X. Jiang, J. C. Bollinger, D. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 15678–15679; e) F.-S. Liu, H.-Y. Gao, K.-M. Song, Y. Zhao, J.-M. Long, L. Zhang, F.-M. Zhu, Q. Wu, *Polyhedron* **2009**, *28*, 673–678.

[25] D. Liguori, R. Cenroe, A. Tuzi, F. Grisi, I. Sessa, A. Zambelli, *Macromolecules* **2003**, *36*, 5451–5458.

[26] W. P. Kretschmer, B. Hessen, A. Noor, F. R. Wagner, R. Kempe, *J. Organomet. Chem.* **2007**, *692*, 4569–4579.

[27] E. Benzing, W. Kornicker, *Chem. Ber.* **1961**, *94*, 2263–2267.

[28] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[29] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found Crystallogr.* **2008**, *64*, 112–122.

[30] L. J. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

[31] M. Albrecht, Y. Song, *Synthesis* **2006**, *18*, 3037–3042.

4.7 Supporting Information

Table S1. Crystallographic data of the compounds investigated by single crystal X-ray structure analysis.

Compound	**2a**	**2b**	**2d**	**3b**
Formula	$C_{35}H_{51}Cl_4N_3Ti$	$C_{37}H_{56}Cl_4N_4Ti$	$C_{103}H_{140}Cl_8N_8Ti_2$	$C_{40}H_{61}Cl_2N_4Ti$
Formula weight	703.49	746.56	1869.63	716.73
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$\mathrm{P}\bar{1}$	$P2_1/n$
a [Å]	19.9830(6)	10.0600(4)	16.0290(7)	11.4880(5)
b [Å]	10.2220(3)	21.2840(8)	16.4230(7)	18.3580(7)
c [Å]	20.3180(6)	18.7930(7)	20.6920(9)	19.0270(7)
α [°]	90.00	90.00	101.305(3)	90.00
β [°]	118.117(2)	90.132(3)	97.266(4)	95.536(3)
γ [°]	90.00	90.00	102.186(3)	90.00
Cell volume [Å^3]	3660.49(19)	4023.9(3)	5140.3(4)	3994.0(3)
Z	4	4	2	4
Crystal size [mm^3]	0.34x0.21x0.11	0.32x0.21x0.17	0.58x0.25x0.17	0.62x0.28x0.17
Habit	block	block	plate	prism
Colour	red	red	red	red
Density [gcm^{-3}]	1.277	1.232	1.208	1.192
T [K]	133(2)	133(2)	133(2)	133(2)
Theta range	1.18–25.64	1.45–25.71	1.02–21.00	1.54–24.10
Unique reflections	6909	7594	10998	6328
Observed reflections [I > 2s(I)]	5887	5309	7915	4946
Parameters	406	427	1114	437
wR_2 (all data)	0.106	0.106	0.131	0.112
R [I > 2s(I)]	0.039	0.045	0.051	0.043

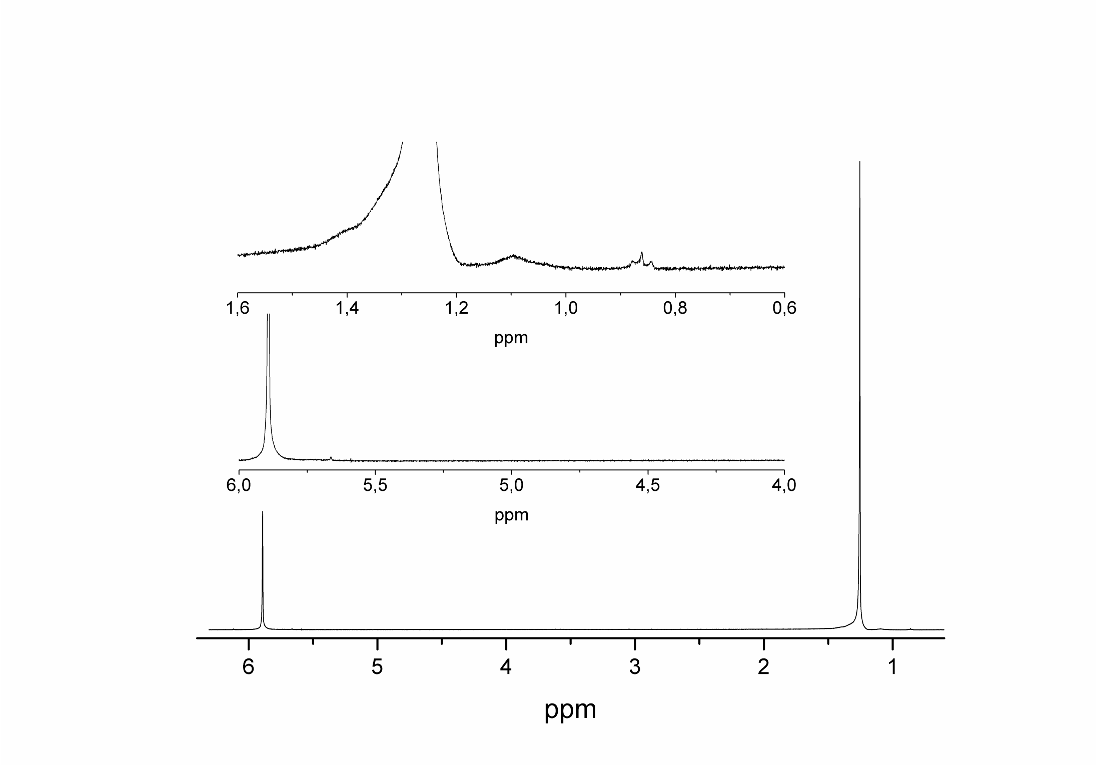


Figure S1.^{1}H NMR spectrum ($C_2Cl_4D_2$, 120°C) of PE obtained with **2b**/MAO catalyst system after acidic workup of the reaction solution.

5 Efficient Synthesis of Aluminium-Terminated Polyethylene by Means of Irreversible Coordinative Chain-Transfer Polymerisation Using a Guanidinatotitanium Catalyst

Johannes Obenauf,[a] Winfried P. Kretschmer,[a] and Rhett Kempe*[a]

[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany. Fax: +49-921-552-157 E-mail: kempe@uni-bayreuth.de Homepage: http://www.ac2.uni-bayreuth.de

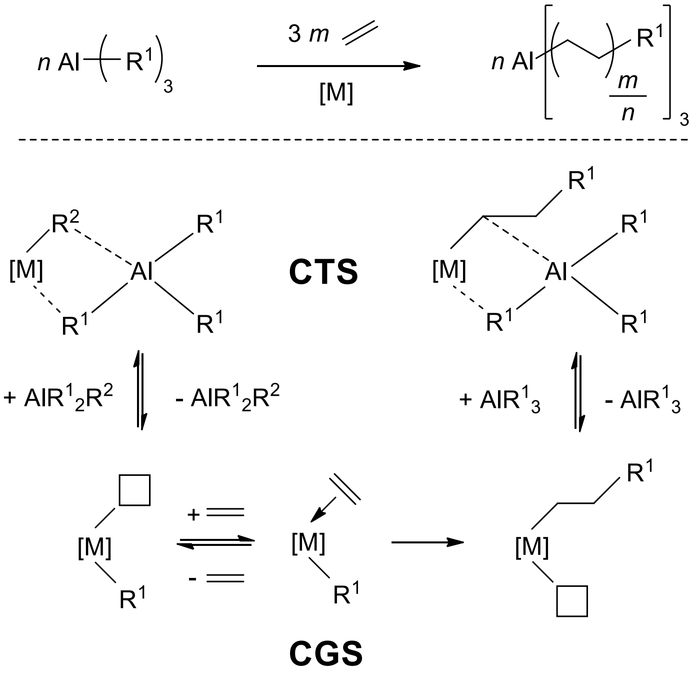
Published in: *Eur. J. Inorg. Chem.* **2014**, *9*, 1446–1453.

5.1 Abstract

A series of guanidinato-ligand-stabilised titanium complexes has been synthesised and characterised. These compounds can be prepared by carbodiimide insertion into titanium-amide bonds. Reaction of carbodiimides *N*,*N*'-bis(2,6-diisopropylphenyl)carbodiimide, *N*,*N*'-bis(2,6-dimethylphenyl)carbodiimide and *N*-*tert*-butyl-*N*'-(2,6-diisopropylphenyl)carbodiimide (**2a**–**2c**, respectively) with [$(Et_2N)TiCl_3$] led to mono(guanidinato)trichloridotitanium(IV) complexes (**3a**–**3c**). Subsequent conversion with methylmagnesium chloride gave the corresponding trimethyl complexes (**4a** and **4b**). Single-crystal X-ray diffraction analyses were carried out for all complexes. Compound **4a** showed very high activities in the polymerisation of ethylene in the presence of very high amounts of triethylaluminium and undergoes polymeryl chain transfer to aluminium. Irreversible coordinative chain-transfer polymerisation and a unique combination of catalyst economy and high activity were observed. In the presence of 1000 equivalents of aluminium, a chain elongation of 83.3% could be achieved with an activity of 9900 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$. The influence of the steric demand of the ligand on the polymerisation capability is significant and was investigated too.

5.2 Introduction

Polyethylene (PE) is the most important plastic worldwide. It is essential for our modern lifestyle because of its low cost and its broad applicability. Unfortunately, its compatibility with other important polymers or materials is limited owing to the rather apolar nature of PE. Compatibility agents that consist of a PE block and a block of another polymer or material could solve this problem. Furthermore, PE-based block copolymers themselves allow for nanostructuring by means of microphase separation and enable access to nanostructured PE materials and to novel applications of such materials.[1] Both approaches rely on an efficient synthesis of PE with an end group that allows the easy introduction of further polymer blocks. Coordinative chain transfer polymerisation (CCTP) is a polymerisation protocol that produces metal-terminated PE that can easily be converted into PE that carries such reactive end groups (Scheme 1).[2–4]



Scheme 1. Net reaction and mechanism of CCTP involving aluminium alkyls. 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; *n*, *m* = natural numbers.

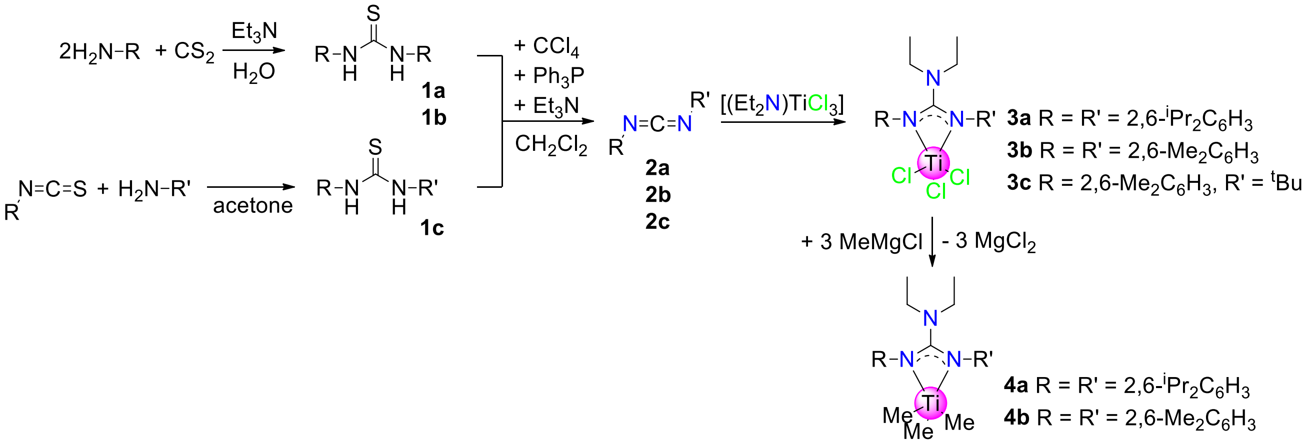
Pioneering work that involved well-defined molecular polymerisation catalysts was reported by Eisenberg and Samsel[5,6] as well as Mortreux and co-workers. Meanwhile, ethylene CCTP catalyst systems that use rare earth metals (RE) and transition metals (TM) in combination with different chain-transfer agents (CTA) such as Mg-,[7–12] Zn-,[13–25] and Al-[5,6,26–39] alkyls, have been developed. Mechanistic studies have been carried out by the groups of Bochman[40,41] and Norton.[42,43] The kinetics of chain growth at Al have been studied when catalysed by a Zr complex. The reaction is first order in [olefin] and [catalyst] and of inverse first order in [AlR_3] (R = PE polymeric chain).[42] This inverse first-order dependence results in a rather low catalyst economy of the catalyst systems reported so far. It prohibits the use of high CTA/catalyst ratios because high amounts of CTA result in a poor overall polymerisation activity. The catalyst is essentially transferring polymeryl chains but is no longer able to grow chains.

