Highly Flexible Synthesis of Linear Alpha Olefins from Ethylene

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Andreas Walter Gollwitzer

geboren in Tirschenreuth

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Acting dean: Prof. Dr. Stefan Peiffer

Examination committee:

Prof. Dr. Rhett Kempe (reviewer)

Prof. Dr. Seema Agarwal (reviewer)

Prof. Dr. Georg Papastavrou (chairman)

Prof. Dr. Rainer Schobert

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Abbreviations

Ar	aryl
avg	average
calcd	calculated
CCTP	coordinative chain transfer polymerization
CGS	chain growing state
Cp	cyclopentadienyl
CTA	chain transfer agent
MAO	methylaluminoxane
d-MAO	dry methylaluminoxane
Me	methyl
Ln	litres under normal conditions (273.15 K, 1.01325 bar, DIN 1343)
NMR	nuclear magnetic resonance
PDI	polydispersity index
α value	alpha value
PE	polyethylene
Hz	Hertz
J	coupling constant (Hz)
ppm	parts per million
THF	tetrahydrofurane
d	doublet
s	singlet
t	triplet
δ	chemical shift
TEA	triethylaluminum
TOA	trioctylaluminum

TMA	trimethylaluminum
DEZ	diethylzinc
rpm	round per minute
acac	acetylacetonate
KTA	Kettentransferagenz
CGS	chain growing state
CTS	chain transfer state
LAO	linear alpha olefin

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1. Zusammenfassung

In der vorliegenden Arbeit wird die Entwicklung eines neuartigen und hochflexiblen Prozesses zur nicht-selektiven Oligomerisierung von Ethylen zu linearen α-Olefinen (LAO) vorgestellt. Die Möglichkeit, Kettenwachstums- von Kettenabbruchreaktionen voneinander zu trennen wird genutzt, um eine enorme Syntheseflexibilität zu realisieren. Durch die gezielte Einflussnahme auf Teilreaktionsraten kann die erhaltene Produktverteilung der LAO sehr einfach und flexibel eingestellt werden.

Die (quasi) zeitliche und räumliche Trennung der Kettenwachstums- und Kettenabbruchsreaktion wird durch eine Kombination von spezialisierten Katalysatoren realisiert. Der Kettenaufbau, ausgehend von Ethylen, wird mittels KKTP-Katalysatoren (koordinative Kettentransferpolymerisation) durchgeführt und die entstandenen Alkylketten auf ein Kettentransferagenz (KTA), basierend auf Al- oder Zn-Alkylen, übertragen. Ein weiterer Katalysator, basierend auf Nickel, katalysiert die Kettenabbruchreaktion (β-H-Eliminierung/Übertragung), wobei diese vereinfacht als Kettenaustauschreaktion verstanden werden kann. Die an das KTA gebundene Alkylkette wird durch Ethylen ersetzt und das korrespondierende alpha Olefin erhalten (Schema 1a). Den Kettentransport zwischen beiden Katalysatoren vermittelt dabei das KTA. In einer Eintopf-Tandemreaktion können dadurch LAO außerordentlich flexibel und hoch effizient hergestellt werden. Die jeweiligen Teilreaktionen wurden getrennt voneinander untersucht, um die Eintopf-Tandemreaktion eingehend untersuchen zu können.
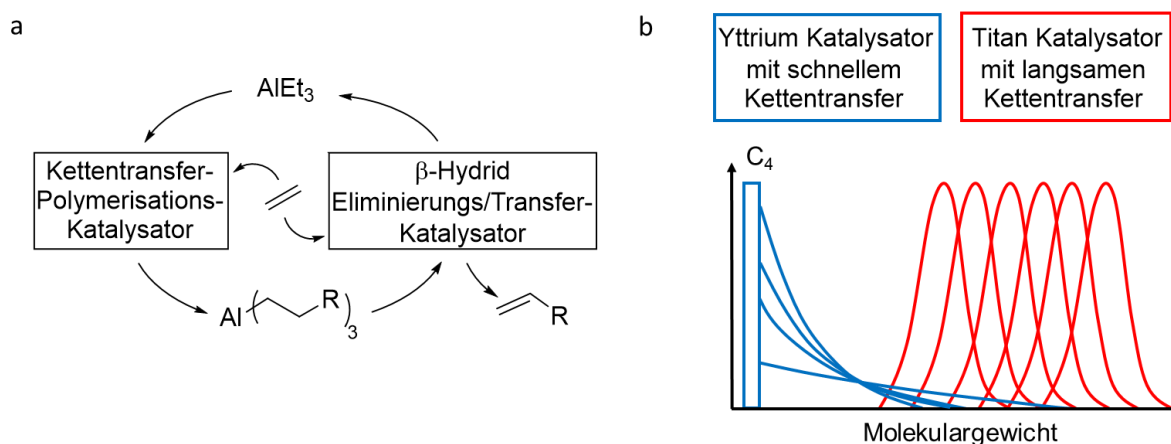
Schema 1. a) Kombination eines KKTP Katalysators mit einem Nickel basierten Austauschkatalysator zur Produktion von LAO aus Ethylen. b) Abhängigkeit des

durchschnittlichen Molgewichtes von der Kettentransferrate des verwendeten KKTP-Katalysators.

Die KKTP Katalysatoren wurden in Polymerisationsexperimenten ohne Nickel untersucht, die Nickel(0) katalysierte Kettenaustauschreaktion wurde mittels ^{1}H-NMR Experimenten beschrieben.

Ein auf Yttrium(III)/Triethylaluminum (TEA) basiertes KKTP System zeigte in der Polymerisation von Ethylen ohne Nickel eine reversible Kettentransferpolymerisation mit sehr hohen Transferraten. Es wird eine lebende Polymerisation beobachtet und Produkte mit einer Poisson-Verteilung erhalten.

Kinetische ^{1}H-NMR Untersuchungen der Nickel katalysierten Kettenaustauschreaktion zeigten eine Reaktion erster Ordnung in Abhängigkeit der Al- bzw. Ni-Konzentration auf.

In der Tandemreaktion aus KKTP und Nickel katalysierter Kettenaustauschreaktion konnten LAO erhalten werden, welche einer Schulz-Flory-Verteilung folgen. Mit Variation der Prozessparameter (Ethylen-, Al-, Y- und Ni- Konzentration) kann die Verteilung der erhaltenen LAO herausragend flexibel reguliert werden. Die Produktverteilung kann dabei von 1-Buten (90 mol-%) bis hin zu LAO mit einem durchschnittlichen Molgewicht von 850 g mol^{-1} eingestellt werden. In einem Batchexperiment konnten die eingesetzten Al-Alkyle bis zu 78mal (TON) wiederverwendet werden, wodurch die Effizienz des Systems wesentlich gesteigert wird.

Anschließend wurde auf ein Titan(IV)/TEA basiertes KKTP Katalysatorsystem zurückgegriffen, welches Alkylketten aus Ethylen erzeugt, irreversibel auf Al überträgt und dabei niedrige Kettentransferraten aufweist. Dabei werden Produkte erhalten, welche vergleichsweise langkettig sind und Dispersitäten (M_w/M_n) von ca. 2 aufweisen.

In der Tandemreaktion mit Nickel wurden ebenfalls relativ langkettige (bis M_n = 7000 g mol^{-1}) LAO erhalten. Durch Änderung des Ethylendrucks und der Aluminiumkonzentration können gezielt LAO mit einem durchschnittlichen Molgewicht zwischen 260 g mol^{-1} und 7000 g mol^{-1} synthetisiert werden. Dieses System ist mit Halbwertszeiten von 126 min herausragend stabil, sodass in Langzeitexperimenten die eingesetzten Aluminiumalkyle ebenfalls unterstöchiometrisch eingesetzt werden können.

Es konnte gezeigt werden, dass die Kettentransferrate des KKTP Katalysators einen entscheidenden Einfluss auf das Molekulargewicht der erhaltenen Produkte besitzt (Schema 1b). Hohe Transferraten haben kurzkettige Produkte, niedrige Transferraten haben vergleichsweise langkettige Produkte zur Folge. Eine weitere Möglichkeit auf die Produktverteilung in der Tandemreaktion Einfluss zu nehmen ist die Verwendung von mehreren KTAs, da die Kettentransferrate stark vom KTA abhängig ist. Um diesen Einfluss zu untersuchen, wurde ein Katalysatorsystem basierend auf Zirkonium/TEA/DEZ (Diethylzink) erarbeitet.

KKTP Experimente mit einem Aminopyridinato-/Cyclopentadienylligand stabilisierten Zr-Katalysator und TEA als KTA, zeigten einen irreversiblen Kettentransfer mit einer relativ niedrigen Kettentransferrate zwischen Zr und Al auf. Die erhaltenen Produkte besitzen ein durchschnittliches Molekulargewicht von $M_n = 3000$ g mol^{-1} ($M_w/M_n = 1.6$). KKTP Experimente in zusätzlicher Anwesenheit von DEZ als KTA zeigten einen reversiblen Kettentransfer mit einer relativ hohen Kettentransferrate zwischen Zr und Zn. Hierbei wurden Produkte mit einem vergleichsweise niedrigen Molekulargewicht erhalten ($M_n = 2200$ g mol^{-1}, $M_w/M_n = 1.2$).

Ähnliche Unterschiede im Reaktionsverhalten wurden in der Nickel katalysierten Kettenaustauschreaktion beobachtet. Kinetische ^{1}H-NMR Untersuchungen unter gleichen Bedingungen ergaben, dass die Kettenaustauschreaktion von Al-Alkylen quantitativer und bis zu 70-mal schneller abläuft als von Zn-Alkylen.

In der Tandemreaktion mit Nickel werden ohne Zinkalkyle aufgrund der niedrigen Transferrate (Zr zu Al) vergleichsweise langkettige LAO (C$_{40+}$) erhalten, in Anwesenheit von Zinkalkylen werden wesentlich kürzerkettige Produkte (C$_4$-C$_{30}$) erzeugt. Die Produktverteilung kann hierbei durch die Zink- und Aluminiumalkylkonzentrationen sehr einfach eingestellt werden.

Mit den vorgestellten Systemen kann Ethylen sehr flexibel und gezielt zu nahezu jeder gewünschten Molmassenverteilung oligomerisiert werden, welche zwischen 1-Buten und 7000 g mol^{-1} liegt. Zudem können die verwendeten Transferagenzien unterstöchiometrisch eingesetzt werden, wodurch eine enorm effiziente Oligomerisierungsreaktion möglich ist. Die gezielte Einflussnahme auf die

Produktverteilung stellt einen enormen Vorteil gegenüber etablierter Oligomerisierungsprozesse dar.

2. Summary

This thesis introduces the development of a novel and highly flexible process for the nonselective oligomerization of ethylene to linear α-olefins (LAO). The ability to separate chain growth from chain termination reactions in time and space enables the realization of enormous production flexibility. An easy and flexible product adjustment can be achieved through the selective influence on partial reaction rates.

Herein, the (quasi) separation of the partial reactions by the combination of two catalysts, which are specialized in the respective reaction, is described. The chain growth from ethylene is mediated by coordinative chain transfer polymerization (CCTP) catalysts and the resulting alkyl chains are transferred on a chain transfer agent (CTA) based on Al or Zn. Another catalyst, based on nickel, catalyzes the chain termination step (β-H elimination/transfer), that could be understood as a chain displacement reaction. The CTA bound alkyl chain gets displaced by ethylene and the corresponding alpha olefin is obtained. The chain transport between the two catalysts is mediated by the CTA (Scheme 1 a). The LAO can, thus, be produced from ethylene extremely flexible and highly efficient in a one-pot tandem reaction. The partial reactions were investigated in detail.
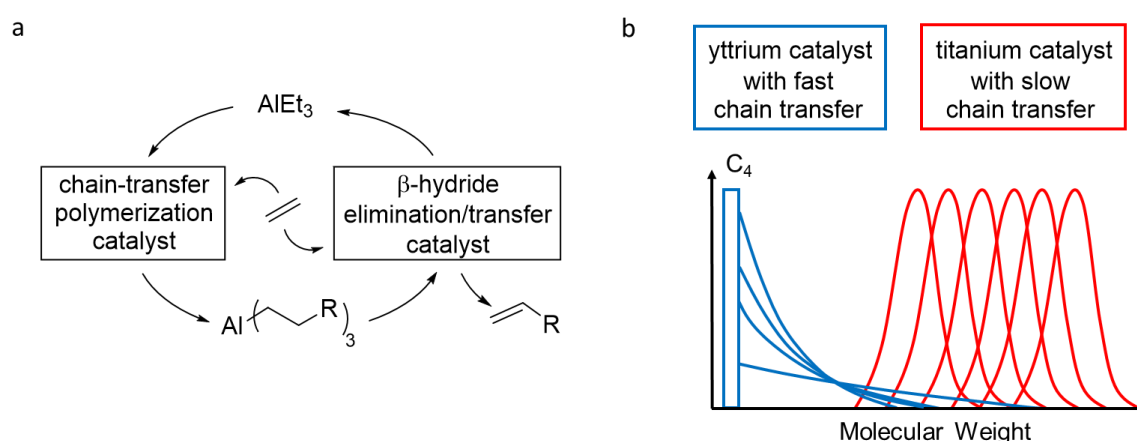
Scheme 1. a) Combination of a CCTP catalyst with a nickel-based displacement catalyst for the production of LAO from ethylene. b) The average molecular weight depends on the chain transfer rate of the CCTP catalyst used.

The CCTP catalysts were examined in polymerization experiments without nickel, whereas the nickel-catalyzed chain termination reaction was described by ^{1}H NMR experiments.

Kinetic ^{1}H NMR studies of the nickel(0)-catalyzed chain displacement reaction showed a first order reaction, depending on the Al or Ni concentration.

A CCTP system based on yttrium(III)/triethylaluminum (TEA) showed a reversible chain transfer polymerization with very high transfer rates in the polymerization of ethylene without nickel.

LAO could be obtained in the tandem reaction of CCTP and the nickel-catalyzed displacement reaction, which follow a Schulz-Flory distribution. The distribution of the resulting LAO can be regulated with outstanding flexibility by altering the process parameters (ethylene, Al, Y and Ni concentration). Thus, product distribution can be adjusted from 1-butene (90 mol-%) to LAO with an average molecular weight of 850 g mol^{-1}. Furthermore, Al alkyls can be re used in a single batch experiment up to 78 times (TON), which increases the efficiency of the system significantly.

Next, a titanium(IV)/TEA-based CCTP system was applied to produce Al capped alkyls chains from ethylene by irreversible chain transfer. The Ti catalyst shows low chain transfer rates and the products show a comparatively high molecular weight and polydispersities (M_w/M_n) of about 2.

Relatively long-chain LAO were could thus be obtained in the tandem reaction with nickel. LAO with an average molecular weight from 260 g mol^{-1} to 7000 g mol^{-1} can be synthesized by altering the ethylene pressure and the aluminum concentration. This system, with a half-life of 126 min, has an outstanding long-term stability, and the Al alkyls applied can also be used substoichiometrically.

As we showed, the chain transfer rate of the CCTP catalyst has a decisive influence on the molecular weight of the products (Scheme 1 b). Another option to influence the product distribution in the tandem reaction is the application of several CTAs, since the chain transfer rate is strongly dependent on the CTA. Consequently, a catalyst system based on zirconium(IV)/TEA/DEZ (diethylzinc) was developed.

CCTP experiments with an aminopyridinato/cyclopentadienyl ligand stabilized Zr-based catalyst with TEA as the CTA showed an irreversible chain transfer behavior with a relatively low chain transfer rate between Zr and Al. The products show a molecular

weight of M_n = 3000 g mol^{-1} (M_w/M_n = 1.6). A significantly lower molecular weight of the products (M_n = 2200 g mol^{-1}, M_w/M_n = 1.2), was observed in CCTP experiments with the additional presence of DEZ as CTA. This indicates a reversible and much faster chain transfer between Zr and Zn.

Similar differences in reaction behavior of the nickel catalyzed chain transfer reaction were found. ^{1}H NMR experiments under equal conditions showed that chain displacement reaction of aluminum alkyls is quantitative and 70 times faster than the corresponding reaction of zinc alkyls.

Comparatively long-chain LAO (C$_{40+}$) are obtained without zinc alkyls in the tandem reaction due to chain transfer is slow between Zr and Al. Much shorter chained products (C$_4$-C$_{30}$) are obtained in the presence of zinc alkyls. Consequently, the product distribution can be flexibly adjusted by the concentrations of zinc and aluminum alkyls.

Ethylene can be oligomerized very flexibly to almost any molecular mass average desired between 1-butene and 7000 g mol^{-1} using the systems presented. In addition, the CTAs can be applied substoichiometrically, which increases the efficiency of the oligomerization reaction.

3. Introduction

The oligomerization of ethylene to linear alpha olefins (LAO) is one of the most important transition metal-catalyzed reactions in the petrochemical industry with an annual production of several megatons and still an intensively investigated field of interest. Ethylene can be produced very easily on a large scale and can be converted into high priced products by oligomerization. Most industrial oligomerization processes are mediated by transition metal catalysts, which perform chain growth and chain termination reactions equally. The product distribution is catalyst-specific and often results in a relatively low adjustability of the molecular weight distribution. Once a process has been implemented, there are only limited possibilities to react to the fluctuating product demands. The simple and tailor-made product synthesis to customer requirements is a constantly increasing demand on new synthesis methods.[1–3] Great efforts have been expended to increase the product selectivity as well as the catalyst activity and lifetime over the past 50 years. The main application for LAO are as co-monomers for the production of polyethylene, lubricants, detergents, plasticizers, oil field and fine chemicals (Figure 1).[4]
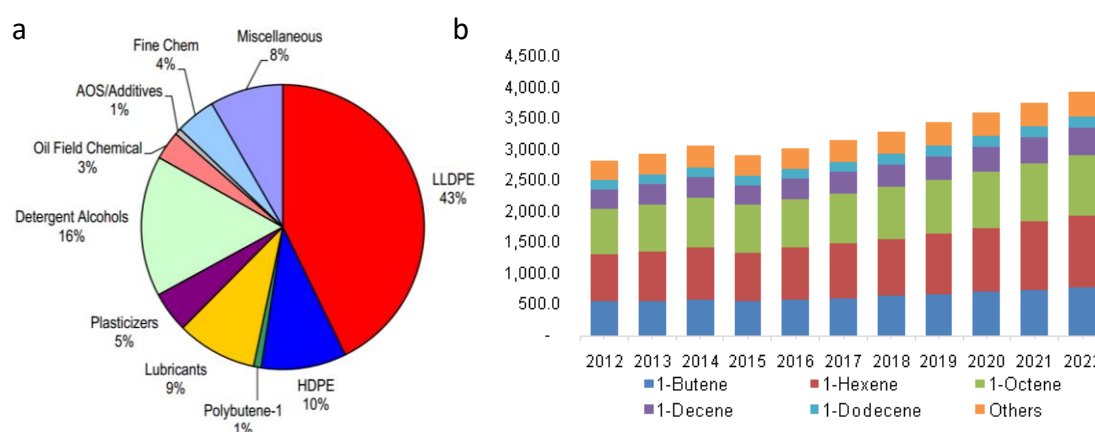

Figure 1. a) Global alpha olefin demand by end use.[5] b) Alpha Olefin market revenue (USD billion)[6]

In 1966, the Gulf Oil Company (Chevron Phillips) developed the first industrial one-step process based on triethylaluminum. Process parameters are adapted in a way that chain growth and chain termination take place equally and products matching a Schulz-Flory[7] distribution are obtained. A two-step process, which implements the recycling of

1-butene, was developed by the Ethyl Company (Ineos) a few years later.[8] Reaction parameters which favor a chain growth are applied in a first reaction step. By increasing the reaction temperature afterwards, the chain displacement is favored and Poisson-distributed LAO can be produced. In the 1970s, the Shell Company developed the Shell Higher Olefin Process (SHOP) for the synthesis of LAO from ethylene with a nickel-based catalyst in a biphasic reaction medium. Subsequent isomerization and olefin metathesis reactions are conducted to realize a better product adjustment. In 1989, Idemitsu Kosan Do. Ltd. commercialized a Zr(IV)-based oligomerization process for the nonselective oligomerization of ethylene. In 2006, the α-Sablin process, based on a Zr(IV)/Al catalyst system, was introduced by Linde and Saudi Basic Industries (SABIC). The Institut Français du Pétrole Energies Nouvelles (IFPEN) developed a catalyst system (Alphaselect) with a similar metal composition. The product distributions from these three processes match a Schulz-Flory distribution. In 2014, Chevron Philips, Ineos and Shell produced almost 90 % of the world's LAO consumption. Nevertheless, the highly lucrative reaction drove the development of many different processes for the oligomerization of ethylene (Table 1).

Table 1. Overview of the most important oligomerization processes of ethylene.[2,3]

| Process	Company	Metal	Co-Catalyst	Product(s)	Distribution
Alphabutol	IFP	Ti	$AlEt_3$	1-Butene	
DIMERSOL	IFP	Ni	$EtAlCl_2$	1-Butene	
	Chevron/Phillips	Cr	$EtAlCl_2/Et_2AlCl$	1-Hexene	
Sasol	Sasol	Cr	MAO	1-Hexene/1-Octene	
Alphaselect	IFP	Zr	$EtAlCl_2/Et_2AlCl$	α-Olefins ($C_4 - C_{10}$)	SF (α = 0.2–0.5)
Linear-1	UOP	Ni	$NaBH_4$ (biphasic)	α-Olefins ($C_4 - C_{10}$)	SF (α = 0.55–0.67)
Linealene	Idemitsu	Zr	$EtAlCl_2/Et_2AlCl$	α-Olefins ($C_4 - C_{24}$)	SF
	Chevron/Phillips	Al	$EtAlCl_2/Et_2AlCl$	α-Olefins ($C_4 - C_{30}$)	SF (α = 0.5–0.75)
α-SabLin	Sabic/Linde	Zr	$EtAlCl_2/Et_2AlCl$	α-Olefins ($C_4 - C_{30+}$)	SF (α = 0.4–0.8)
SHOP	Shell	Ni	none (biphasic)	α-Olefins ($C_4 - C_{30+}$)	SF (α = 0.75–0.8)
Ethyl	INEOS	Al	$AlEt_3$	α-Olefins ($C_4 - C_{30}$)	Poisson

SF = Schulz-Flory, α = alpha value

In principle, there are two major ethylene oligomerization reaction pathways, named after their products. The *selective ethylene oligomerization* pathway formally produces one single product (1-hexene or 1-octene) in high yields (Scheme 2).[9]
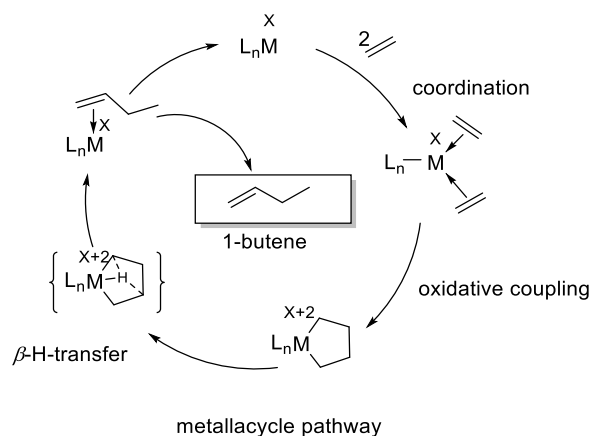
Scheme 2. Metallacycle reaction pathway for the selective oligomerization of ethylene.[2]