Recently, we communicated a guanidinatotitanium catalyst (**3a**) that showed very high activity in the presence of very high amounts of CTA (triethylaluminium).[37] The catalyst system seemed to be able to mediate chain growth and chain transfer in a parallel fashion. Unfortunately, the chain transfer was not highly reversible. In such a regime, multiple insertions might also compensate efficiency loss caused by high CTA/catalyst ratios.[44,45] Herein, we report in more detail on such guanidinatotitanium catalysts. In particular, we discuss structural features that enable high catalyst economy and address the issue of transfer efficiency. As a result, a cheap metal catalyst system (Ti–Al) is provided that efficiently allows the production of end-group-functionalised PE.

5.3 Results and Discussion

Ligand and Complex Synthesis

Guanidinato-trichloridotitanium(IV) complexes are generally accessible through carbodiimide insertion into titanium–amide bonds (Scheme 2).[37] The required carbodiimides are accessible by desulfurisation of *N*,*N*'-substituted thioureas with a three-component system of PPh_3, CCl_4 and triethylamine[46] and subsequent fractional crystallisation from ethanol. Symmetric thioureas **1a** and **1b** are accessible from the reaction of two equivalents of aniline and carbon disulfide in the presence of two equivalents of triethylamine in water.[47] After recrystallisation from dichloromethane, the resulting thioureas can be obtained in high yields. Nonsymmetric thioureas can be synthesised from the reaction of isothiocyanates with the corresponding aniline in acetone solution.[48] After removal of Ph_3PS (crystallisation from ethanol), **2c** can be obtained by distillation as a colourless oil. The synthesis of the guanidinatotitanium(IV) complexes **3a**–**3c** (Scheme 2) were performed by the reaction of equimolar amounts of the corresponding carbodiimides and diethylamido trichloridotitanium(IV) in toluene. They were obtained in high yields. Guanidinatotitanium(IV) alkyl complexes can be synthesised by means of a salt-elimination reaction. Treatment of the trichlorido complexes with three equivalents of an appropriate Grignard reagent (methylmagnesium chloride; Scheme 2) led to the trialkyl complexes **4a** and **4b**. After two hours of reaction time, the solvent was removed and the residue was extracted with hexane. Bright yellow crystals could be obtained from a concentrated hexane solution at −30 °C. All complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy along with elemental analysis. The molecular structures of the complexes were confirmed by single-crystal structure analysis.



Scheme 2. Synthesis of symmetric and nonsymmetric guanidinatotitanium(IV) complexes **3a**–**4b**.

Structural Investigations

The molecular structures of **3b**, **3c**, **4a** and **4b** are presented in Figures 1, (**4a**) 2 (**3b** and **4b**) and 3 (**3c**). Selected bond lengths and angles are listed in Table 1. Crystallographic details are available in the Supporting Information (Table S1). The structure analysis revealed mono(guanidinato)titanium(IV) complexes, as expected. For all compounds a distorted trigonal-bipyramidal coordination of the titanium atoms was observed. The metal atom is coordinated by two nitrogen atoms and three chlorine or carbon atoms. The Ti–N bond lengths of the chlorido complexes are about 2.01 Å and become significantly extended (to about 2.09 Å) for the methyl compounds. The exchange of the chlorido by the methyl ligands also results in a reduction of the N1–Ti1–N2 bond angle from 65.41° (**3b**) and 65.68° (**3c**) to 62.70° (**4a**) and 62.96° (**4b**). The sum of bond angles around N3 and C1 is approximately 360° and confirms sp2-hybridised nitrogen and carbon atoms. It indicates the participation of the lone pair of the non-coordinating nitrogen atom in the π system of the ligand, which can increase the electron density at the titanium metal to result in stronger bonding of the ligand.

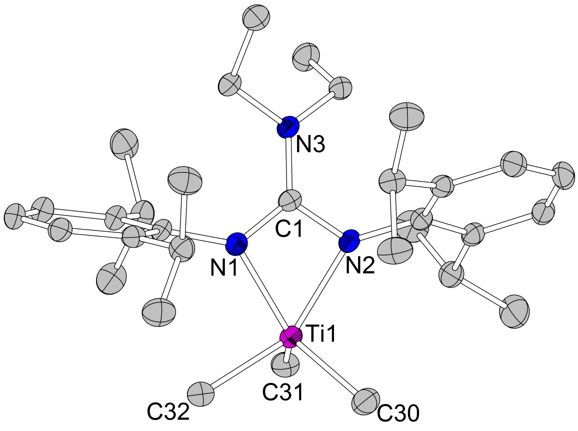


Figure 1. Molecular structure of **4a**. Hydrogen atoms are omitted for clarity. Ellipsoids are at 30% probability level.

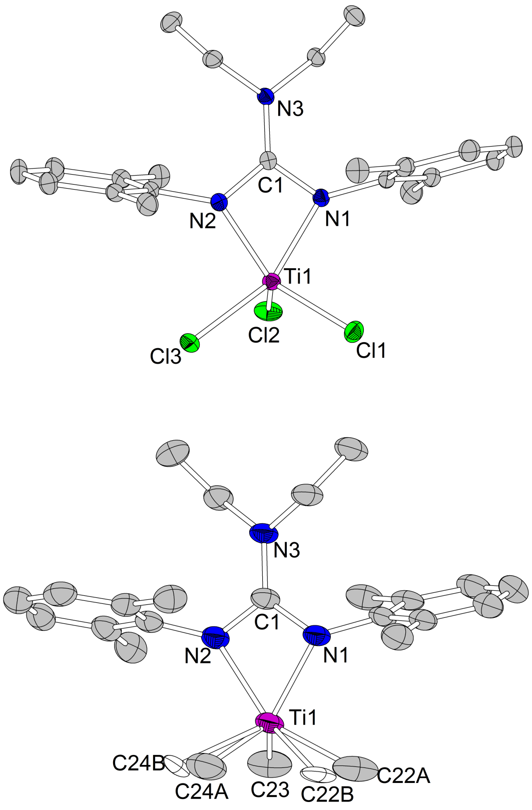


Figure 2. Molecular structures of **3b** (top) and **4b** (bottom). Hydrogen atoms are omitted for clarity. Ellipsoids are at 30 % probability level. The carbon atoms C22 and C24 are disordered (C22A/C22B and C24A/C24B; 88/12%).

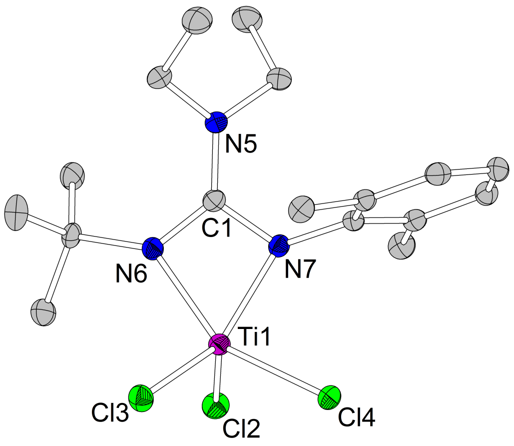


Figure 3. Molecular structure of **3c**. Hydrogen atoms are omitted for clarity. Ellipsoids are at 30% probability level.

Table 1. Selected bond lengths [Å] and bond angles [°] for complexes **3a**,[37] **3b**, **3c**, **4a** and **4b**.

	3a	3b	3c	4a	4b
Ti1–N1	2.015(3)	2.0174(14)	1.9979(12)	2.1082(19)	2.087(4)
Ti1–N2	2.027(4)	2.0115(14)	2.0214(13)	2.0895(19)	2.112(4)
Ti1–Cl (avg.)	2.2385	2.2410	2.2524	–	–
Ti1–C_{methyl} (avg.)	–	–	–	2.080	2.041
C1–N1	1.368(6)	1.366(2)	1.3450(19)	1.329(3)	1.341(6)
C1–N2	1.356(5)	1.358(2)	1.3674(19)	1.367(3)	1.350(6)
C1–N3	1.352(5)	1.326(2)	1.3473(18)	1.367(3)	1.355(6)
N1–Ti1–N2	65.11(14)	65.41(6)	65.68(5)	62.70(7)	62.96(15)
N1–C1–N2	106.0(3)	106.10(14)	106.95(12)	108.22(18)	109.2(4)
∑<(C1)	359.9	359.99	359.98	359.97	360.00
∑<(N3)	359.5	360.00	359.88	359.71	360.00

Ethylene Polymerisation

We recently developed a titanium-based catalyst system stabilised by bulky guanidinato ligands, which is highly efficient in CCTP.[37] We pointed out that the variation of the substituents at the non-coordinating nitrogen atom has only a marginal influence on the catalytic performance. As a result, we became interested in the variation of the steric bulk of the ligand at the coordinating N atoms and the exchange of the chlorido ligands with alkyls to drastically reduce the catalyst induction period. Initial polymerisation studies (Table 2) showed that significantly higher activities could be achieved by replacing chlorido ligands with methyl ligands. Activities of up to 12000 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ in the presence of 25000 equivalents of aluminium were obtained at 50 °C and 2 bar ethylene pressure. The resulting PE showed a molecular weight of 2550 $gmol^{-1}$ and a molecular-weight distribution of 1.9 (Table 2, entry 4). High-temperature ^1H NMR spectroscopic experiments are indicative of polymeryl chain transfer to aluminium owing to the absence of olefinic resonances after hydrolytic workup of the resulting polymers (Figure S1 in the Supporting Information). Furthermore, the activity increases significantly as the Al/Ti ratio increases. It appears that the fraction of elongated chains significantly decreased as the aluminium amount increased from 42 % at 250 equiv. to 1.6 % at 25000 equiv. (under the given conditions). The percentage of elongated chains expresses how many of the ethyl groups of the CTA triethylaluminium were extended/elongated in the polymerisation process. It is a crucial number and should be as high as possible to avoid unused triethylaluminium in the CCTP.

Table 2. Initial polymerisation studies investigating the chain-extension efficiency of complex **4a**. Conditions: p = 2 bar, T = 50 °C, t = 15 min, toluene 150 mL, activator ammonium borate {$[R_2N(CH_3)H][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$), Ti/B = 1:1.1} and triethylaluminium.

Entry	**4a** [µmol]	Al:Ti	Activity[a]	M_n [$gmol^{-1}$]	M_w/M_n	N_{exp}/N_{theo}[b] [%]
1	2	250	1900	3000	2.2	42.0
2	0.2	5000	7000	2400	1.8	9.8
3	0.2	10000	13000	2450	2.1	8.9
4	0.1	25000	12000	2550	1.9	1.6

[a] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]. [b] $N_{exp.}$: experimental chain number [yield PE (in g)/M_n]; $N_{theo.}$: theoretical chain number, assuming three growing chains per Al atom.

The reduction of the steric bulk of the guanidinato ligand from 2,6-diisopropylphenyl to 2,6-dimethylphenyl substituents led to a significant decrease in the activity, especially when high amounts of triethylaluminium were used (Table 3, entries 5–8). A lower steric protection of the guanidinato ligand allows an easier transfer of the ligand towards aluminium.[36] It becomes especially relevant at high Al concentrations. Compound **3b** is almost inactive with 10000 equivalents of aluminium. The use of the corresponding trimethyl compound **4b** could increase the activity (Table 3, entries 9 and 10) but on a significantly lower level relative to **4a**. In both cases, the methyl compounds are more active than the chlorido complexes. The use of the chlorido complexes goes along with a long induction period as can be seen from the ethylene consumption profiles. Within the induction periods, ligand transfer to Al can be especially relevant, because the cation, which binds the N ligand more strongly, is not yet formed.[32,33] Hence, the methyl complexes show more activity since more of the catalytically active species are generated. The nonsymmetric guanidinatotitanium(IV) complex **3c** showed almost no activity in the polymerisation of ethylene under the same conditions. Ligand transfer to aluminium proceeds so fast that no further active catalyst can be formed. Reduction to Ti^{III} species indicated by colour changes was not observed during the activation of any of the catalysts.