The first step of the metallacycle pathway is the coordination of two ethylene monomers, followed by the formation of a metallacycle from oxidative coupling, which increases the oxidation state by two. At this stage, further monomer insertions into the metal-carbon bond, are possible. The next reaction step is a concerted β-hydride/reductive elimination, where the metal center is reduced to its original oxidation state and the α–olefin is formed through decoordination.[10]

By contrast, oligomerization processes can be *nonselective* and a mixture of alpha olefins is obtained, which can be described mostly by a Schulz-Flory distribution (Scheme 3a).[10,11,12] The second ethylene oligomerization pathway can be described by a degenerative polymerization (Cossee-Arlman)[13] mechanism, paired with a relatively fast β-hydride elimination. After each monomer insertion step, the catalyst can catalyze another ethylene insertion (chain propagation) or a β-hydride elimination (chain termination). The product distribution is dependent on the propagation probability (α–value) and/or the termination probability (1-α) (Scheme 3b).
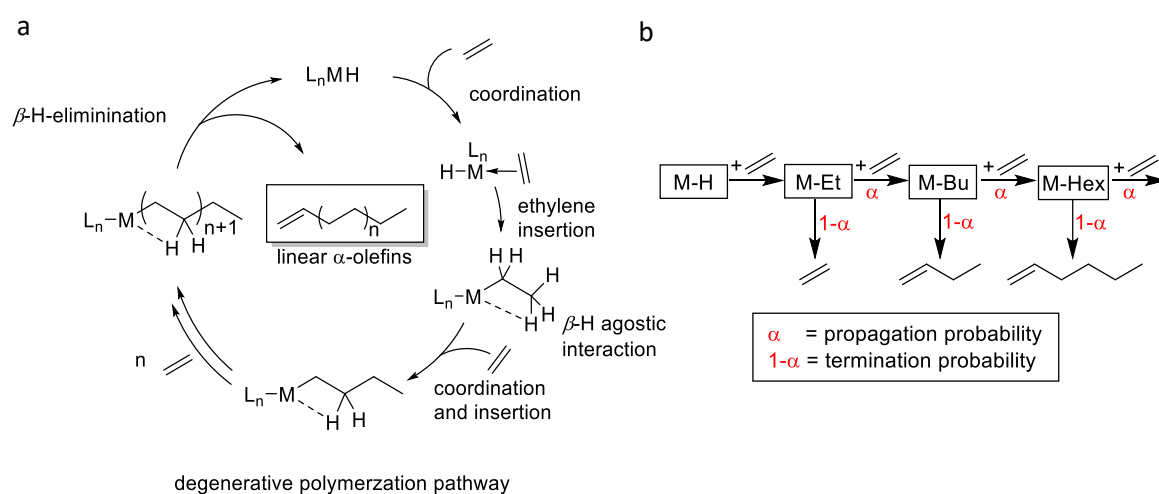
Scheme 3. a) Degenerative polymerization reaction pathway for the selective oligomerization of ethylene. b) Illustration of the propagation and termination probabilities.

The propagation probability α is used to describe the Schulz-Flory distribution (Equation 1).[12]

$$C_p = c \cdot (1 - \alpha) \cdot \alpha^{(n-1)} \tag{1}$$

C_p is the quantity of moles of α-olefin with *n* monomer units inserted, α is the probability of chain propagation and *c* is the total quantity (moles) of α-olefins produced. The Schulz-Flory distribution is described as a first order linear homogeneous recurrence relation with constant parameters. Figure 2 illustrates the influence of different propagation probabilities on the product distribution.
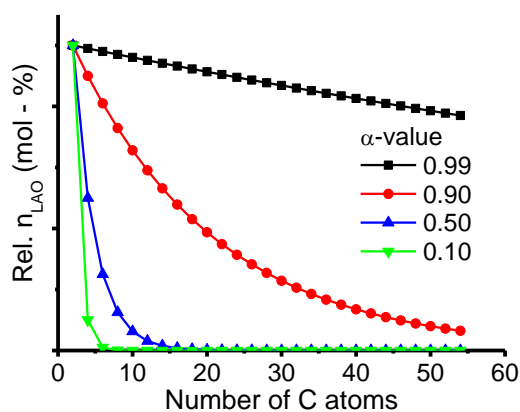

Figure 2. Examples of Schulz-Flory-like olefin distributions for different α-values.

A conceptually new approach to gain a high flexibility of the oligomerization process is to separate the chain propagation from the chain termination step in time and space by applying one catalyst for each partial reaction. The reaction rates can be tuned independently by separation and the product distribution can be varied over a broad range.

A coordinative chain transfer polymerization (CCTP) protocol for the insertion (chain propagation) step is applied. This technique is normally used for the polymerization of ethylene in a highly controlled way to produce narrowly distributed main group metal- (or Zn-) terminated polymer chains. The CCTP is conducted by a polymerization catalyst which can produce alkyl chains by degenerative ethylene insertion polymerization (chain growing state: CGS) followed by a coordinative chain transfer (chain transfer state: CTS)

to a chain transfer agent (CTA; Scheme 4). The most common CTAs are Al[14], Mg[15] and Zn[16,17] alkyls.[18] These end capped products can be used for further functionalization.[19]
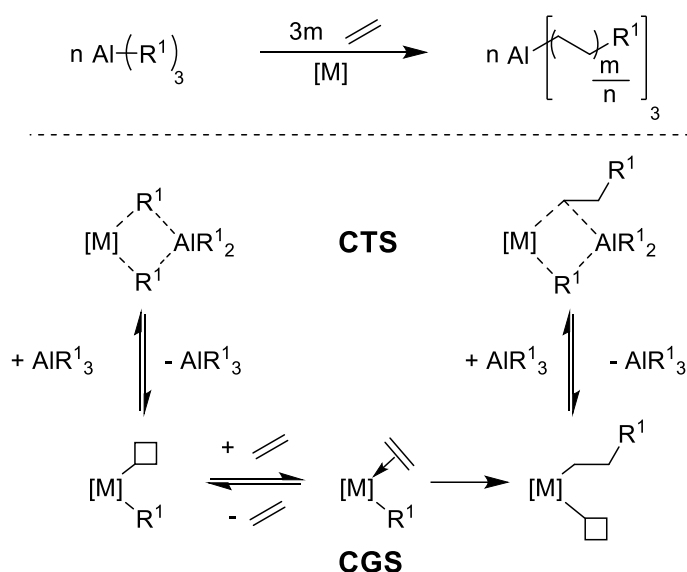

Scheme 4. Net reaction and mechanism of the CCTP of ethylene with aluminum alkyls as the CTA. The catalyst can be switch between two states: CTS (chain transfer state) and CGS (chain growing state). [M] = transition or rare earth metal complex. R^1 are alkyl groups.

We focus here on the reaction of aluminum alkyls with a nickel-based displacement catalyst which can displace aluminum bound alkyls with ethylene via β-hydride elimination/transfer to produce the corresponding α-olefin and triethylaluminum (Scheme 5).[20] The *"Nickeleffekt"* was first mentioned by Ziegler and co-workers in 1955.[21] During an *"Aufbaureaktion"* experiment, 1-butene was produced after one of Ziegler's co-workers left impurities of nickel in the autoclave. Since then, the *"Nickeleffekt"* has been investigated intensively and in addition to Ni, displacement catalysts based on Co[22], Fe[23] and Pt[24] were also described.[25]
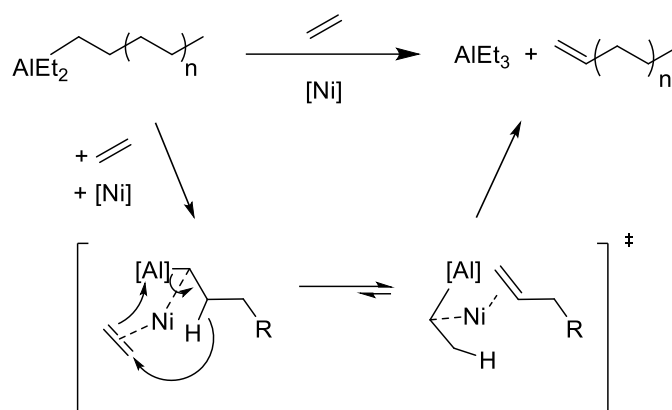
Scheme 5. Example of the nickel catalyzed displacement (β-hydride elimination/transfer) reaction.

Combined with the CCTP of ethylene, the "*Nickeleffekt*" can be utilized as the chain terminating step. The highly flexible oligomerization of ethylene is performed in a one-pot tandem reaction. The chain transport between both catalysts is realized by the CTA (Scheme 6).
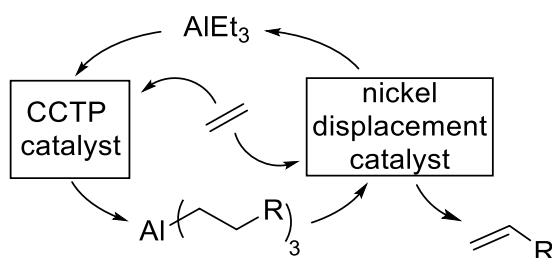

Scheme 6. Example of the combined reaction of a CCTP catalyst and a nickel-based displacement catalyst to produce LAO from ethylene with TEA as the CTA.

The first approach of this tandem reaction was reported by the group of Gibson.[17] In a first step, an iron-catalyzed CCTP of ethylene was performed with diethyl zinc as the CTA. In the next step, the zinc-terminated alkyls were displaced by the addition of [Ni(acac)$_2$] as the displacement pre-catalyst in an ethylene atmosphere. After five hours, 90 % of the alkyls bound to zinc were displaced by ethylene and the corresponding LAO were obtained (Scheme 7).
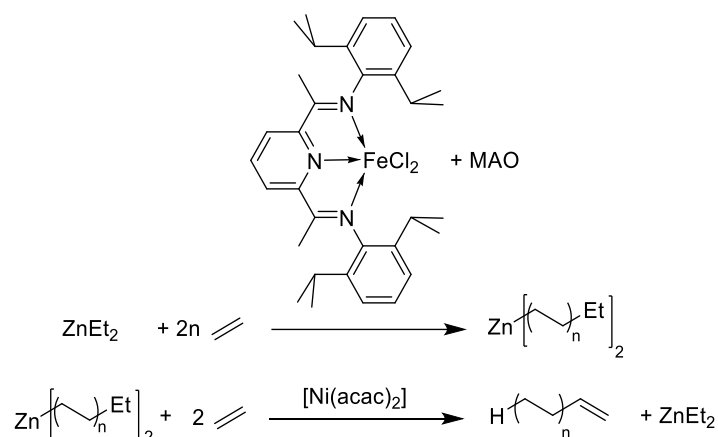
Scheme 7. The combination of an iron-catalyzed CCTP and nickel-catalyzed displacement reaction to produce linear α-olefins in a two-step procedure reported by Gibson and co-workers.[17]

Cariou and Shabaker used the same iron CCTP pre-catalyst in combination with an iron-based displacement catalyst to obtain LAO in a one-pot tandem reaction.[23] A very slow chain displacement reaction rate yielded products with a multimodal distribution. Furthermore, poisoning of the CCTP catalyst by the displacement catalyst was observed (Scheme 8).
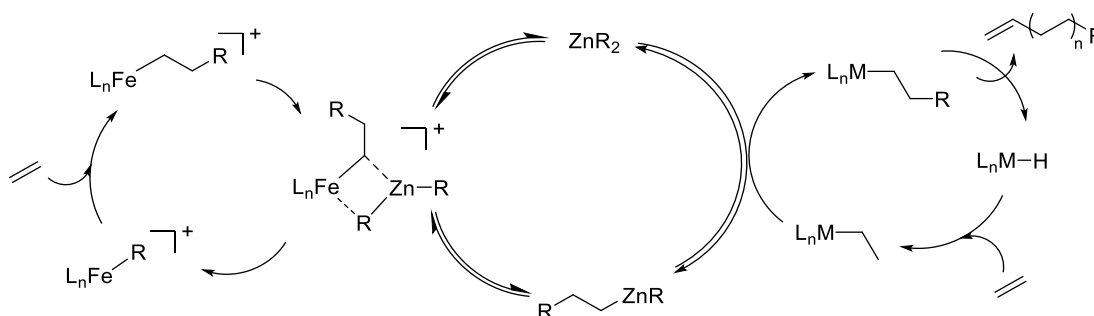
Scheme 8. Tandem Fe-catalyzed CCTP and displacement reaction to produce LAO in a one-pot reaction.