Table 3. Polymerisation studies comparing complexes **3b** and **4b**. Conditions: Precatalyst 2 µmol, p = 2 bar, T = 50 °C, t = 15 min, toluene 150 mL, activator ammonium borate {$[R_2N(CH_3)H][B(C_6F_5)_4]$ ($R = C_{16}H_{33}$–$C_{18}H_{37}$), Ti/B = 1:1.1} and triethylaluminium.

Entry	Precat [µmol]	Al:Ti	Activity[a]	M_n [$gmol^{-1}$]	M_w/M_n	N_{exp}/N_{theo}[b] [%]
5	**3b**	100	500	6000	2.0	
6	**3b**	500	450	2200	2.0	
7	**3b**	1000	360	1700	1.5	
8	**3b**[c]	10000	traces	n.d.	n.d.	n.d.
9	**4b**	500	920	2200	1.6	
10	**4b**	1000	900	1800	1.6	

[a] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]. [b] $N_{exp.}$: experimental chain number [yield PE (in g)/M_n]; $N_{theo.}$: theoretical chain number, assuming three growing chains per Al atom. [c] 0.2 µmol.

Owing to the relevance of steric protection and the higher activity of the methyl complexes, we focused on **4a** in further studies. By increasing the ethylene pressure from 2 to 5 bar, the molecular weight of the polymer was more than doubled from 2450 to 5800 gmol^{-1} in the presence of 10000 equivalents of triethylaluminium (Table 4, entry 12). The polydispersity slightly increased from 2.1 (Table 2, entry 3) to 2.6 (Table 4, entry 12). In all polymerisation experiments at 50 °C a precipitation of the polymer could be observed whereby the reaction solution became turbid after a short period of time. To achieve an increased solubility of the resulting aluminium-terminated polyethylene, the temperature of the experiments was increased from 50 to 80 °C. This resulted in a clear reaction solution over the entire reaction time. The number of elongated chains could be increased from 31.6 up to 51.7 % in the presence of 1000 equivalents of aluminium (Table 4, entry 13) owing to an increase in activity. In the presence of 10000 equiv., the reaction solution still became slightly turbid after longer reaction times (90 min).

Table 4. Variation of the polymerisation conditions by increasing the ethylene pressure using complex **4a**. Conditions: p = 5 bar, T = 50 °C, t = 15 min, toluene 150 mL, activator ammonium borate {$[R_2N(CH_3)H][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$-$C_{18}H_{37}$), Ti/B = 1:1.1} and triethylaluminium.

Entry	4a [µmol]	Al:Ti	Activity[b]	M_n [gmol^{-1}]	M_w/M_n	N_{exp}/N_{theo}[c] [%]
11	2	1000	3800	2000	1.9	31.6
12	0.2	10000	7600	5800	2.6	5.5
13	2[a]	1000	4520	3700	2.0	51.7
14	0.2[a]	10000	13200	4100	2.2	13.4

[a] T = 80 °C. [b] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]. [c] $N_{exp.}$: experimental chain number [yield PE (in g)/M_n]; $N_{theo.}$: theoretical chain number, assuming three growing chains per Al atom.

To gain more insight into the nature of the chain-transfer process, time-dependent experiments were performed in the presence of 10000 and 5000 equivalents of triethylaluminium [80 °C and 5 bar ethylene pressure (Table 5)]. Reversible chain transfer is indicated by an increase in the molecular weight of the polymer over time. Irreversible chain transfer would lead to more polymer of the same molecular weight. In the case of both 10000 and 5000 equivalents of triethylaluminium, a significant decrease in the activity was observed with increased reaction time and the system almost became inactive after 90 min. The molecular weight remained more or less constant and the number of elongated chains increased over time. A slight increase of the molecular weight distribution was obtained, likely on account of the increased viscosity of the reaction solution and the corresponding deterioration of ethylene diffusion. An experiment with a constant amount of triethylaluminium and varied catalyst concentrations showed that for an Al/Ti ratio of 500 a chain-elongation percentage of 73.5% was achieved (Table 6, entry 25). It seems that the maximum percentage of elongated chains lies between 70 and 80%.

Table 5. Time-dependent polymerisation experiments using complex **4a**. Conditions: Precatalyst 0.1 µmol (entries 15–18), 0.2 µmol (entries 19 and 22), p = 5 bar, T = 80 °C, toluene 150 mL, activator ammonium borate: $[R_2N(CH_3)H][B(C_6F_5)_4]$ ($R = C_{16}H_{33}$–$C_{18}H_{37}$), Ti/B = 1:1.1, triethylaluminium = 1 mmol.

Entry	t [min]	Al:Ti	Activity[a]	M_n [gmol^{-1}]	M_w/M_n	N_{exp}/N_{theo}[b] [%]
15	15	10000	15400	6400	1.9	10.1
16	30	10000	12100	6400	1.9	15.7
17	60	10000	8200	7000	1.9	19.4
18	90	10000	5600	5500	2.2	25.4
19	15	5000	15200	6900	1.9	18.5
20	30	5000	10600	6800	1.9	26.0
21	60	5000	5600	7500	2.1	25.0
22	90	5000	4200	7000	2.5	30.1

[a][$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]. [b]$N_{exp.}$: experimental chain number [yield PE (in g)/M_n]; $N_{theo.}$: theoretical chain number, assuming three growing chains per Al atom.

Table 6. Polymerisation experiments using several concentrations of complex **4a** with a constant amount of triethylaluminium. Conditions: *p* = 5 bar, *T* = 80 °C, *t* = 15 min, toluene 150 mL, activator ammonium borate {$[R_2N(CH_3)H][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$), Ti/B = 1:1.1} and triethylaluminium (0.54 mL, 25 wt.-% in toluene).

Entry	**4a** [µmol]	Al:Ti	Activity[a]	M_n [gmol^{-1}]	M_w/M_n	N_{exp}/N_{theo}[b] [%]
23	0.2	5000	27200	7200	2.1	31.7
24	0.8	1250	17700	8900	2.1	66.7
25	2.0	500	8600	9700	2.2	73.5

[a] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]. [b] $N_{exp.}$: experimental chain number [yield PE (in g)/M_n]; $N_{theo.}$: theoretical chain number, assuming three growing chains per Al atom.

Finally, we became interested in the question of what happens after the maximum chain elongation is reached (Table 7). A CTA/catalyst ratio of 1000 was used for this investigation. A maximum of 83.3% for the elongated chains was achieved after 30 min. After 30 min and at lower percentage of elongated chains, the catalyst was still active and chains were still elongated/extended. After the maximum chain elongation was reached, a significant decrease in the activity was observed. In addition, the formation of a high-molecular-weight polymer fraction could be observed (Figure 4).

Table 7. Time-dependent polymerisation experiments using complex **4a**. Conditions: precatalyst 1.0 µmol, *p* = 5 bar, *T* = 80 °C, toluene 150 mL, activator ammonium borate: $[R_2N(CH_3)H][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$), Ti/B = 1:1.1, triethylaluminium: 1 mmol (Al/Ti = 1000:1).

Entry	t [min]	Activity[a]	M_n [gmol^{-1}]	M_w/M_n	N_{exp}/N_{theo}[b] [%]
26	30	9900	9800	2.4	83.3
27	60	4000	11200	5.5	58.5
28	90	3200	10600	3.9	75.0
29	120	2300	11700	5.8	65.5

[a][$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]. [b]$N_{exp.}$: experimental chain number [yield PE (in g)/M_n]; $N_{theo.}$: theoretical chain number, assuming three growing chains per Al atom.

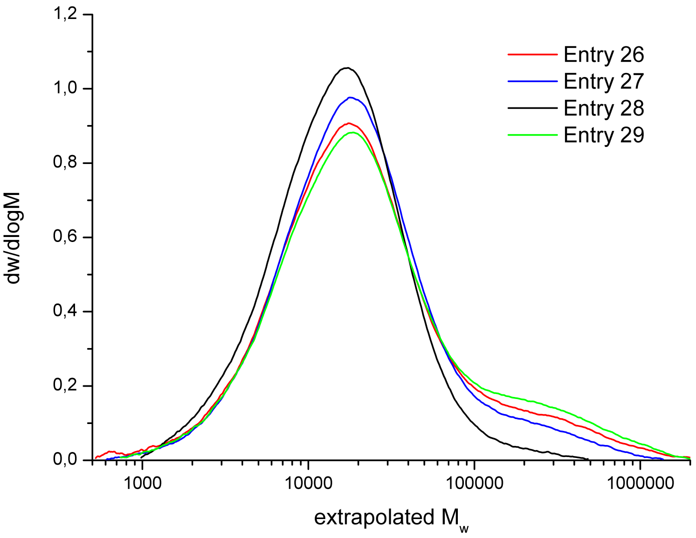


Figure 4. Molecular-weight distribution plot of polymerisation experiments described in Table 7.

A comparison of **4a** with other CCTP catalysts in terms of catalyst economy, activity and percentage of extended chains is difficult but possible. There are not many examples with CTA catalyst ratios of 1000 (and higher). Recently we reported a very good catalyst system in terms of high CTA/catalyst ratio and high activity, as well as irreversible CCTP.[30] There, we observed 5200 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ for a CTA/catalyst ratio of 10000. Unfortunately, the chain elongation for such runs is only very low: 3%. One can push the chain elongation to 66% but only with a CTA/ catalyst ratio of 100 (activity at 5600 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$). With the irreversible CCTP catalyst system described here, we observed (with a CTA-to-catalyst ratio of 10000 and with a chain elongation of 10%) an activity of 77000 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$. Under maximum chain elongation conditions, we observed an activity of 50000 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ at a CTA/catalyst ratio of 1000. Mortreux and co-workers have published the best reversible system (and the only one that was explored at high CTA/catalyst ratios).[7,12] It shows an activity of 40 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ with a CTA/catalyst ratio of 1000 and a chain elongation of 100 %.

5.4 Conclusion

Trichlorido-guanidinatotitanium(IV) complexes are accessible through carbodiimide insertion into titanium–amide bonds. Alkylation of these trichlorido complexes with methylmagnesium chloride selectively leads to the corresponding trimethyl complexes in high yields. These complexes are suitable precatalysts for the polymerisation of ethylene in the presence of high aluminium alkyl amounts if sterically demanding guanidinato ligands are used. Reduction of the steric demand of the ligands results in a significant decrease in the activity. The absence of olefinic resonances in the high-temperature NMR spectra of the resulting polymers after hydrolytic workup indicates chain transfer to aluminium. We observed no increase in the molecular weight over time but did note an increase in the number of elongated chains over time. These observations indicate irreversible coordinative chain-transfer polymerisation. A quantity of elongated chains of up to 83.3% in the presence of 1000 equivalents of aluminium could be achieved with an activity of 9900 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$. With increasing reaction time (>30 min) at such high Al/catalyst ratios, no continuous increase in elongated chains was observed but rather a decomposition of the catalyst towards a species that produces high-molecular-weight PE. The catalyst system discussed here is ideally suited to produce Al-terminated high-density PE with a unique combination of high activity and high catalyst economy.

5.5 Experimental Section

General: All manipulations and reactions were carried out under dry argon or nitrogen using standard Schlenk and glovebox techniques. Solvents were purified by distillation from potassium, Na/K alloy or sodium ketyl of benzophenone under argon immediately before use. Toluene used for ethylene polymerisation (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3–11-supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over BASF R3-11-supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). *N*,*N*'-Bis(2,6-dimethylphenyl)thiourea (**1b**),[47] *N*-*tert*-butyl-*N*'-(2,6-dimethylphenyl)thiourea (**1c**),[48] *N*,*N*'-bis(2,6-dimethylphenyl)carbodiimide (**2b**), *N*-*tert*-butyl-*N*'-(2,6-diisopropylphenyl)carbodiimide (**2c**),[46] *N*',*N*''-bis(2,6-diisopropylphenyl)-*N*,*N*-diethylguanidinatotrichloridotitanium(IV) (**3a**)[37] and $[(Et_2N)TiCl_3]$[49] were prepared according to the published procedures. Commercial *n*-butyllithium (2.5 M in *n*-hexane), methylmagnesium chloride (3.0 M in thf) (Aldrich), *N*,*N*'-bis(2,6-diisopropylphenyl)carbodiimide (**2a**), triethylaluminium (TEA, 25 wt.-% in toluene, Aldrich), $[R_2N(CH_3)H][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–

$C_{18}H_{37}$), 6.2 wt.-% $B(C_6F_5)_4^-$ in Isopar (Dow Chemicals) and all other chemicals were used as received without further purification.

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

NMR Spectroscopy: NMR spectra were recorded with 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 by using the residual solvent resonances. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. Chemical shifts (δ) are reported in ppm.

Gel Permeation Chromatography (GPC): Gel permeation chromatography analysis was carried out with a PL-GPC 220 (Agilent, Polymer Laboratories) high-temperature chromatographic unit equipped with differential pressure (DP) and refractive index (RI) detectors and three linear mixed-bed columns (Olexis, 13-micron particle size). GPC analyses were performed at 150 °C and with 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.05 wt.-%, c = 1 mgmL^{-1}) 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 linear PE (M_w = 520–3200000 gmol^{-1}) as standard. 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 [λ(Mo-K_α) = 0.71073 Å] equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished with SIR97,[50] SHELXL-97[51] and WinGX.[52]

CCDC-973107 (for **3b**), -973108 (for **3c**), -973106 (for **4a**) and -973109 (for **4b**) 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.

Ethylene Polymerisation: The polymerisation experiments were carried out in a 300 mL glass autoclave (Büchi) with ethylene flow display equipped with external heating (water bath) at constant ethylene pressure. The autoclave was evacuated and purged with ethylene. Toluene (150 mL) was added into the autoclave and saturated with ethylene. The stock solutions of precatalyst and co-catalyst were prepared in a glovebox. After addition of the co-catalyst and complete saturation with ethylene, the precatalyst was added. To stop the polymerisation, the reactor was vented and acidified ethanol was added. The obtained polymers were filtered, washed with ethanol and dried at 60 °C.

Synthesis of Complex 4a: Methylmagnesium chloride (1.1 mL, 3.27 mmol) was added dropwise at –78 °C to a solution of *N*',*N*''-bis(2,6-diisopropylphenyl)-*N*,*N*-diethylguanidinatotrichloridotitanium(IV) **3a** (0.506 g, 0.86 mmol) in toluene (30 mL), thereby resulting in a colour change of the solution from red to yellow. The solution was warmed to room temperature and stirred for an additional 2 h. Toluene was removed under reduced pressure and the residue was extracted with *n*-hexane (30 mL) and filtered. Storage of the concentrated filtrate at –20 °C led to bright yellow crystals. Yield 0.45 g (89 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.33 [t, *J* = 7.1 Hz, 6 H, $N(CH_2CH_3)_2$]; 1.25 [d, *J* = 6.9Hz, 12 H, $CH(CH_3)_2$]; 1.35 [d, *J* = 6.7 Hz, 12 H, $CH(CH_3)_2$]; 1.87 [s, 9 H, $Ti(CH_3)_3$]; 2.77 [q, *J* = 7.8Hz, 4 H, $N(CH_2CH_3)_2$]; 3.67 [sept, *J* = 6.8 Hz, 4 H, $CH(CH_3)_2$]; 7.10 (s, 6 H, Ar*H*) ppm. 13C NMR (75.4 MHz, C_6D_6): δ = 11.6 [$N(CH_2CH_3)_2$]; 24.4 [$CH(CH_3)_2$]; 25.9 [$CH(CH_3)_2$]; 28.4 [$CH(CH_3)_2$]; 40.9 [$N(CH_2CH_3)_2$]; 72.4 [$Ti(CH_3)_3$]; 124.4, 125.6, 143.5, 143.9 (ArC); 169.9 (NCN) ppm. $C_{35}H_{53}N_3Ti$ (527.65): calcd. C 72.84, H 10.12, N 7.96; found C 72.41, H 10.86, N 8.08.

Synthesis of Complex 3b: Compound **2b** (197 mg, 0.787 mmol) and [$(Et_2N)TiCl_3$] (206 mg, 0.787 mmol) were dissolved in toluene (40 mL) and stirred overnight. Dark red crystals could be obtained by layering a concentrated toluene solution with *n*-hexane. Yield 341 mg (85 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.18 [t, *J* = 7.2 Hz, 6 H, $N(CH_2CH_3)_2$]; 2.35 [q, *J* = 7.2 Hz, 4 H, $N(CH_2CH_3)_2$]; 2.43 (s, 12 H, $ArCH_3$); 6.85–7.00 (m, 6 H, Ar*H*) ppm. ^{13}C NMR (75.4 MHz, C_6D_6): δ = 11.7 [$N(CH_2CH_3)_2$]; 19.6 ($ArCH_3$);

41.6 [$N(CH_2CH_3)_2$]; 127.3, 129.3, 132.8, 147.1 (ArC) 167.0 (NCN) ppm. $C_{21}H_{28}Cl_3N_3Ti$ (476.69): calcd. C 52.91, H 5.92, N 8.81; found C 52.77, H 6.00, N 8.88.

Synthesis of Complex 4b: Compound **4b** was prepared similarly to **4a** by using **3b** (500 mg, 1.05 mmol) and MeMgCl (1.05 mL, 3.15 mmol). Yield 390 mg (78 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.30 [t, *J* = 7.2 Hz, 6 H, $N(CH_2CH_3)_2$]; 1.72 [s, *J* = 7.2 Hz, 6 H, $Ti(CH_3)_3$], 2.35 (s, 12 H, $ArCH_3$), 6.80–7.10 (m, 6 H, Ar*H*) ppm. ^{13}C NMR (75.4 MHz, C_6D_6): δ = 11.7 [$N(CH_2CH_3)_2$]; 19.3 ($ArCH_3$), 40.4 [$N(CH_2CH_3)_2$]; 71.8 [$Ti(CH_3)_3$], 124.5, 129.0, 132.9, 146.3 (ArC), 169.9 (NCN) ppm. $C_{24}H_{37}N_3Ti$ (415.44): calcd. C 69.39, H 8.98, N 10.11; found C 68.94, H 9.17, N 10.11.

Synthesis of Complex 3c: Compound **2c** (456 mg, 2.25 mmol) and [$(Et_2N)TiCl_3$] (510 mg, 2.25 mmol) were dissolved in toluene and stirred overnight, whereby a crystalline solid precipitated. Dark red crystals suitable for single-crystal analysis could be obtained from a concentrated chloroform solution at room temperature. Yield 850 mg (88 %). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.03 [t, *J* = 7.1 Hz, 6 H, $N(CH_2CH_3)_2$]; 1.70 [s, 9 H, $C(CH_3)_3$]; 2.30 (s, 6 H, $ArCH_3$); 3.00 [q, *J* = 7.2 Hz, 4 H, $N(CH_2CH_3)_2$]; 7.06 (s, 3 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 12.8 [$N(CH_2CH_3)_2$]; 19.7 ($ArCH_3$), 31.5 [$C(CH_3)_3$]; 43.5 [$N(CH_2CH_3)_2$]; 59.0 [$C(CH_3)_3$] 127.3, 129.0, 132.5, 152.0 (ArC), 170.3 (NCN) ppm. $C_{17}H_{28}Cl_3N_3Ti$ (428.65): calcd. C 47.63, H 6.58, N 9.80; found C 47.57, H 6.43, N 9.76.

Supporting Information (see footnote on the first page of this article): Crystallographic details and high-temperature 1H NMR spectrum of the obtained PE.

Acknowledgments

This work was supported by NANOCAT, international graduateprogram within the Elitenetzwerk Bayern, and by SASOL Germany GmbH.

5.6 References

[1] F. S. Bates, M. a. Hillmyer, T. P. Lodge, C. M. Bates, K. T. Delaney, G. H. Fredrickson, *Science* **2012**, *336*, 434–440.

[2] R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764–2773.

[3] L. R. Sita, *Angew. Chem. Int. Ed.* **2009**, *48*, 2464–2472; *Angew. Chem.* **2009**, *121*, 2500–2508.

[4] A. Valente, A. Mortreux, M. Visseaux, P. Zinck, *Chem. Rev.* **2013**, *113*, 3836–3857.

[5] E. Samsel, *EP 0539876*, **1992**.

[6] E. Samsel, D. Eisenberg, *EP 0574854*, **1993**.

[7] T. Chenal, X. Olonde, J.-F. Pelletier, K. Bujadoux, A. Mortreux, *Polymer* **2007**, *48*, 1844–1856.

[8] W. Kaminsky, Ed. **1999**, DOI: 10.1007/978-3-642-60178-1.

[9] X. Olonde, A. Mortreux, F. Petit, K. Bujadoux, *J. Mol. Catal.* **1993**, *82*, 75–82.

[10] J.-F. Pelletier, K. Bujadoux, X. Olonde, E. Adisson, A. Mortreux, T. Chenal, *US 5779942*, **1995**.

[11] J. F. Pelletier, A. Mortreux, F. Petit, X. Olonde, K. Bujadoux, *Catalyst Design for Tailor-Made Polyolefins. Studies in Surface Science and Catalysis*, vol. 89 (Eds.: K. Soga, M. Terano), Kodansha and Elsevier, Tokyo and Amsterdam, **1994**.

[12] J.-F. Pelletier, A. Mortreux, X. Olonde, K. Bujadoux, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1854–1856; *Angew. Chem.* **1996**, *108*, 1980–1982.

[13] D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* **2006**, *312*, 714–719.

[14] G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, P. J. Maddox, M. van Meurs, *Angew. Chem. Int. Ed.* **2002**, *41*, 489–491; *Angew. Chem.* **2002**, *114*, 507–509.

[15] G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, M. Van Meurs, *J. Am. Chem. Soc.* **2004**, *126*, 10701–10712.

[16] F. Deplace, Z. Wang, N. a. Lynd, A. Hotta, J. M. Rose, P. D. Hustad, J. Tian, H. Ohtaki, G. W. Coates, F. Shimizu, K. Hirokane, F. Yamada, Y.-W. Shin, L. Rong, J.

Zhu, S. Toki, B. S. Hsiao, G. H. Frederickson, E. J. Kramer, *J. Polym. Sci., Part B Polym. Phys.* **2010**, *48*, 1428–1437.

[17] A. Hotta, E. Cochran, J. Ruokolainen, V. Khanna, G. H. Fredrickson, E. J. Kramer, Y.-W. Shin, F. Shimizu, A. E. Cherian, P. D. Hustad, J. M. Rose, G. W. Coates, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15327–32.

[18] P. D. Hustad, R. L. Kuhlman, E. M. Carnahan, T. T. Wenzel, D. J. Arriola, *Macromolecules* **2008**, *41*, 4081–4089.

[19] P. D. Hustad, R. L. Kuhlman, D. J. Arriola, E. M. Carnahan, T. T. Wenzel, *Macromolecules* **2007**, *40*, 7061–7064.

[20] P. D. Hustad, G. R. Marchand, E. I. Garcia-Meitin, P. L. Roberts, J. D. Weinhold, *Macromolecules* **2009**, *42*, 3788–3794.

[21] H. Kaneyoshi, Y. Inoue, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 5425–5435.

[22] S. Li, R. A. Register, B. G. Landes, P. D. Hustad, J. D. Weinhold, *Macromolecules* **2010**, *43*, 4761–4770.

[23] J. O. Ring, R. Thomann, R. Mülhaupt, J.-M. Raquez, P. Degée, P. Dubois, *Macromol. Chem. Phys.* **2007**, *208*, 896–902.

[24] M. van Meurs, G. J. P. Britovsek, V. C. Gibson, S. A. Cohen, *J. Am. Chem. Soc.* **2005**, *127*, 9913–9923.

[25] W. Zhang, J. Wei, L. R. Sita, *Macromolecules* **2008**, *41*, 7829–7833.

[26] G. C. Bazan, J. S. Rogers, C. C. Fang, *Organometallics* **2001**, *20*, 2059–2064.

[27] C. Boisson, V. Monteil, D. Ribour, R. Spitz, F. Barbotin, *Macromol. Chem. Phys.* **2003**, *204*, 1747–1754.

[28] C. Döring, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2010**, *18*, 2853–2860.

[29] M. Ganesan, F. P. Gabbaï, *J. Organomet. Chem.* **2005**, *690*, 5145–5149.

[30] I. Haas, W. P. Kretschmer, R. Kempe, *Organometallics* **2011**, *30*, 4854–4861.

[31] C. J. Han, M. S. Lee, D.-J. Byun, S. Y. Kim, *Macromolecules* **2002**, *35*, 8923–8925.

[32] W. P. Kretschmer, T. Bauer, B. Hessen, R. Kempe, *Dalton Trans.* **2010**, *39*, 6847–6852.