Only a few examples of this tandem reaction have been published in literature and we became interested to see whether the concept has a potential to be established in a new process. The main topic of this thesis is the development of a process based on CCTP catalysts in combination with nickel-based displacement catalysts to produce LAO from ethylene in a highly flexible and efficient way by applying the reactants and catalysts substoichiometrically. The influence of the transfer rate from the CCTP catalyst to the CTA

and the displacement rate of aluminum and zinc alkyls on the product distribution obtained were investigated.

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4. Synopsis

This thesis contains three publications which are presented in chapters 6 – 8. Two are published and one has been submitted.

During the last few years, the Kempe group has focused on the development of highly active CCTP catalysts for the synthesis of aluminum-capped oligo-/polyethylenes. Under CCTP conditions, ethylene can be polymerized with a high control of the molecular weight obtained. Since nickel is known to catalyze the β-hydride elimination/transfer step of aluminum alkyls, which normally occurs at elevated temperatures, we became interested to see whether both reactions can be combined in a one-pot reaction (Figure 3a).
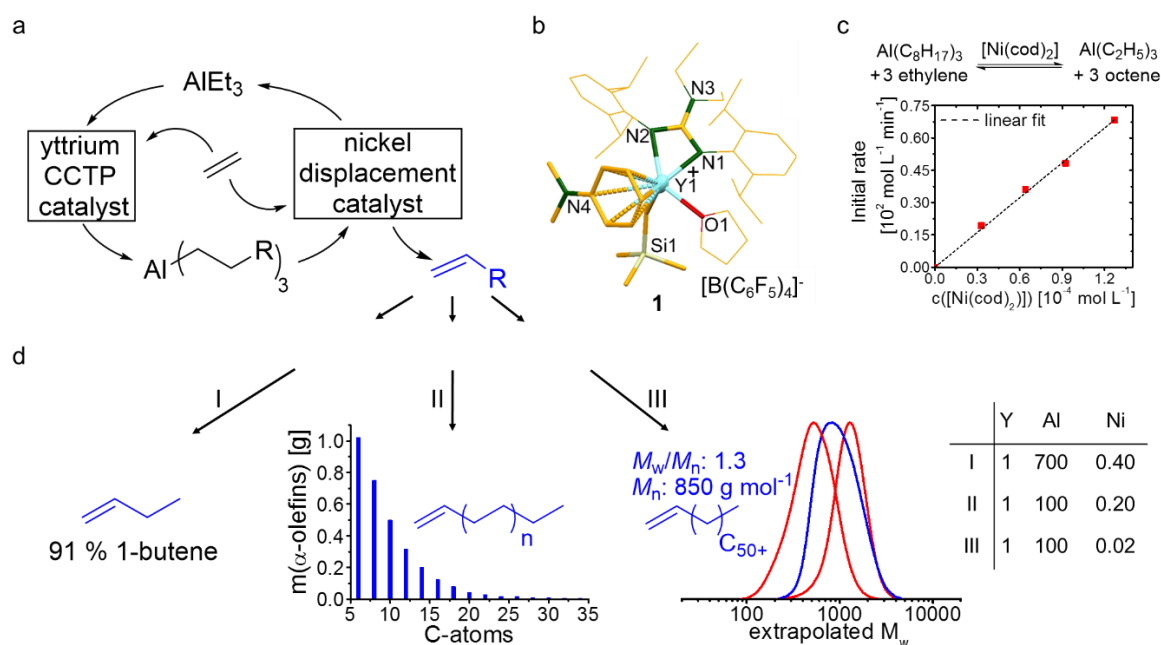
Figure 3. A broadly tunable synthesis of linear α-olefins applying a trimetallic catalyst system. (a) The combination of an yttrium coordinative chain transfer polymerization (CCTP) catalyst, triethylaluminum (TEA), and a nickel chain displacement catalyst (β-H elimination/transfer) permits the highly flexible formation of α-olefins via variation of the rates of the two catalytic steps. It is not essential that all three ethyl groups on aluminum are displaced; partial chain exchange to Al can be sufficient. (b) Molecular structure of the yttrium catalyst determined by X-ray single crystal structure analysis. (c) Kinetic investigations (^{1}H NMR spectroscopy-based) of the [Ni(COD)$_2$]-catalyzed octyl chain displacement reaction of Al alkyls. Plot of the initial rates versus different Ni catalyst concentrations indicating the reaction is first order regarding Ni. (d) Product scope. Variation of the concentrations of the catalysts and TEA lead to extremely different products, such as 91 % selective 1-butene (I), adjustable Schulz-Flory α-olefin distributions (II) or III olefin distributions (blue) similar to Poisson distributed products of the pure CCTP

runs (red). The corresponding Y-Al-Ni ratios (I-III) responsible for these different products are given in the table.

Therefore, an Y(III)-based CCTP catalyst was synthesized and characterized. Single crystal structure analysis showed that the free coordination site is stabilized by η^6-coordination of *N*,*N*-dimethylaniline, which is part of the activator applied (Figure **3**b).

In CCTP experiments, the catalyst showed a living, very fast and reversible chain transfer polymerization of ethylene with triethylaluminum as the CTA. Consequently, the products showed a narrow dispersity of the molecular weight after acidic workup. Furthermore, the activity of the catalyst showed an inverse first order dependence on the Al concentration.

After the chain growing step could be described, various Ni precursor complexes (nickel(II)acetylacetonate, nickel(II)stearate and bis(cyclooctadiene)nickel(0)) were added to the CCTP runs. The products were analyzed by gas chromatography and ^{1}H NMR. The overall activity of the trimetallic system was not reduced and, in most cases, LAO could be obtained. The precursor Ni(COD)$_2$ showed the best performance regarding the yield (alkanes to alkenes) and purity (internal to terminal) of the α-olefins.

The kinetics of the Ni^0-catalyzed chain displacement reaction of aluminum alkyls was investigated separately by ^{1}H NMR. The knowledge about the reaction order in catalysis is an important information to be able to influence the product distribution. Therefore, different Ni and Al concentrations were placed in a J. Young NMR valve with tube attached, followed by ethylene condensation. The displacement reaction was started by warming to room temperature and the reaction was monitored. The results revealed a first order dependence of the Al and Ni concentration on the initial rate (Figure 3c). The displacement rate during further tandem reactions can, thus, be easily tuned by varying the Ni concentration.

Next, the catalysts and Al alkyls were combined to produce LAO matching a Schulz-Flory distribution and we became interested to determine to which extent the α-value of the LAO obtained can be tuned. Therefore, the ethylene, Al, Ni and Y concentrations were

adjusted separately and their influence on the product distribution was examined (Figure 3d).

The ethylene concentration influences the insertion rate of the CCTP catalyst, which results in an increasing propagation probability with increasing ethylene pressure and vice versa. Therefore, the α-value is directly dependent on the ethylene pressure.

By increasing the Ni concentration, the displacement rate is increased and, therefore, the termination probability. Consequently, the α-value is indirectly dependent on the nickel concentration.

Higher Y concentrations lead to the formation of LAO distributions with higher α-values due to the more active catalyst in the solution and, therefore, the propagation probability is increased. The α-value of the products, is directly dependent on the Y concentration.

By increasing the Al concentration, the catalyst is preferably in the chain transfer state during the tandem reaction. Consequently, the propagation probability is reduced due to an increase of the chain transfer rate. Therefore, the α-value is inversely dependent on the Al concentration. Higher Al concentrations lead to the formation of products with comparatively lower molecular weight.

Overall, we are able to adjust the product distribution from 90 mol-% 1-butene to the formation of α-olefins with an average molecular weight of about 850 g mol^{-1}, covering nearly the whole range of the short-chain Schulz-Flory regime. In conclusion, the Y catalyst exhibits a very high chain transfer rate and, therefore, comparatively low molecular weight LAO are obtained. Furthermore, the aluminum alkyls applied can be used substoichiometrically and recycled up to 78 times within one tandem.

After we had gathered information about the Y-Al-Ni trimetallic system, we became interested to see whether we could extend the product range to higher molecular weight LAO. These products can be functionalized easily and applied as compatibilizers for the recycling of PE materials, an upcoming application which is becoming more important due to the increase of plastic waste. Therefore, a Ti-based CCTP catalyst which exhibits a low chain transfer rate was applied in the tandem reaction (Figure 4a). A low transfer rate

(and a comparatively high propagation probability) should lead to LAO with a distinctively higher molecular weight compared to the products formed by the Y-Al-Ni system.

The CCTP experiments of ethylene and TEA as CTA showed that the Ti catalyst can produce Al-terminated alkyls by an irreversible chain transfer polymerization. Experiments with various Al concentrations showed an inverse dependency on the molecular weight of the products.

Next, screenings of process parameters were conducted to quantify their influence on the product distribution (Figure 4b).
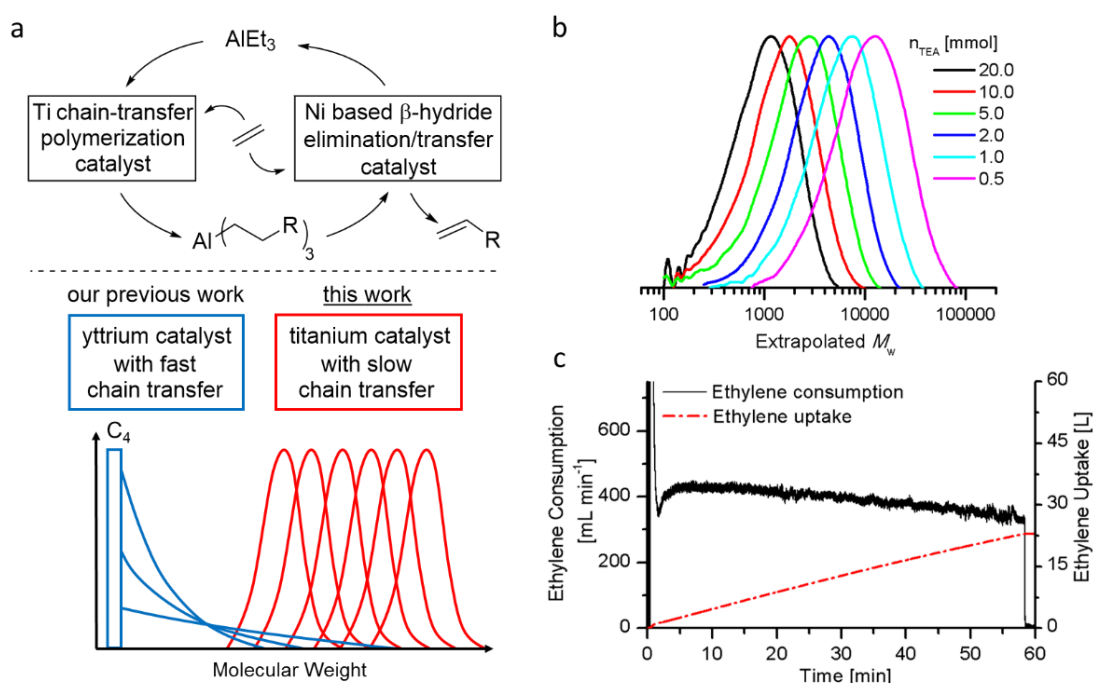
Figure 4. a) The novel trimetallic linear α-olefin (LAO) synthesis concept, the previous work (bottom left, blue LAO products) and the synthesis of various LAO distributions with flexible mean molecular weight (bottom right, red). b) Normalized molecular weight distributions of the LAO that can be obtained by varying the Al concentration. c) Ethylene consumption for the high yield synthesis of LAO with the Ti-Al-Ni catalyst system. The half-life of the catalyst system, assuming a linear decay, is 126 min.