[33] W. P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, *Chem. Eur. J.* **2006**, *12*, 8969–8978.

[34] R. L. Kuhlman, T. T. Wenzel, *Macromolecules* **2008**, *41*, 4090–4094.

[35] G. Mani, F. P. Gabbaï, *Angew. Chem. Int. Ed.* **2004**, 43, 2263–2266; *Angew. Chem.* **2004**, *116*, 2313–2316.

[36] J. Obenauf, W. P. Kretschmer, T. Bauer, R. Kempe, *Eur. J. Inorg. Chem.* **2013**, 537–544.

[37] S. K. T. Pillai, W. P. Kretschmer, M. Trebbin, S. Förster, R. Kempe, *Chem. Eur. J.* **2012**, *18*, 13974–13978.

[38] J. S. Rogers, G. C. Bazan, *Chem. Commun.* **2000**, *2*, 1209–1210.

[39] F. Rouholahnejad, D. Mathis, P. Chen, *Organometallics* **2010**, *29*, 294–302.

[40] M. Bochmann, S. J. Lancaster, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1634–1637; *Angew. Chem.* **1994**, *106*, 1715.

[41] M. Bochmann, S. Lancaster, *J. Organomet. Chem.* **1995**, *497*, 55–59.

[42] R. A. Petros, J. R. Norton, *Organometallics* **2004**, *23*, 5105–5107.

[43] J. M. Camara, R. A. Petros, J. R. Norton, *J. Am. Chem. Soc.* **2011**, *133*, 5263–5273.

[44] K. Michiue, R. F. Jordan, *Organometallics* **2004**, *23*, 460–470.

[45] S. Murtuza, O. L. Casagrande, R. F. Jordan, *Organometallics* **2002**, *21*, 1882–1890.

[46] R. Appel, R. Kleinstück, K. Ziehn, *Chem. Ber.* **1971**, *104*, 1335–1336.

[47] M. Findlater, N. J. Hill, A. H. Cowley, *Dalton Trans.* **2008**, 4419–4423.

[48] W. Walter, G. Randau, *Justus Liebigs Ann. Chem.* **1969**, *722*, 52–79.

[49] E. Benzing, W. Kornicker, *Chem. Ber.* **1961**, *94*, 2263–2267.

[50] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[51] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[52] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

5.7 Supporting Information

Table S1. Crystallographic data of the compounds characterised by single crystal X-ray structure analysis.

Compound	**3b**	**3c**	**4a**	**4b**
Formula	$C_{21}H_{28}Cl_3N_3Ti$	$C_{17}H_{28}Cl_3N_3Ti$	$C_{32}H_{53}N_3Ti$	$C_{24}H_{37}N_3Ti$
Formula weight	476.71	428.67	527.67	415.47
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1$	$P2_1/c$
a [Å]	11.1583(4)	9.4746(6)	9.4210(4)	14.8109(12)
b [Å]	15.2612(6)	10.0290(12)	17.1525(7)	9.8163(8)
c [Å]	14.0413(5)	12.5389(8)	10.3406(4)	17.5973(13)
α [°]	90.000	88.054(5)	90.000	90.000
β [°]	101.740(3)	86.140(5)	109.374(3)	107.817(6)
γ [°]	90.000	62.019(5)	90.000	90.000
Cell volume [Å^3]	2341.06(15)	1049.79(16)	1576.35(11)	2435.7(3)
Z	4	2	2	4
Crystal size [mm^3]	0.293x0.257x0.255	0.227x0.208x0.112	0.283x0.243x0.179	0.348x0.230x0.147
Habit	block	block	block	block
Colour	red	red	yellow	yellow
Density [gcm^{-3}]	1.353	1.356	1.112	1.133
T [K]	133(2)	133(2)	133(2)	133(2)
Theta range	1.34–25.74	1.63–26.02	2.09–25.01	1.22–25.60
Unique reflections	4263	24566	5266	4461
Observed reflections [I > 2s(I)]	3602	15479	4744	2625
Parameters	259	225	338	283
wR_2 (all data)	0.0747	0.1132	0.0841	0.1877
R [I > 2s(I)]	0.0277	0.0488	0.0339	0.0712

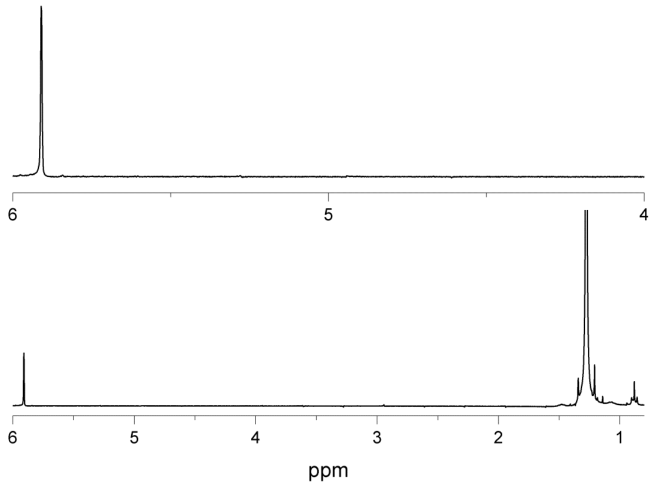


Figure S1. ^{1}H NMR spectrum ($C_2Cl_4D_2$, 120°C) of PE obtained with **4a** (Table 2, Entry 3) after acidic workup of the reaction solution.

6 Highly Controlled and Efficient Polymerization of Ethylene

Johannes Obenauf, Winfried P. Kretschmer and Rhett Kempe*

Lehrstuhl für Anorganische Chemie II – Catalyst Design
Universität Bayreuth, 95440 Bayreuth, Germany

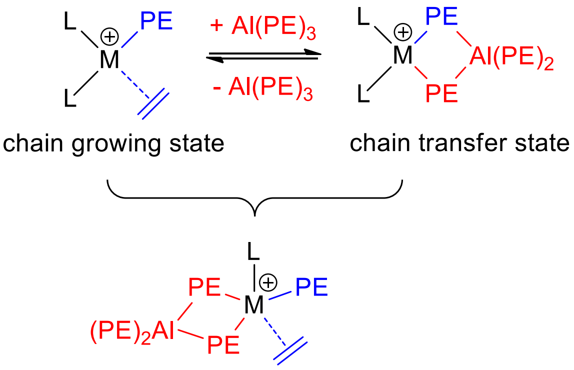
to be submitted.

6.1 Abstract

The controlled and efficient polymerization of ethylene, the most important monomer to produce plastics, could open up a variety of novel applications of polyethylene materials. Coordinative chain-transfer polymerization, a protocol characterized by polymeryl chain-transfer between dormant states of a chain-transfer agent and a polymerization catalyst responsible for the chain growth, already allows the controlled polymerization of ethylene. A fundamental problem associated with coordinative chain-transfer polymerization is the low efficiency or low catalyst economy. An inverse first-order dependence of the chain growth on the chain-transfer agent concentration restricts the number of chains that can be grown by a catalyst molecule. Herein, we introduce a concept to solve this problem and a catalyst system that combines control and efficiency in ethylene polymerization.

6.2 Introduction

Multi-block copolymers can undergo microphase separation leading to an infinite variety of reproducible formed polymer nanostructures.[1] Such structuring leads, for instance, to polymers having unique pore structures,[2,3] highly ordered materials,[4] supermolecules[5] and towards many applications based on the structuring. Polyethylene (PE) is one of the most important or the most important synthetic polymer worldwide,[6] but is difficult to produce in a highly controlled fashion. In consequence, multi-block copolymer formation and structuring based on it is restricted. PE blocks for such purpose are usually made from butadiene via hydrogenation of 1,4-polybutadiene.[5] Classic protocols to polymerize ethylene in a highly controlled fashion such as anionic or living coordinative polymerization are inefficient for PE (and polypropylene, the second most important polymer).[7] Coordinative chain-transfer polymerization (CCTP),[8] the rapid migration of polymeryl chains between two different metal sites, seems to be the most promising concept to solve this problem.[9] One of them, the chain growing state (Scheme 1, top left) or catalyst, is responsible for chain growth via ethylene insertion without chain termination other than chain-transfer. The other, the chain-transfer agent (CTA), an inexpensive main group metal alkyl (Al in Scheme 1) or Zn alkyl added in excess, acts as the dormant state or as the polymeryl chain resting state. If chain exchange via the chain-transfer state (Scheme 1, right) is faster than chain propagation, all polymeryl chains grow with the same rate leading to very low polydispersities and time-dependent chain growth.



Scheme 1. Top: Chain-growing state and chain-transfer state in coordinative chain-transfer polymerization and their equilibrium. PE = polyethylene; M = group 4 metal; L = anionic ligand. An increase in $Al(PE)_3$ concentration decreases (first-order dependence) the rate of chain growth. Bottom: Bifunctional group 4 metal catalyst which is stabilized only by one (bulky) anionic ligand and simultaneously grows and transfers polymeryl chains. In consequence, chain growth is independent from the aluminium concentration.

CCTP is associated with a fundamental problem, the problem of catalyst economy. The CTA binds to the active catalyst in a rapidly maintained equilibrium to form heterobimetallic complexes,[10-12] which are responsible for the chain-transfer (Scheme 1, top right). Thus, chain growth depends inverse first-order on the CTA concentration.[13] This inverse first-order dependence has restricted CCTP towards low CTA to catalyst ratios or a low number of chains a catalyst molecule can grow.

Here we propose how to overcome the catalyst economy problem using a novel bifunctional catalyst. This group 4 metal based catalyst family enables PE chain growth and transfer simultaneously (Scheme 1, bottom). In combination with fast reversible chain-transfer and catalyst stability at high CTA concentrations, the controlled and efficient polymerization of ethylene is possible. Temperature dependent studies show constant ethylene consumption over one hour up to 70 °C. Very high activities have been observed for CTA to catalyst ratio of 10000 and above in combination with growth of all alkyl chains. Time dependent studies of the polymerization process revealed an increase of the molecular weight by time. Polymerization studies varying the CTA to catalyst ratio between 12000 and 20000 revealed no inverse first-order dependence of the chain growth on the CTA concentration.

6.3 Results and Discussion

Various catalyst systems based on lanthanides and transition metals have been reported for the CCTP of ethylene.[9] Reports on high CTA to catalyst ratios are rare and if reported very low activity/productivities have been observed. In their pioneering contribution, Mortreux[14] and co-workers describe experiments with Mg to Sm ratios of 10, 20 and 50 giving rise to productivities of 564, 396 and 348 $kg_{PE}mol_{cat}^{-1}h^{-1}$, respectively. Furthermore, a Mg/Sm ratio of 1000, the highest ratio reported for reversible CCTP so far, was used. In this experiment, the productivity decreases to 37 $kg_{PE}mol_{cat}^{-1}h^{-1}$. We reported on the highly controlled formation of Al-terminated PE using a group 3 metal organo cation as a catalyst.[15] Here, activities of 375 and 168 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ were observed for Al/Y ratios of 50 and 100, respectively. At higher CTA/catalyst ratios, no polymer formation is observed and the catalyst decomposes via ancillary ligand transfer to the CTA.

A bifunctional group 4 metal catalyst as shown in Scheme 1, bottom, in which the ancillary ligand binds strongly enough to avoid its transfer to the electron deficient CTA could overcome these limitations. Group 4 metal catalysts can operate in the +4 oxidation state and host four anionic ligands compensating this charge. One of them is used for ancillary ligand coordination providing catalyst solubility and activity. The second and the third are needed for the active sites for ethylene coordination and the polymeryl chain growth. The fourth anionic ligand can now be an aluminate enabling simultaneous polymeryl chain-transfer and chain growth. Zirconium complexes stabilized by one bulky guanidinato ligand looked promising to us. Guanidinato ligands are highly electron rich anionic N-ligands binding strongly to electron deficient metals. Sterically demanding versions of such ligands could be kinetically inert against ligand transfer deactivation processes,[16] and zirconium is extremely stable in the +4 oxidation state.

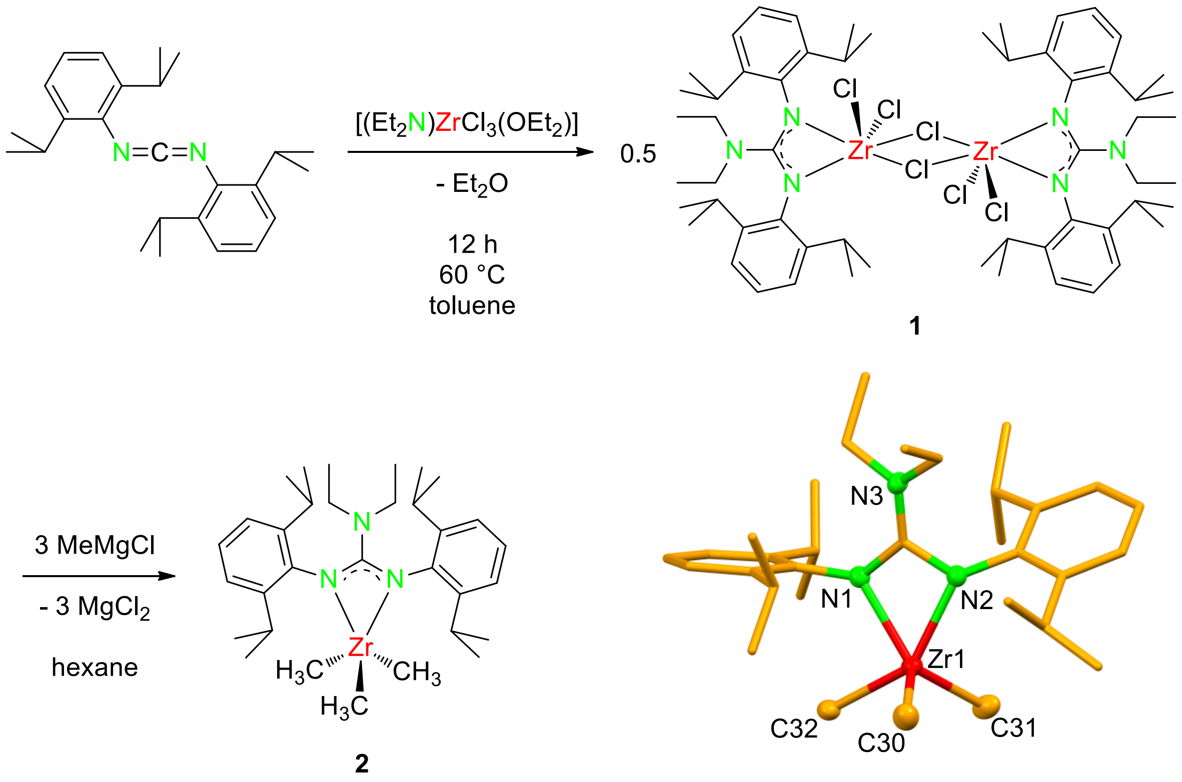


Figure 1. Synthesis and molecular structure of **2** (determined by single crystal X-ray analysis). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1–N1 2.238(3), Zr1–N2 2.201(2), Zr1–C30 2.240(3), Zr1–C31 2.228(4), Zr1–C32 2.260(3), C1–N1 1.338(4), C1–N2 1.366(4), C1–N3 1.346(4), N1–Zr1–N2 59.23(9), N1–C1–N2 108.4(3).

The guanidinato ligand stabilized zirconium complex **1** was synthesized via carbodiimide insertion into a zirconium amide bond (Figure 1, top). The reaction of *N*,*N*'-methanediylidene bis(2,6-diisopropylaniline) with the [$(Et_2N)ZrCl_3(OEt_2)$] (Et = ethyl)[17] allows the isolation of compound **1** in excellent yields. **1** was subsequently reacted with methylmagnesium chloride (three equivalents) to give the precatalyst **2** (Figure 1). Colorless crystals of **2** in very good isolated yields can be obtained from a concentrated hexane solution. The molecular structure of **2** was determined via X-ray single crystal structure analysis. It is shown in Figure 1, bottom left.

Initial ethylene polymerization studies with the novel guanidinato ligand stabilized zirconium complex **2** in the presence of triethylaluminium (TEA) and an ammonium borate as an activator revealed high polymerization activities (Table 1). Polymeryl chain-transfer to aluminium is indicative due to the absence of olefinic proton resonances in the high-temperature ^{1}H NMR of the synthesized PE materials after hydrolytic workup (Figure S2, Supporting Information). To find conditions under which the catalyst operates stable without thermal decomposition the catalyst based on **2** was tested at a TEA to catalyst ratio of 10000 at various temperatures (Table 1, Figure 2). For experiments at higher CTA to catalyst ratios (20000 equivalents of aluminium), see Table S2 of the Supporting Information.

Table 1. Temperature-dependent polymerization experiments using precatalyst **2**. Conditions: precatalyst 1 µmol, p = 2 bar, toluene 280 mL, activator ammonium borate: $[R_2N(CH_3)H][B(C_6F_5)_4]$ ($R=C_{16}H_{33}-C_{18}H_{37}$), Zr/B=1/1.1, triethylaluminium = 10 mmol, Al/Zr 10000/1, 1000 rpm.

Entry	T [°C]	m_{Pol} [g]	Activity[a]	M_n [gmol^{-1}]	M_w/M_n	N_{exp}/N_{theo}[b] [%]
1	60	30.0	15000	1050	1.5	95
2	70	33.8	16900	1160	1.4	97
3	80	19.5	9800	650	1.5	100
4	90	5.1	2600	1400	1.8	12

[a] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$], [b] N_{exp}, experimental chain number (yield PE (in g)/M_n)), N_{theo}, theoretical chain number, assuming three growing chains per Al atom.

At temperatures of 70°C and below, ethylene consumption is constant over one hour of reaction time. Ethylene consumption plots for a temperature of 70, 80 and 90 °C (entries 2, 3 and 4 in Table 1) are shown in Figure 2. At temperatures higher than 70 °C, the reaction starts with high ethylene consumptions but significantly decreases with increasing reaction time (Figure 2). A lower overall activity due to catalyst deactivation is observed for the 80 °C run (entry 3, Table 1) and for the 90 °C run (entry 4, Table 1). At 90 °C, the catalyst becomes already inactive after 30 minutes of reaction time (green plot in Figure 2) due to fast thermal decomposition. An elongation of all aluminium alkyl chains as indicated by the N_{exp}/N_{theo} value was found for the 60, the 70 and the 80 °C runs (Table 1, entries 1-3). N_{exp} is the experimentally determined number of chains that has been extended by the catalyst. It is calculated by dividing the yield of PE by the M_n. N_{theo} is the number describing the theoretically available number of chains assuming three chains per Al atom. PE with a narrow molecular weight distribution and an activity of 16900 $kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$ could be observed for the 70 °C run (Table 1, entry 1). Based on the good long-time stability and the efficient polymerization ability at 70°C, all further experiments were performed at this temperature.

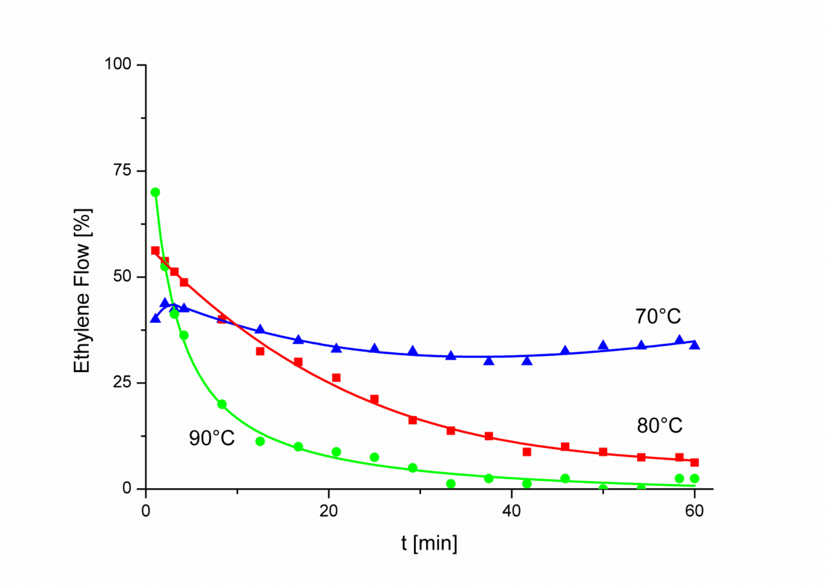


Figure 2. Ethylene flow-plots related to experiments described in Table 2 (Entry 2–4, Entry 1 is omitted for clarity). Long-term stability was observed for 60°C and 70°C.

To understand the transfer ability (reversible *versus* irreversible chain-transfer) of the catalyst described here, a time-dependent polymerization experiment was performed in which several samples were taken from one polymerization run and analyzed (Table 2). The experiment clearly shows time-dependent chain growth and therefore indicates reversible chain-transfer to aluminium. The molecular weight distribution plots of selected polymerization experiments listed in Table 2 are shown in Figure 3. Initially, a non-linear increase of the molecular weight can be observed with the ethylene consumption. Doubling of the ethylene consumption does not result in a doubled molecular weight indication. For such high amounts of aluminium, a certain level of ethylene consumptions is needed to observe elongation of all chains.

Table 2. Time-dependent polymerization experiment using precatalyst **2**. Conditions: precatalyst 1 µmol, T = 70°C, p = 2 bar, toluene 300 mL, activator ammonium borate: $[R_2N(CH_3)H][B(C_6F_5)_4]$ ($R=C_{16}H_{33}$–$C_{18}H_{37}$), Zr/B=1/1.1, triethylaluminium = 10 mmol, Al/Zr 10000/1, 1000 rpm.

Entry	t [min]	Ethylene consumption [nL]	Activity[a]	M_n [gmol^{-1}]	M_w/M_n
5	15	10.0	25000	590	1.5
6	30	16.2	20300	820	1.5
7	60	21.6	13500	1080	1.5
8	90	25.1	10500	1270	1.5
9	120	32.0	10000	1440	1.5

[a] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$] calculated from ethylene consumption.

The investigation of the activity from the CTA/catalyst ratio revealed no inverse dependence. The successive increase of the Al/Zr ratio between 12000 and 20000 (Table 3) did not result in a significant decrease of the polymerization ability or activity and oligoethylenes with narrow molecular weight distributions were obtained.

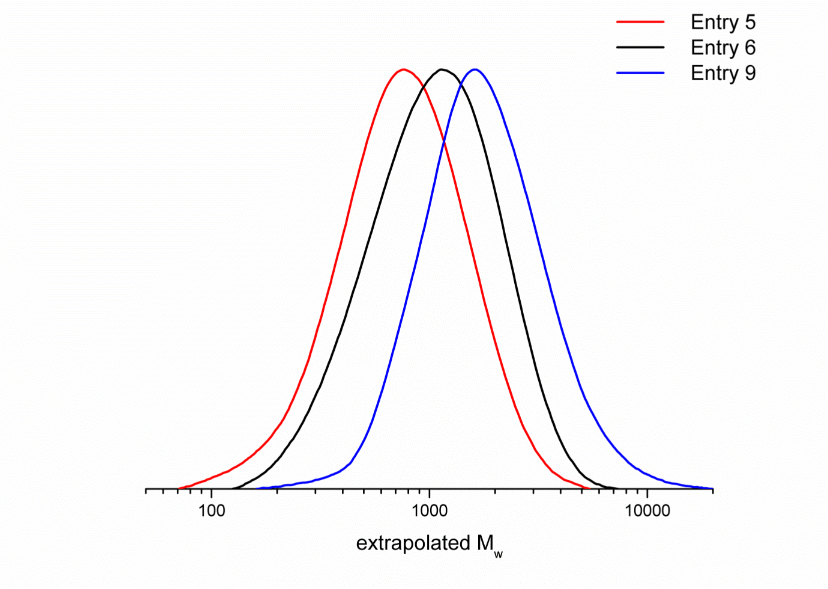


Figure 3. Time-dependent increase of the molecular weight of polymers described in Table 2. Entry 7 and 8 are omitted for clarity.

Table 3. CTA-dependent polymerization experiments using precatalyst **2**. Conditions: precatalyst 1 µmol, T = 70°C, p = 2 bar, toluene 280 mL, t = 60 min, activator ammonium borate: $[R_2N(CH_3)H][B(C_6F_5)_4]$ ($R=C_{16}H_{33}-C_{18}H_{37}$), Zr/B=1/1.1, CTA triethylaluminium, 1000 rpm.

Entry	Al/Zr	Activity[a]	M_n [$gmol^{-1}$]	M_w/M_n
10	20000	9100	450	1.5
11	18000	7000	450	1.4
12	16000	8000	400	1.4
13	15000	9000	520	1.3
14	14000	9000	500	1.4
15	13000	9100	550	1.4
16	12000	9700	620	1.4

[a] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$] calculated from ethylene consumption.