A variation of the ethylene pressure showed a direct dependency on the propagation probability and an increase in ethylene pressure yields in the formation of products with a higher molecular weight.

By varying the Ni concentration, no influence on the chain length was observed due to the irreversible chain transfer behavior of the Ti catalyst. Nevertheless, the α-olefin content can be increased by increasing the amount of Ni. Compared to the Y-Al-Ni system, overall higher Ni concentrations have to be applied because displacement of the Al alkyl chains has to be accomplished before precipitation.

An alteration of the Ti concentration gave no modification of the molecular weight of the products under the conditions applied.

The propagation probability is reduced by increasing the Al concentration due to the increase of the chain transfer rate. Consequently, the molecular weight of the LAO obtained is inversely dependent on the Al concentration and a decrease in molecular weight can be observed by increasing the Al concentration. LAO showing an average molecular weight of 260 g mol^{-1} (closing the gap to the Y-Al-Ni system) could be obtained with a high Al concentration and an additionally low ethylene pressure. An uptake of 19 liters of ethylene with 0.5 µmol of Ti within 60 min could be observed in an upscaling experiment. The catalytic system is remarkably stable in the long-term and the half-life, assuming a linear decay, is 126 min with a turnover number of Al alkyls of 4.2 per Al chain (Figure 4c). With this Ti-Al-Ni system LAO showing a M_n between 260 and 7000 g mol^{-1} can be produced flexibly.

Ethylene can be oligomerized with both systems in a highly flexible and efficient manner to any distribution within the range of 1-butene to olefins showing a M_n of 7000 g mol^{-1}. The most effective way to adjust the product distribution in both systems is to influence the chain propagation probability of the CCTP catalyst by varying the Al concentration. Therefore, we became interested to see whether there are any differences in the chain transfer rate (and, thus, the chain propagation rate) to other CATs, such as Zn alkyls. In addition to Al, Zn is one of the most frequently used CTA in CCTP and is known to show a different chain transfer behavior. Therefore, we introduced a new CCTP system with two CTAs, namely TEA and DEZ, and investigated the product distribution. Furthermore, we became interested to see whether there are any differences in the displacement rate between Al and Zn.

Three Zr-based catalysts were synthesized and characterized and suitable crystals for Xray single crystal structure analysis could be obtained by crystallization from supernatant toluene solution at -30 °C (Figure 5a).
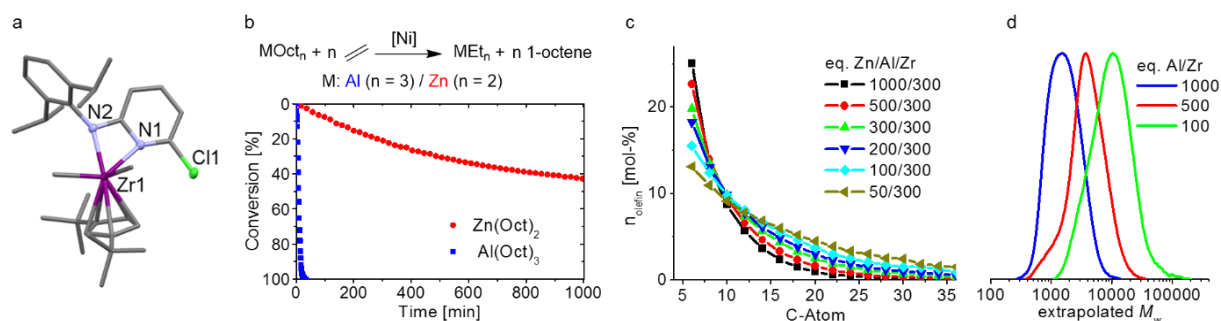

Figure 5. a) Molecular structure of a pre-catalyst applied in the CCTP and tandem catalysis. Hydrogen atoms are omitted for clarity. b) Conversion over time plot of the nickel-catalyzed chain displacement reaction of Al(Oct)$_3$ and Zn(Oct)$_2$. c) α-Olefin distribution of the products by the combination of Zr-Al-Zn-Ni. d) Molecular weight distribution of the products by the combination of Zr-Al-Ni.

Polymerization experiments with Al and Zn alkyls were conducted to find a suitable CCTP catalyst and the catalyst showing the best activity was chosen for further reactions.

If only Al alkyls were present in CCTP experiments, products with comparatively high molecular weight were obtained (M_n > 3000 g mol^{-1}). The CCTP catalyst did not show any activity in the presence of only Zn alkyls.

If Al and Zn alkyls were applied, the products showed a remarkably lower average molecular weight (2200 g mol^{-1}). Time-dependent CCTP experiments showed a growing molecular weight if Zn alkyls are applied additionally. The results indicate a fast and reversible chain transfer to Zn and a slow and irreversible behavior to Al.

We became interested to see whether there are also any differences between Al- and Zn-bound alkyls in the nickel-catalyzed chain displacement reaction and performed kinetic studies, which were monitored by ^{1}H NMR (Figure 5 b). The results showed that the initial rate of the displacement reaction of Al-bound alkyls is almost 70 times higher than that of Zn-bound alkyls. Furthermore, the conversion is quantitative after 25 min for Al alkyls under the equal conditions. A tandem reaction mediated solely by Zn alkyls would afford quite high amounts of Ni to ensure a fast and quantitative displacement of all Zn-bound alkyls.

Next, tandem reactions in the presence of Zn and/or Al alkyls were performed to examine the influence of the CTAs and mixtures of them on the product distribution. The alteration of the Zn-to-Zr ratio between 100 and 1000 maintaining a constant Al-to-Zr ratio of 300 allows the synthesis of low molecular weight LAO showing α-values ranging from 0.72 to 0.87. A decreasing α-value is observed with increasing Zn alkyl concentrations (Figure 4 c). α-Olefins showing a high molecular weight are obtained if solely Al alkyls are applied and a decreasing M_n with an increasing Al concentration was observed (Figure 4 d). Overall, short chain LAO can be obtained in the presence of both CTAs, long chain LAO can be obtained in the sole presence of Al alkyls.

5. Individual Contribution to Joint Publications

The publications and manuscripts in this thesis were realized by collaboration with colleagues. The individual contributions of the co-authors are mentioned below. The corresponding author is marked by the asterisk.

5.1 Chapter 6

This work is published in Nature Communications (*Nature Commun.,* **2017**, *8*, 1226), with the title

"A broadly tunable synthesis of linear α-olefins".

Authors: Andreas Gollwitzer, Thomas Dietel, Winfried P. Kretschmer, Rhett Kempe*

I synthesized and characterized the CCTP pre-catalysts. Furthermore, I conducted all catalytic experiments and did the analysis. Thomas Dietel did the single Xray analysis of the applied catalyst complex and solved the crystal structure. Winfried P. Kretschmer conducted the high temperature gel permeation chromatographic measurements.and analysis. Rhett Kempe and I designed and planned all experiments. The publication was written by me and Rhett Kempe who supervised the work.

5.2 Chapter 7

This work is published in Organometallics (*Organometallics* **2018***, 37,* 2395–2398), with the title

"Synthesis of Linear α-Olefin Distributions with Flexible Mean Molecular Weight by a Ti-Al-Ni Catalyst System".

Authors: Andreas Gollwitzer, Winfried P. Kretschmer, and Rhett Kempe*

I conducted all the catalytic experiments and did the analysis. Winfried P. Kretschmer conducted the high temperature gel permeation chromatographic measurements and analysis. Rhett Kempe and I designed and planned all experiments. The publication was written by me and Rhett Kempe who supervised the work.

5.3 Chapter 8

This work is submitted to Dalton Transactions with the title

"Tailor-made α-Olefins by Coordinative Chain Transfer Polymerization, Displacement Reaction and Two Chain Transfer Agents".

Authors: Andreas Gollwitzer, Winfried P. Kretschmer, and Rhett Kempe*

I synthesized the CCTP pre-catalysts, conducted the catalytic experiments and did the analysis. Winfried P. Kretschmer conducted the high temperature gel permeation chromatographic measurements and analysis. Thomas Dietel did the Xray crystal structure analysis. Rhett Kempe and I designed and planned all experiments. The publication was written by me and Rhett Kempe who supervised the work.

6. A broadly tunable synthesis of linear α-olefins

Authors: Andreas Gollwitzer, Thomas Dietel, Winfried P. Kretschmer, Rhett Kempe*
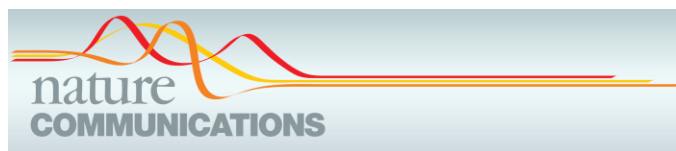
ARTICLE

A broadly tunable synthesis of linear α-olefins

Andreas Gollwitzer [1], Thomas Dietel [1], Winfried P. Kretschmer[1] & Rhett Kempe [1]

The catalytic synthesis of linear α-olefins from ethylene is a technologically highly important reaction. A synthesis concept allowing the formation of selective products and various linear α-olefin product distributions with one catalyst system is highly desirable. Here, we describe a trimetallic catalyst system (Y–Al–Ni) consisting of a rare earth metal polymerization catalyst which can mediate coordinative chain transfer to triethylaluminum combined with a simultaneously operating nickel β-hydride elimination/transfer catalyst. This nickel catalyst displaces the grown alkyl chains forming linear α-olefins and recycles the aluminum-based chain transfer agent. With one catalyst system, we can synthesize product spectra ranging from selective 1-butene formation to α-olefin distributions centered at 850 gmol^{-1} with a low polydispersity. The key to this highly flexible linear α-olefin synthesis is the easy tuning of the rates of the Y and Ni catalysis independently of each other. The reaction is substoichiometric or formally catalytic regarding the chain transfer agent.

[1] Lehrstuhl für Anorganische Chemie II—Katalysatordesign, Universitätsstr. 30, Universität Bayreuth, 95440 Bayreuth, Germany. Correspondence and requests for materials should be addressed to R.K. (email: kempe@uni-bayreuth.de)

ARTICLE

The oligomerization of ethylene to linear α-olefins (LAOs) is an important industrial process with an increasing annual total world production of multiple megatons[1]. It is one of the most important technological applications of homogeneous catalysis and, thus, intensively investigated in industry and academia[2–5]. The LAOs produced range from 1-butene to various product distributions and are used to produce detergent alcohols, lubricants, plasticizers, fine and oil field chemicals, and as co-monomers for polyethylenes[2–5]. Highly flexible syntheses of LAOs with just one catalyst system would be highly desirable to match the frequently changing market demands. Coordinative chain-transfer polymerization (CCTP)[6–8], a polymerization protocol characterized by polymeryl chain-transfer between dormant states of a chain-transfer agent (CTA) and a polymerization catalyst responsible for the chain growth, allows the controlled polymerization of ethylene towards metal-terminated poly-ethylenes. A fundamental problem associated with CCTP is the inverse first-order dependence of the rate of the chain growth from the CTA concentration, which restricts the number of chains that can be grown efficiently by a catalyst molecule, also called (low) catalyst economy[9]. A solution to this problem would be a CCTP process that features a substoichiometric or formally catalytic use of the chain-transfer agent. Gibson and coworkers described the sequential combination of CCTP via chain growth at zinc and the subsequent displacement using a nickel catalyst[10]. In this two-step procedure, product formation is stoichiometric to the Zn alkyl. It was shown recently that the addition of [Ni(acac)₂] (acac-H=pentane-2,4-dione) to the Gibson CCTP catalyst, to run a tandem process, does not influence the CCTP process, as no displacement reaction was observed[11]. The

addition of iron complexes, such as [(bipy)FeEt₂] (bipy=2,2′bi-pyridine, Et=ethyl), permits CTA recycling and result in a poi-soning of the CCTP catalyst in combination with a very slow displacement reaction[11]. A slow displacement reaction reduced the flexibility of the synthesis drastically. We expected that by choosing the right combination of CCTP catalyst, displacement catalyst and CTA, a broadly tunable LAO synthesis process would become feasible which permits the synthesis of different olefin product distributions and selective LAO formation with one catalyst system. Recently, we introduced the corresponding con-cept, the combination of CCTP and alkyl chain displacement via β-H elimination/transfer for α-olefin synthesis[12].

Herein, we report on a highly flexible synthesis of LAO in which a trimetallic catalyst system permits the selective formation of an α-olefin, namely 1-butene, or of various LAO distributions. The catalyst system consists of an yttrium polymerization catalyst able to mediate controlled chain transfer towards triethylalumi-num (TEA) and a Ni complex capable of controlled and efficient β-hydride elimination/transfer of aluminum alkyls of various chain lengths.The key to the broad product spectrum is the independent adjustability of the rates of the Y- and Ni-catalyzed subprocesses. In addition, the two catalysts do not poison each other significantly. Our LAO synthesis protocol is also sub-stoichiometric or formally catalytic regarding Al. Thus, the pro-blem of low catalyst economy or low CTA to catalyst ratios is addressed by efficient CTA recycling.

Results

The trimetallic LAO synthesis concept and catalysts mediating it. The concept is schematically shown in Fig. 1a.
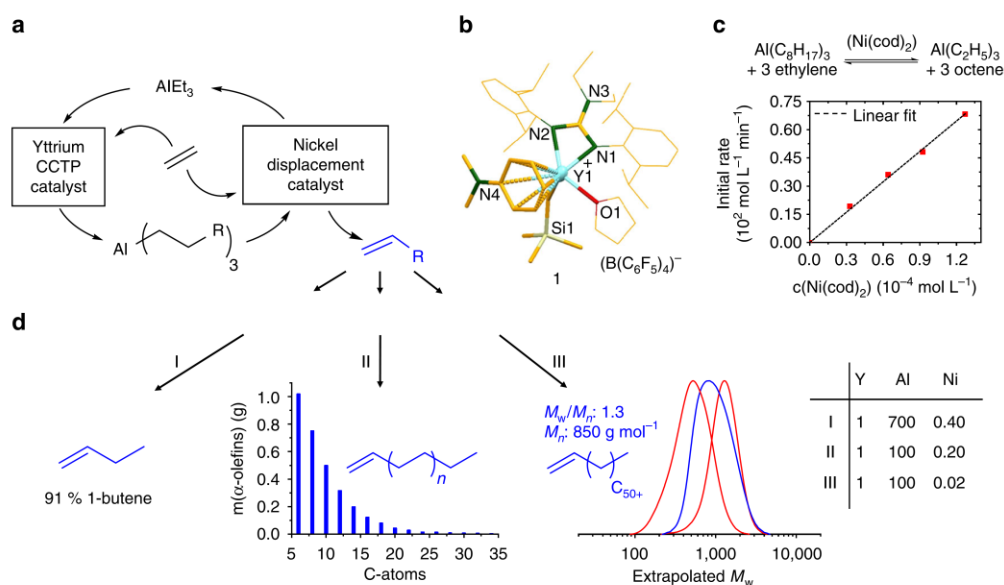
Fig. 1 A broadly tunable synthesis of linear α-olefins applying a trimetallic catalyst system. **a** Combination of an yttrium coordinative chain transfer polymerization (CCTP) catalyst, triethylaluminum (TEA), and a nickel chain displacement catalyst (β-H elimination/transfer) permits the highly flexible formation of α-olefins via variation of the rates of the two catalytic steps. It is not urgent that all three ethyl groups on aluminum are exchanged; partial chain exchange to Al can be sufficient. **b** Molecular structure of the yttrium catalyst **1** determined by X-ray single crystal structure analysis. **c** Kinetic investigations (¹H NMR spectroscopy based) of the [Ni(cod)₂]-catalyzed octyl chain displacement reaction (β-H elimination/transfer) of Al alkyls. Plot of the initial rates (−dc(Al(C₈H₁₇)₃)/dt (10² mol⁻¹ l⁻¹ min⁻¹)) vs. different Ni catalyst concentrations (10⁻⁴ mol l⁻¹) indicating the reaction is first order regarding Ni (slope = 0.5385 ± 0.0080×10⁶ min⁻¹, linear fit: adj. R square = 0.9988). **d** Product scope. Variation of the concentrations of the catalysts and triethyl aluminum (TEA) lead to extremely different products, such as 91% selective 1-butene (I), adjustable Schulz-Flory α-olefin distributions (II) or III olefin distributions (blue) similar to Poisson distributed products of the pure CCTP runs (red, see also Table 1 entries 1 and 2). The corresponding Y–Al–Ni ratios (I–III) responsible for these different products are given in the table

ARTICLE

Table 1 Time-dependent CCTP of ethylene using catalyst 1 and 1 mmol of TEA

$$n \; \diagup\diagup \; \xrightarrow[\text{2) acidic workup}]{\text{1) } \mathbf{1} \text{ / AlEt}_3} \; \diagdown\!\diagup\!\diagdown\!\diagup\!\diagdown_{n-2}$$

Entry	Time (min)	Ni precatalyst	V_{eth} (L)	M_n (g mol^{-1})	α-Olefin content (mol%)	PDI	Productivity[a]
1	5	–	1.8	450	0	1.3	2,700
2	10	–	2.8	1,150	0	1.2	2,100
3	15	–	4.0	1,540	0	1.2	2,000
4	20	–	4.7	1,770	0	1.2	1,750
5	25	–	5.4	2,250	0	1.1	1,620
6	30	–	5.9	2,560	0	1.1	1,400
7	30	[Ni(acac)$_2$]	6.2	n.d.	80	n.d.	1,550
8	30	[Ni(O$_2$CR^1)$_2$]	3.8	n.d.	90	n.d.	970
9	30	[Ni(cod)$_2$]	4.8	n.d.	99	n.d.	1,200

n.d. not determined, R^1 = C$_7$H$_{15}$
Reaction conditions: catalyst **1** (n = 10 μmol), p_{eth} = 9.0 bar, T = 80 °C, n_{TEA} = 1 mmol, V_{tol} = 250 ml
[a]kg$_{ethylene}$ mol$_{cat}^{-1}$ h^{-1}

The yttrium catalyst forms alkyl Al compounds via CCTP starting from TEA and ethylene. In parallel, a displacement catalyst, here Ni-based, recycles the TEA via β-hydride elimination/transfer forming LAOs that match the length of the alkyl chains formed. Thus, CTA can be used substoichiometric or formally catalytic. Not all three ethyl groups on aluminum have to be extended; partial chain exchange to Al and extension can be sufficient. Assuming both reactions are not zero order regarding the catalysts, the variation of the catalyst concentration permits the independent tuning of the rates of one or the other partial reaction, CCTP and displacement. If the rate of the CCTP step is increased and/or that of the displacement step is reduced, short chain LOAs can be produced up to the selective 1-butene formation. Inversely, long chain LOA distributions should be accessible. We expected the use of catalysts based on very different transition metals is crucial, for example, a group 3 and a group 10 metal catalyst, to avoid poisoning between the two catalysts. Both metals show a very different coordination chemistry, and ligands that stabilize one metal only bind weakly to the other. Olefins, for instance, bind comparatively weakly to Y[13]. Thus, the stabilization of the displacement catalyst by olefin ligands would not or only weakly harm the active site of the group 3 metal polymerization catalyst if both catalysts are combined. We used a well-defined yttrium catalyst for the CCTP step[14, 15]. Its molecular structure determined by X-ray single crystal structure analysis is shown in Fig. 1b (Supplementary Fig. 1). Anilinium borate [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] was used to activate the corresponding guanidinato-dialkyl precatalyst (Supplementary Fig. 2) complex. See Supplementary Methods for more information of the synthesis of the CCTP catalyst. Notably, the metal center is stabilized by η^6-arene coordination by *N,N*-dimethylaniline[16]. Controlled CCTP has been observed in toluene in the presence of ethylene (9.0 bar) and TEA (Al/Y=100/1). Samples taken during a CCTP run indicate an increase in the molecular weight of the polyethylene samples obtained over time. A narrow polydispersity indicating a very fast and reversible chain transfer between the CCTP catalyst and the Al-based CTA is observed under the conditions applied (Table 1). Furthermore, different Ni complexes were additionally added to the CCTP run listed as entry 6 in Table 1. The nickel compounds were added as stock solutions in toluene and the products were analyzed after 30 min via gas chromatography, ^{1}H NMR and high temperature gel permeation chromatography.

The best results regarding activity and α-olefin content or selectivity were obtained by using the [Ni(cod)$_2$] (cod=cycloocta-1,5-diene). A comparison of the productivity of the pure CCTP run (Table 1, entry 6) and the tandem process with [Ni(cod)$_2$] as the precatalyst (Table 1, entry 9) revealed no significant catalyst poisoning. No branched or internal olefins were obtained and the linear α-olefins follow a Schulz–Flory distribution[17, 18]. Gas consumption profiles of entry 9 in Table 1 (Supplementary Fig. 11) indicate that the trimetallic catalyst system is still active after 30 min. The half-life of the catalyst system, calculated from this profile assuming a linear decay, is 19 min. We concluded that 30 min is a suitable time for further experiments applying the trimetallic catalyst system. The other Ni-based precatalysts either reduce the activity of the CCTP catalyst or are less selective regarding LAO formation. To find an explanation for the fast and highly selective β-hydride elimination/transfer reaction of aluminum alkyls by [Ni(cod)$_2$], we investigated the conversion of trioctylaluminum into 1-octene and TEA by NMR spectroscopy (Fig. 1c). Trioctylaluminum and [Ni(cod)$_2$] were placed in a Young valve NMR tube followed by the condensation of an excess of ethylene. The reaction was started by heating the mixture to the temperature desired. Different Ni catalyst concentrations were applied and the initial rates were determined. A plot of the initial rates of the Al alkyl displacement reaction vs. the nickel catalyst concentration indicate that the reaction is first order regarding Ni (Fig. 1c). We assume a nickel complex based ß-hydride elimination/transfer process as proposed by Wilke/Eisch and coworkers[19, 20].

Tunability of the Y–Al–Ni concept. Ideally, the product(s) formed in a tandem process should be altered independently by changing the concentration of the Y or Ni catalysts. In addition, different product distributions can be synthesized by changing the concentration of ethylene or TEA. Here, a change in concentration may affect both partial reactions. An increase in the TEA concentration, for instance, reduces the rate of chain growth (inverse first order)[9] and increases the rate of the Ni-mediated β-hydride elimination/transfer.