6.4 Conclusion

Several conclusions can be drawn from the present study. Mono(guanidinato) zirconium(IV) complexes can be synthesized in high yields via methanediimine insertion into zirconium amide bonds. Subsequent conversion with methylmagnesium chloride leads to a monomeric methylated species. The activation of this precatalyst with *N*,*N*,*N*-trialkylammonium tetrakis(pentafluorophenyl)borate gave rise to a highly active, long-term stable coordinative chain-transfer polymerization catalyst in the presence of very high amounts of triethylaluminium along with complete number of elongated chains. Time-dependent increase of molecular weight was observed which confirms reversible chain-transfer to aluminium. No inverse first-order dependence of the reaction in aluminium allows the use of chain-transfer agent to catalyst rations higher than 10000. The coordinative chain-transfer polymerization of ethylene with suchlike system represents a highly efficient catalyzed version of the Ziegler's “Aufbaureaktion”.

6.5 References

1. Bates, F. S., Hillmyer, M. A., Lodge T. P., Bates C. M., Delaney K. T. & Fredrickson, G. H. Multiblock polymers: Panacea or Pandora's box? *Science* **336,** 434–440 (2012).
2. Seo, M. & Hillmyer, M. A. Reticulated Nanoporous Polymers by Controlled Polymerization-Induced Microphase Separation. *Science* **336,** 1422–1425 (2012).
3. Sai, H., Tan, K. W., Hur, K., Asenath-Smith, E., Hovden, R., Jiang, Y., Riccio, M., Muller, D. A., Elser, V., Estroff, L. A., Gruner, S. M. & Wiesner, U. Hierarchical Porous Polymer Scaffolds from Block Copolymers. *Science* **341,** 530–534 (2013).
4. Warren, S. C., Messina, L. C., Slaughter, L. S., Kamperman, M., Zhou, Q., Gruner, S. M., DiSalvo, F. J. & Wiesner, U. Ordered Mesoporous Materials from Metal Nanoparticle-Block Copolymer Self-Assembly. *Science* **320,** 1748–1752 (2008).
5. Gröschel, A. H., Walther, A., Löbling, T. I., Schacher, F. H., Schmalz, H. & Müller, A. H. E. Guided hierarchical co-assembly of soft patchy nanoparticles. *Nature* **503,** 247–251 (2013).
6. Kaminsky, W. & Böhm, L. *Polyolefins: 50 years after Ziegler and Natta I.* **257,** (Springer Berlin Heidelberg, 2013).
7. Domski, G. J., Rose, J. M., Coates, G. W., Bolig, A. D. & Brookhart, M. Living alkene polymerization: New methods for the precision synthesis of polyolefins. *Prog. Polym. Sci.* **32,** 30–92 (2007).
8. Kempe, R. How to Polymerize Ethylene in a Highly Controlled Fashion? *Chem. Eur. J.* **13,** 2764–2773 (2007).
9. Valente, A., Mortreux, A., Visseaux, M. & Zinck, P. Coordinative Chain Transfer Polymerization. *Chem. Rev.* **113,** 3836–3857 (2013).
10. Bochmann, M. & Lancaster, S. J. Monomer-Dimer-Gleichgewichte in homo- und heterodinuclearen kationischen Alkylzirconiumkomplexen: zur Rolle von Alkylaluminiumverbindungen bei der Stabilisierung katalytisch aktiver Zentren. *Angew. Chem.* **106,** 1715–1718 (1994).
11. Bochmann, M. & Lancaster, S. J. Monomer–Dimer Equilibria in Homo- and Heterodinuclear Cationic Alkylzirconium Complexes and Their Role in Polymerization Catalysis. *Angew. Chem. Int. Ed. Engl.* **33,** 1634–1637 (1994).

12. Bochmann, M. & Lancaster, S. J. Cationic group IV metal alkyl complexes and their role as olefin polymerization catalysts: The formation of ethyl-bridged dinuclear and heterodinuclear zirconium and hafnium complexes. *J. Organomet. Chem.* **497,** 55–59 (1995).

13. Camara, J. M., Petros, R. A. & Norton, J. R. Zirconium-Catalyzed Carboalumination of α-Olefins and Chain Growth of Aluminum Alkyls: Kinetics and Mechanism. *J. Am. Chem. Soc.* **133,** 5263–5273 (2011).

14. Pelletier, J.-F., Mortreux, A., Olonde, X. & Bujadoux, K. Synthesis of New Dialkylmagnesium Compounds by Living Transfer Ethylene Oligo- and Polymerization with Lanthanocene Catalysts. *Angew. Chem. Int. Ed. Engl.* **35,** 1854–1856 (1996).

15. Kretschmer, W. P., Meetsma, A., Hessen, B., Schmalz, T., Qayyum, S. & Kempe, R. Reversible Chain Transfer between Organoyttrium Cations and Aluminum: Synthesis of Aluminum-Terminated Polyethylene with Extremely Narrow Molecular-Weight Distribution. *Chem. Eur. J.* **12,** 8969–8978 (2006).

16. Jones, C. Bulky guanidinates for the stabilization of low oxidation state metallacycles. *Coord. Chem. Rev.* **254,** 1273–1289 (2010).

17. Brenner, S., Kempe, R. & Arndt, P. Mixed Chloro(dialkylamido) Complexes of Zirconium and Hafnium. *Z. a. allg. Chem.* **621,** 2021–2024 (1995).

6.6 Supporting Information

Experimental Section

General: All manipulations and reactions were carried out under dry argon or nitrogen using standard Schlenk and glovebox techniques. Solvents were purified by distillation from potassium, Na/K alloy or sodium ketyl of benzophenone under argon immediately before use. Toluene used for ethylene polymerization (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3–11-supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over BASF R3-11-supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). $Zr(NEt_2)_4$[1,2] and trichloro dietylamido zirconium(IV) etherate $[(Et_2N)ZrCl_3(OEt_2)]$[3] were prepared according to the published procedures. Commercial $ZrCl_4$ (ABCR), Et_2NH (Merck), methylmagnesium chloride (3.0 M in THF) (Aldrich), *N*,*N'*-bis(2,6-diisopropylphenyl) carbodiimide (TCI), triethylaluminium (97%, Sasol Germany GmbH), $[R_2N(CH_3)H][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$–$C_{18}H_{37}$), 6.2 wt.-% $B(C_6F_5)_4^-$ in Isopar (Dow Chemicals) and all other chemicals were used as received without further purification.

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

NMR Spectroscopy: NMR spectra were recorded with 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 by using the residual solvent resonances. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. Chemical shifts (δ) are reported in ppm.

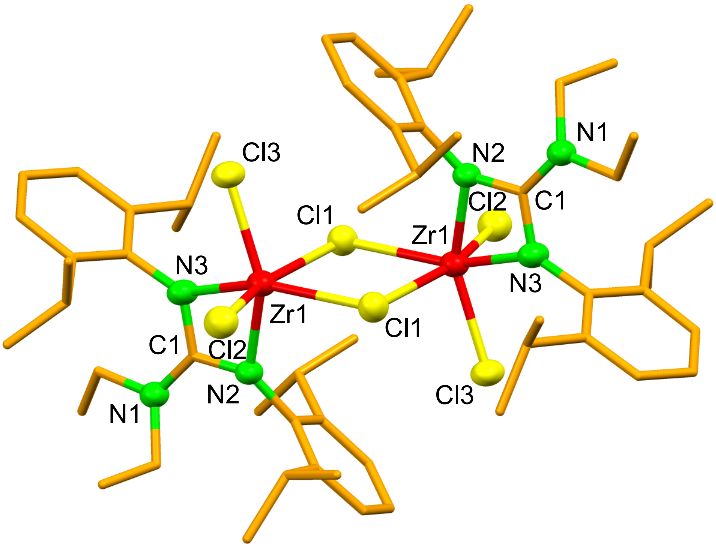
Gel Permeation Chromatography (GPC): Gel permeation chromatography analysis was carried out with an Agilent (Polymer Laboratories Ltd.) PL-GPC 220 high-temperature chromatographic unit equipped with differential pressure (DP), refractive index (RI) and light scattering (LS) (15° and 90°) detectors and three linear mixed bed columns (Olexis). GPC analyses were performed at 150°C and with 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.05 wt.-%, c = 1 mgmL^{-1}) 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 polystyrene standards (M_w = 518–2500000 gmol^{-1}, K = 12.100 and α = 0.707) and were corrected with K and Alpha values for linear PE (K = 40.600 and α = 0.725).

X-ray Crystallography: X-ray crystal structure analyses were performed with a STOE-IPDS II diffractometer [λ(Mo-$K\alpha$) = 0.71073 Å] equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished with SIR97,[4] SHELXL-2013[5] and WinGX.[6]

Ethylene Polymerization: The catalytic ethylene polymerization reactions were performed in a 0.8 L stainless steel autoclave (Büchi) 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 polymerization runs, pressure, ethylene flow, inner and outer reactor temperature were monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 hour at 120°C prior to use. Toluene (150 mL) was added into the autoclave and saturated with ethylene. After addition of triethylaluminium, the co-catalyst and complete saturation with ethylene, the precatalyst was added. The stock solutions of precatalyst and co-catalyst were prepared in a glovebox. Time-dependent experiments were performed in a 1 L stainless steel autoclave (Büchi) with a bottom outlet valve. For sampling, stirring was turned off and five milliliters of the reaction solution were taken out. The polymerization was stopped by venting the reactor and quenched by the addition of acidified ethanol. The reaction solution was cooled with an ice bath and the obtained polymers were filtered, washed with ethanol and dried at 60°C.

Synthesis of Di-μ-chlorido-bis[2,3-bis(2,6-diisopropylphenyl)-1,1-diethylguanidinato]-tetrachlorido-dizirconium(IV) (1): $[(Et_2N)ZrCl_3(OEt_2)]$ (6.736 g, 19.6 mmol) and *N*,*N*'-bis(2,6-diisopropylphenyl) carbodiimide (7.103 g, 19.6 mmol) were dissolved in toluene (100 mL) and stirred for 24 hours at 60°C. Toluene was removed under reduced pressure and the residue washed with hexane (30 mL). Drying in vacuuo gave a white solid. Crystals suitable for X-ray single crystal analysis were obtained by layering a toluene solution with hexane. Yield 12.6 g (91 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.23 [t, ^3J = 7.0 Hz, 6 H, $N(CH_2CH_3)_2$]; 1.18 [d, ^3J = 6.8Hz, 12 H, $CH(CH_3)_2$]; 1.50 [d, ^3J = 6.6 Hz, 12 H, $CH(CH_3)_2$]; 2.61 [q, ^3J = 6.8 Hz, 4 H, $N(CH_2CH_3)_2$]; 3.55 [m, 4 H, $CH(CH_3)_2$]; 7.04–7.13 (s, 6 H, Ar*H*) ppm. ^{13}C NMR (75.4 MHz, C_6D_6): δ = 11.4 [$N(CH_2CH_3)_2$]; 24.2 [$CH(CH_3)_2$]; 26.1 [$CH(CH_3)_2$]; 29.0 [$CH(CH_3)_2$]; 41.5 [$N(CH_2CH_3)_2$]; 110.3, 124.8, 127.3, 141.0, 143.5 (ArC); 169.9 (NCN) ppm. Elemental analysis: $C_{58}H_{88}Cl_6N_6Zr_2$ (1264.53) calcd. C 55.09, H 7.01, N 6.65; found C 54.13 H 6.95, N 6.53.