The influence of the concentration of the Y-based CCTP catalyst on the α-value of the α-olefin distribution was examined by applying 5–15 μmol of **1** in tandem runs (Table 2, entries 1–4). As expected, the α-value increases with a higher Y catalyst concentration. A higher Y catalyst concentration leads to faster

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Table 2 Influence of the Y and Ni catalysts concentration as well as TEA concentration and ethylene pressure on the α-value, TON Al (formal Al turnover number) and productivity

Entry	p_{eth}	n_{Ni} (µmol)	n_Y (µmol)	n_{TEA} (mmol)	α-value	TON Al	Productivity[a]
1	9	2	5	1	0.48	15	900
2	9	2	7	1	0.52	37	1,100
3	9	2	10	1	0.56	48	1,200
4	9	2	15	1	0.64	69	1,400
5	9	8.0	10	1	0.35	30	800
6	9	4.0	10	1	0.47	33	960
7	9	1.0	10	1	0.70	40	1,200
8	9	0.5	10	1	0.84	39	1,300
9	9	0.2	10	1	–	4	1,120
10	9	4	10	7.0	0.09	5	500
11	9	2	10	6.0	0.13	4	550
12	9	2	10	4.0	0.21	7	700
13	9	2	10	2.0	0.49	15	850
14	9	2	10	0.5	0.80	78	1,650
15	4.0	2	10	1	0.40	15	520
16	6.5	2	10	1	0.45	36	850
17	11.5	2	10	1	0.63	50	1,400
18	14.0	2	10	1	0.71	54	1,600

Reaction conditions: catalyst **1** ($n = 10$ µmol), $T = 80\,°C$, $t = 30$ min, $V_{tol} = 250$ ml
[a]$kg_{ethylene}\,mol_{cat}^{-1}\,h^{-1}$

chain growth and the formation of longer Al alkyl chains prior to the Ni-mediated chain displacement, which proceeds at the same rate for all experiments listed in Table 2, entries 1–4. Interestingly, the productivity (given in $kg_{ethylene}\,mol_{cat}^{-1}\,h^{-1}$) also increases with increasing Y catalyst concentration. The catalyst's productivity is also affected by the catalyst-CTA ratio[9]. The state of the active polymerization is in equilibrium with the chain-transfer state where the alkyl chains are transferred via a bimetallic complex towards Al[21–23]. Lower CTA to Y catalyst ratios resulting from a higher Y catalyst concentration will shift the equilibrium towards the chain-growing state leading to an increase in productivity. It is highly interesting that the turnover number (TON) for Al is significantly increased at higher Y catalyst concentrations. The TON of Al is calculated by dividing the moles of the α-olefins obtained by the moles of TEA used. One would expect that the rate of the displacement reaction is similar for all runs, since the number of alkyl Al chains and the Ni catalyst concentration are the same. Consequently, the real Al TON should be the same as well. The way we measure the TON of Al shown in Table 2 does not display the real Al TON, since we do not see ethyl recycling. We only monitor the recycling of chains longer than ethyl. The number of these chains increase with increasing Y catalyst concentrations. An increase of the Y catalyst concentration leads to an extension of the Al alkyl chain lengths, indicated by the higher α-values, and, in addition, to an increase of the number of extended Al alkyl chains, indicated by the increased TON of Al.

The results (Table 2, entries 5–8, Supplementary Figs. 3 and 4) show an expected dependence of the α-value from the Ni catalyst concentration. Higher Ni concentrations lead to a faster displacement of built up and transferred Al alkyl chains. As a result, the higher the Ni concentration, the smaller the α-value of the α-olefin distribution obtained will be. We believe that there is a maximum amount of Ni concentration in this system. The

maximum is reached if every alkyl chain gets immediately displaced directly after its first transfer from the CCTP catalyst to Al. If chain transfer is significantly faster than chain growth, selective 1-butene formation becomes feasible (vide infra). The smallest chain extension possible is transferred and displaced immediately in such a case. At a very low concentration of the displacement catalyst, not all built up alkyl chains are displaced during the tandem reaction and a fraction of alkanes related to the amount of CTA is formed after the workup. Similarly, a very slow displacement reaction can lead to mixtures of alkanes and olefins even at high displacement catalyst concentrations[11]. Interestingly, the TON of Al is about the same in all experiments listed in Table 2, entries 5–8. One would expect an increase in the TOF of Al with a faster displacement reaction resulting from a higher Ni catalyst concentration. Here again, the number of extended Al alkyl chains is relevant, since we can only monitor their β-hydride elimination/transfer. Because the Y catalyst concentration and the CTA concentration are the same in all experiments listed in entries 5–8 in Table 2, the number of extended chains is similar to the TON of Al. The increase of the productivity can be explained as less blocking of the polymerization catalyst by the displacement catalyst.

We were next interested in how the α-value of the α-olefins produced is influenced by varying the Al alkyl concentration (see Table 2, entries 11–14, see Supplementary Fig. 5). Different amounts of TEA from 0.5 to 6.0 mmol were added as stock solutions to the tandem reaction. We noticed a strong effect of the TEA concentration on the α-value of the α-olefins obtained. The α-value can be adjusted by increasing the CTA concentration over a large range from 0.80 to 0.13, which are quite different olefin distributions (Supplementary Fig. 6). Changes in the TEA concentration has two major impacts on the tandem reaction. Since the catalyst productivity is inverse first order regarding the Al alkyl concentration, high amounts of Al lead to low monomer

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insertion. Consequently, relatively short chains are transferred to Al. Another effect of high Al concentrations is an increase in the chain displacement rate. Chain displacement is first order regarding Al. The constructive combination of both influences permits the alteration of the α-value over such a large range.

Finally, we were interested in how the pressure of ethylene influences the product distribution obtained (Table 2, entries 15–18). The solubility of ethylene in toluene is influenced by the pressure applied and, therefore, the rate of monomer insertion can be tuned. We observed the expected increase of the α-value with increasing ethylene pressure (Supplementary Figs. 7 and 8). The length of the mean alkyl chain formed at Al is dependent mainly on the number of monomer insertions done by the CCTP catalyst within a given time frame, where time is defined as the mean time after which displacement takes place. It has been kept constant (Table 2, entries 15–18). The productivity increases linearly with increased pressure over the pressure range investigated. The increasing TON of Al can again be explained by the presence of more extended alkyl Al chains in the high-pressure experiments.

With our knowledge about the flexibility of the Y–Al–Ni catalyst system, we can now adjust the catalyst system to obtain many of the product distributions desired (Fig. 1d). This led us to push towards extremes regarding the products formed (Table 2, entries 9 and 10). The CTA concentration was varied, since it has the strongest influence on the α-value (Table 2, entry 10). In addition, we varied the Ni concentration. Ethylene pressure and Y catalyst concentration were kept constant. A very small α-value of 0.09 can be obtained by using 7.0 mmol CTA and a Y–Ni ratio of 2.5. More than 90% of the product obtained consists of 1-butene (Table 2, entry 10). A second extreme product distribution can be obtained by using 1.0 mmol CTA and very small amounts of the Ni precursor (Y/Ni=50). This experiment leads to olefins with chain lengths centered around $850\,\mathrm{g\,mol^{-1}}$ with a $M_\mathrm{w}/M_\mathrm{n}$ of 1.3 (HT-GPC) and a vinyl content of 92% (^{1}H NMR, see Supplementary Fig. 9) (Table 2, entry 9). This product distribution (blue, Fig. 1d, III) is similar to Poisson distributed runs of the pure CCTP polymerization (Table 1, entries 1 and 2, red in Fig. 1d, III).

Discussion

A highly flexible trimetallic synthesis concept of LAOs from ethylene has been introduced. The selective formation of an α-olefin, namely 1-butene, or of various LAO distributions with one catalyst system has been demonstrated. The catalyst system consists of a Y-based CCTP catalyst and an Ni-based ß-hydride elimination/transfer catalyst. Both catalysts do alkyl or polymeryl chain transfer with Al alkyls in a similar rate regime. The Y catalyst permits controlled chain growth at Al, forming trialkylaluminum from ethylene and TEA. The Ni catalyst mediates β-hydride elimination/transfer forming olefins matching the chain length of the alkylaluminum chains grown and transferred by the Y catalyst. In addition, TEA is formed and, thus, recycled. The key to the many product spectra or selective LAO formation is the (independent) adjustability of the rates of the Y- and Ni-catalyzed sub-processes. We have demonstrated that these rates can be adjusted by the concentration of the Y catalyst, the Ni catalyst and the chain-transfer agent, and the ethylene pressure. In addition, it is important that the two catalysts do not poison each other significantly. Our broadly tunable synthesis concept of LAOs is also substoichiometric or formally catalytic regarding Al. The problem of low catalyst economy in CCTP is addressed by multiple usage of the chain-transfer agent.

Methods

General. All manipulations of air sensitive compounds were performed with exclusion of oxygen and moisture using standard Schlenk techniques or a nitrogen or argon filled glove box (mBraun) with a high capacity circulator (<0.1 p.p.m. O_2). All solvents used for air and moisture sensitive reactions were dried and purified by distillation from Na/benzophenone or CaH_2 (halogenated solvents) under argon atmosphere.

Typical semi batch poly-/oligomerization run. The autoclave was evacuated (1×10^{-3} mbar) and heated at 100 °C for 30 min. Afterwards, the polymerization temperature was adjusted, charged with the desired amount toluene (typically 250 ml) and pressurized with ethylene. Subsequently activator, CTA and nickel solution were added as stock solutions via a syringe. Afterwards the catalyst (1 ml) stock solution was added. The ethylene flow was measured over the course of the polymerization procedure and is given as V_eth under normal conditions. After the procedure the reaction mixture was quenched with acidified ethanol and the obtained products were analyzed.

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Acknowledgements

Author contributions
A.G. carried out the synthesis of the catalyst, the poly-/oligomerizations and the kinetic experiments. T.D. carried out the X-ray characterization of the catalyst. W.P.K. carried out the high temperature GPC analysis. A.G. and R.K. designed the experiments and co-wrote the manuscript.