Synthesis of 2,3-Bis(2,6-diisopropylphenyl)-1,1-diethylguanidinato trimethanido zirconium(IV) (2): To a suspension of **1** (1176 mg, 0.93 mmol) in hexane (50 mL) methylmagnesium chloride (1.9 mL, 5.58 mmol) was added dropwise at -78°C. The mixture was warmed to room temperature and stirred overnight. Storage of the concentrated filtrate at –30 °C led to colourless crystals. Yield 903 mg (85 %). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ = 0.26 [t, ^{3}J = 7.1 Hz, 6 H, $\mathrm{N(CH_2C}\mathit{H}_3\mathrm{)_2}$]; 0.86 [s, 9 H, $\mathrm{Zr(C}\mathit{H}_3\mathrm{)_3}$]; 1.24 [d, ^{3}J = 6.9Hz, 12 H, $\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$]; 1.36 [d, ^{3}J = 7.1 Hz, 12 H, $\mathrm{CH(C}\mathit{H}_3\mathrm{)_2}$]; 2.74 [q, ^{3}J = 7.1 Hz, 4 H, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_3)_2}$]; 3.62 [sept, ^{3}J = 6.8 Hz, 4 H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$]; 7.09 (s, 6 H, Ar*H*) ppm. ^{13}C NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ = 11.3 [$\mathrm{N(CH_2CH_3)_2}$]; 24.0 [$\mathrm{CH(CH_3)_2}$]; 25.9 [$\mathrm{CH(CH_3)_2}$]; 28.5 [$\mathrm{CH(CH_3)_2}$]; 40.8 [$\mathrm{N(CH_2CH_3)_2}$]; 51.4 [$\mathrm{Zr(CH_3)_3}$]; 124.3, 125.5, 142.7, 143.3 (ArC); 169.5 (NCN) ppm. Elemental analysis: $\mathrm{C_{32}H_{53}N_3Zr}$ (571.01): calcd. C 67.31, H 9.36, N 7.36; found C 67.15, H 9.46, N 7.33.



Supplementary Figure S1. Molecular structure of compound **1** investigated by single crystal structure analysis. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1–N1 2.152(6), Zr1–N2 2.168(6), Zr1–Cl1 2.584(2), Zr1–Cl2 2.388(2), Zr1–Cl3 2.3935(19), C1–N1 1.376(9), C1–N2 1.347(9), C1–N3 1.331(9), N1–Zr1–N2 60.7(2), N1–C1–N2 106.5(6).

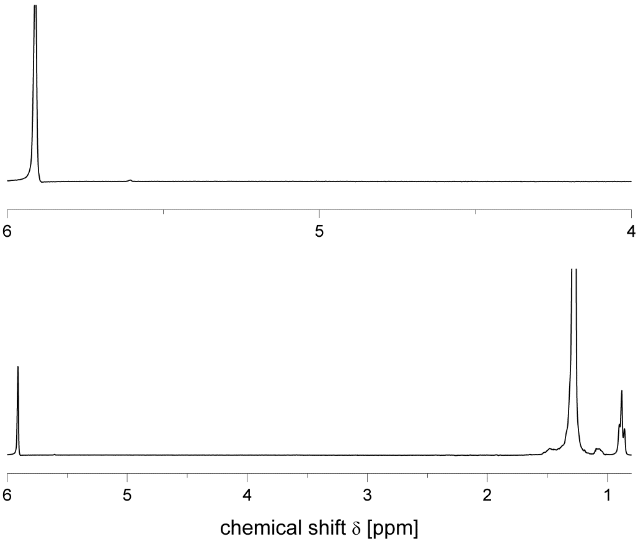
Supplementary Table S1. Crystallographic data of the compounds characterized by single crystal X-ray structure analysis.

Compound	**1**	**2**
Formula	$C_{58}H_{88}Cl_6N_6Zr_2$, 2 (C_7H_8)	$C_{32}H_{53}N_3Zr$
Formula weight	1448.75	570.99
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a [Å]	10.9383(10)	9.4553(4)
b [Å]	20.6555(18)	17.2321(7)
c [Å]	16.4615(16)	10.3607(4)
α [°]	90	90
β [°]	100.105(5)	108.682(3)
γ [°]	90	90
Cell volume [Å^3]	3661.6(6)	1599.17(11)
Z	2	2
Crystal size [mm^3]	0.267x0.190x0.163	0.177x0.159x0.147
Habit	block	block
Color	Colorless	Colorless
Density [gcm^{-3}]	1.414	1.186
T [K]	133	133(2)
Theta range	1.26–25.65	2.08–27.11
Unique reflections	6909	6693
Observed reflections [I > 2s(I)]	3487	5468
Parameters	399	338
wR_2 (all data)	0.2158	0.0724
R [I > 2s(I)]	0.0872	0.0379

Supplementary Table S2. Temperature-dependent polymerization experiments using precatalyst **2**. Conditions: precatalyst 1 µmol, p = 2 bar, toluene 280 mL, activator ammonium borate: $[R_2N(CH_3)H][B(C_6F_5)_4]$ ($R=C_{16}H_{33}-C_{18}H_{37}$), Zr/B=1/1.1, triethylaluminium = 20 mmol, Al/Zr 20000/1, 1000 rpm.

Entry	T [°C]	m_{Pol} [g]	Activity[a]	M_n [$gmol^{-1}$]	M_w/M_n
22	50	10.3	5300	455	1.4
23	60	15.7	8700	400	1.7
24	70	17.0	9100	450	1.5
25	80	19.1	10100	390	1.5
26	90	6.7	3400	370	1.5

[a] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$].



Supplementary Figure S2. High-temperature ^1H NMR ($C_2Cl_4D_2$, 120°C) of the polymer obtained of entry 2 (Table 1) after hydrolytic workup. The absence of olefinic resonances indicates chain-transfer to aluminium.

Supplementary Table S3. CTA-dependent polymerization experiments using precatalyst **2**. Conditions: precatalyst 1 μmol, T = 70°C, p = 2 bar, toluene 280 mL, t = 60 min, activator ammonium borate: $[R_2N(CH_3)H][B(C_6F_5)_4]$ ($R=C_{16}H_{33}$–$C_{18}H_{37}$), Zr/B=1/1.1, CTA triethylaluminium, 1000 rpm.

Entry	Al/Zr	Activity[a]	M_n [$gmol^{-1}$]	M_w/M_n
27	5000	11500	1770	1.9
28	4000	11500	2360	1.9
29	3000	10800	2750	2.0
30	2000	11000	3430	2.1
			94400	2.7
31	1000	12200	6040	1.7
			362300	1.9

[a] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]; calculated from ethylene consumption.

References

1. Bradley, D. C. & Thomas, I. M. Metallo-organic Compounds containing Metal-Nitrogen bonds. Part I. Some Dialkylamino-derivatives of Titanium and Zirconium. *J. Chem. Soc.* 3857–3861 (1960).
2. Diamond, G. M., Jordan, R. F. & Petersen, J. L. Synthesis of Group 4 Metal *rac*-(EBI)M(NR_2)$_2$ Complexes by Amine Elimination. Scope and Limitations. *Organometallics* **15,** 4030–4037 (1996).
3. Avtomonov, E. V. & Rufonav, K. A. Zirconium Reagents for Organometallic Synthesis. Crystal Structures of ZrCl4*2Et20 and (Et2N)ZrCl3*Et20. *Zeitschrift für Naturforsch.* **54b,** 1563–1567 (1999).
4. Altomare, A. *et al.* SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **32,** 115–119 (1999).
5. Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. A.* **64,** 112–22 (2008).
6. Farrugia, L. J. WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32,** 837–838 (1999).

7 List of Publications

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

1. J. Obenauf, W. P. Kretschmer, T. Bauer, R. Kempe, *Eur. J. Inorg. Chem.* **2013**, *4*, 537–544.

   "An Efficient Titanium Amidinate Catalyzed Version of Ziegler's 'Aufbaureaktion'"

2. J. Obenauf, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2014**, *9*, 1446–1453.

   "Efficient Synthesis of Aluminium-Terminated Polyethylene by Means of Irreversible Coordinative Chain-Transfer Polymerisation Using a Guanidinatotitanium Catalyst"

3. J. Obenauf, W. P. Kretschmer, R. Kempe, *to be submitted.*

   "Highly Controlled and Efficient Polymerization of Ethylene"

4. A. P. Sobaczynski, J. Obenauf, R. Kempe, *Eur. J. Inorg. Chem.* **2014**, *7*, 1211–1217.

   "Alkane Elimination Reactions between Yttrium Alkyls and Tungsten Hydrides"

5. D. Forberg, J. Obenauf, M. Friedrich, S.-M. Hühne, W. Mader, G. Motz, R. Kempe, *Catal. Sci. Technol.* **2014**, *4*, 4188-4192.

   "The synthesis of pyrroles via acceptorless dehydrogenative condensation of secondary alcohols and 1,2-amino alcohols mediated by a robust and reusable catalyst based on nanometer-sized iridium particles"

8 Acknowledgment

First of all I would like to thank my academic supervisor

Prof. Dr. Rhett Kempe

for giving me the opportunity to work in his research group on this very interesting topic. I am grateful for his constant interest on the progress of this work, highly interesting scientific discussions and the liberties granted to me.

I would like to thank Dr. Winfried P. Kretschmer for his support, scientific discussions and high-temperature GPC analysis and help with NMR spectra.

Financial support from Sasol Germany GmbH is gratefully acknowledged. Thanks to Dr. Albert Boddien and Christian Köster for scientific discussions on the CAP project.

Thanks are due to all those who facilitated a trouble-free everyday laboratory life for me: employees of the central materials and consumables for the supply with all necessary consumables, the electronics workshop, metal workshops, glassblowing workshops. I thank Anna Dietel and Heidi Maisel for providing dried solvents and other lab equipment.

My thanks also go to my interns Sven Hafke, Martin Meyer, Bastian Klose and Fabian Kallmeier for their commitment and their help during their advanced lab courses and bachelor thesis.

I furthermore wish to thank Dr. Tobias Bauer for introducing me at the STOE IPDS-II X-ray diffractometer and his help with crystal structure analysis. Dr. Benjamin Oelkers, Dr. Isabelle Haas, Dr. Awal Noor and Dr. Mikhail Butovskii are gratefully acknowledged for their help at X-ray crystal structure analysis.

Thanks to my lab mates Simone Hoch, Martin Friedrich, Dr. Justus Herrmannsdörfer, Dr. Adam Sobaczynski, Dr. Muhammad Hafeez, Walter Kremnitz, Dominic Tilgner and Andreas Gollwitzer for the great atmosphere and the time we spent together.

Additionally, I thank Walter Kremnitz for his commitment to make everyone's daily lab routine as enjoyable as possible. My special thanks goes to Marlies Schilling for help in all administrative and organizational matters.

I especially thank all my other colleagues Dr. Tobias Bauer, Dr. Isabelle Haas, Dr. Awal Noor, Walter Kremnitz, Dr. Benjamin Oelkers, Susanne Ruch, Sina Rösler, Sabrina Sachau, Sonja Fehn, Stefan Schwarz, Dr. Stefan Michlik, Theresa Winkler, Julia Ewert, Toni Hille, Daniel Forberg, Nick Deibl for having a great time as well inside as outside the lab.

I thank the other members of the Kempe Group Dr. Christine Denner, Dr. Sadaf Qayyum, Dr. Saravana Pillai, Dr. Emmanuel Sobgwi Tamne and Dr. Muhammad Hafeez, Dr. Muhammad Zaheer for their help in many respects.

I thank Dr. Torsten Irrgang and Dr. Benjamin Oelkers for proofreading of publications and this thesis.

I would like to thank Dr. Wolfgang Milius for his support at the X-ray diffractometers.

My special thanks go to my family for their never-ending support and encourage not only during my PhD-time.

Finally, I would like to thank Julia with all my heart for her endless love and her confidence, her encouraging words and her never-ending patience.

9 Declaration

(Eidesstattliche) Versicherungen und Erklärungen

(§5 Nr. 4 PromO)

Hiermit erkläre ich, dass keine Tatsachen vorliegen, die mich nach den gesetzlichen Bestimmungen über die Führung akademischer Grade zur Führung eines Doktorgrades unwürdig erscheinen lassen.

(§8 S. 2 Nr. 5 PromO)

Hiermit erkläre ich mich damit einverstanden, dass die elektronische Fassung meiner Dissertation unter Wahrung meiner Urheberrechte und des Datenschutzes einer gesonderten Überprüfung hinsichtlich der eigenständigen Anfertigung der Dissertation unterzogen werden kann.

(§8 S. 2 Nr. 7 PromO)

Hiermit erkläre ich eidesstattlich, dass ich die Dissertation selbstständig verfasst und keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt habe.

(§8 S. 2 Nr. 8 PromO)

Ich habe die Dissertation nicht bereits zur Erlangung eines akademischen Grades anderweitig eingereicht und habe auch nicht bereits diese oder eine gleichartige Doktorprüfung endgültig nicht bestanden.

(§8 S. 2 Nr. 9 PromO)

Hiermit erkläre ich, dass ich keine Hilfe von gewerblichen Promotionsberatern bzw. -vermittlern in Anspruch genommen habe und auch künftig nicht nehmen werde.

Bayreuth, den 17.03.2015 Johannes Obenauf