Additional information

Supporting Information

Supplementary Figure 1. Molecular structure of **1** with 50 % probability of thermal ellipsoids, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:Y1-O1 2.37(1), N1-Y1 2.27(1), N2-Y1 2.36(1), C30 Y1 2.33(2), N1-C13 1.34(2), N2-C13 1.36(2), C13-N3 1.40(2), "centroid: C34 C39 C35 C38 C36 C37" Y1 2.549; O1-Y1-C30 100.7(6), N1-Y1-N2 58.1(4), N1-C13-N2 113(1), O1-Y1-N1 86.3(5).
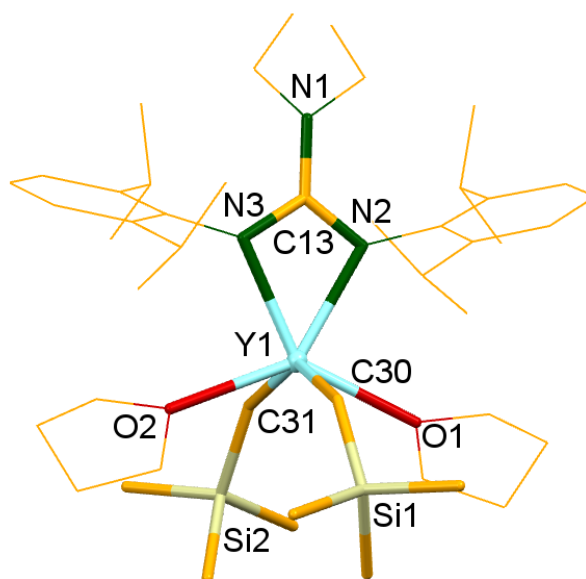
Supplementary Figure 2. Molecular structure of the precatalyst with 50% probability of thermal ellipsoids, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:O1-Y1 2.409(6), Y1-O2 2.448(6), C31-Y1 2.421(8), C30-Y1 2.439(9), N2-Y1 2.361(6), N3-Y1 2.347(6), N2-C13 1.35(1), N3-C13 1.34(1), N1-C13 1.38(1); O1-Y1-C31 85.5(2), C31-Y1-O2 80.6(2), O2-Y1-C30 84.8(2); C30-Y1-O1 82.6(2), N3-Y1-N2 55.9(2), N3-C13-N2 110.0(7).
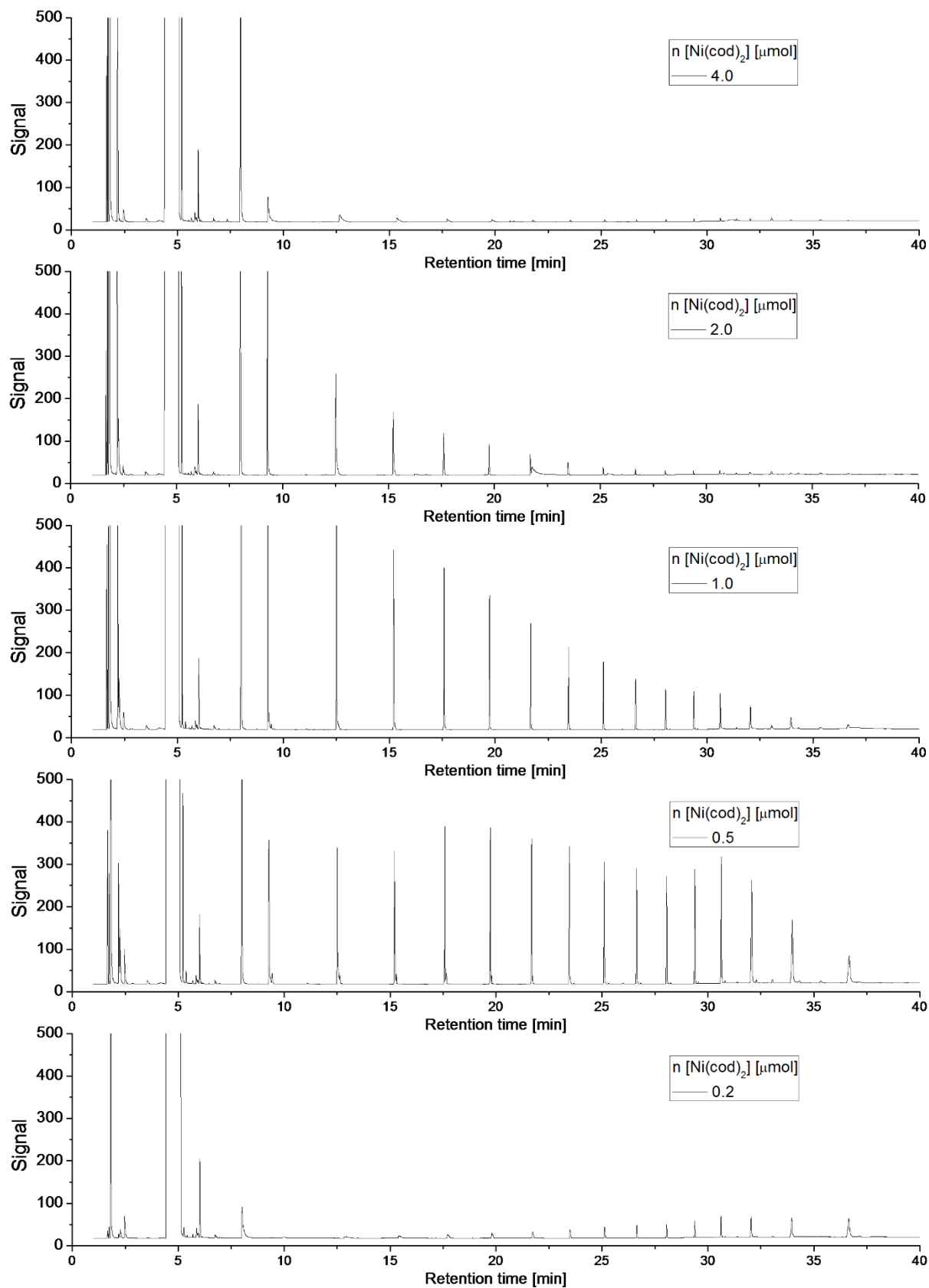
Supplementary Figure 3. Selected gas chromatograms of the products obtained from experiments described in Table 2, (entry 6-9).
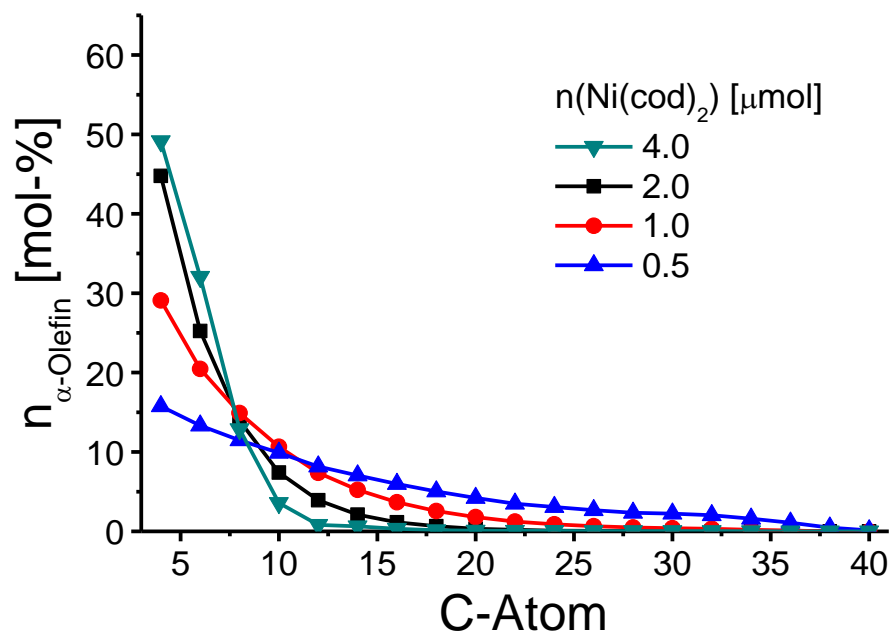
Supplementary Figure 4. Selected product distributions in mol-% obtained from experiments described in Table 2 (entry 3, 6-8).
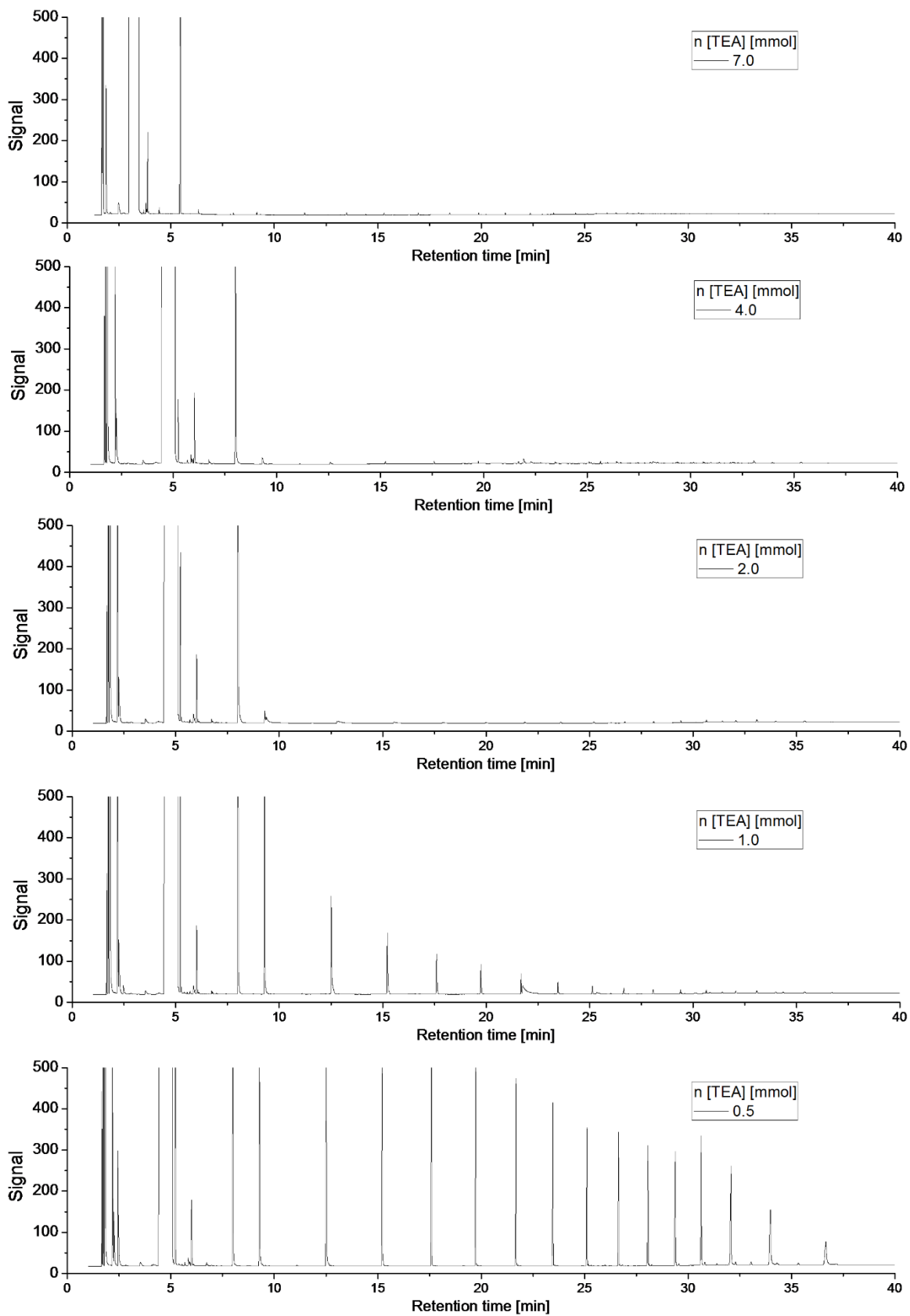
Supplementary Figure 5. Selected gas chromatograms of the products obtained from experiments described in Table 2, (entry 3, 10, 12, 13 and 14).
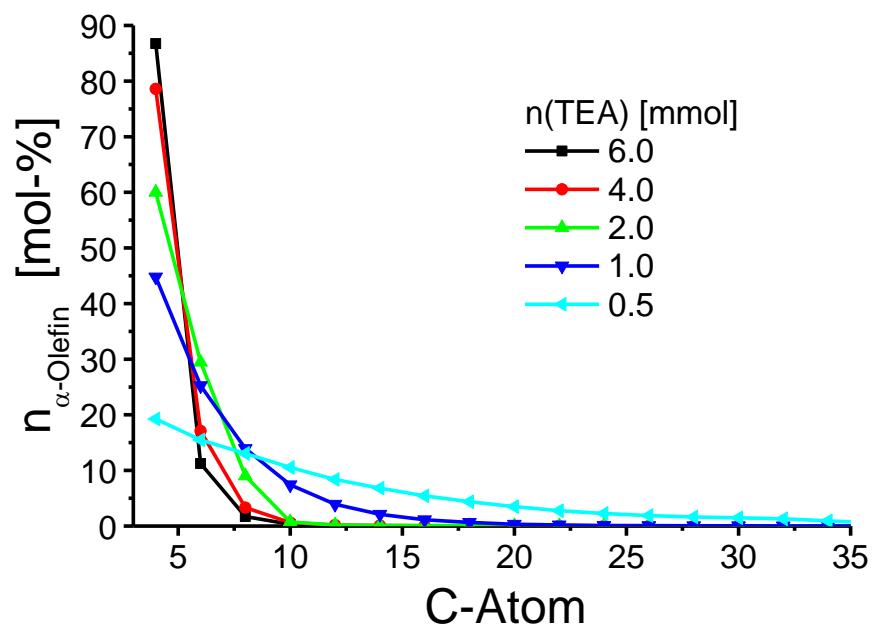
Supplementary Figure 6. Selected product distributions in mol-% obtained from experiments described in Table 2, (entry 10-14).
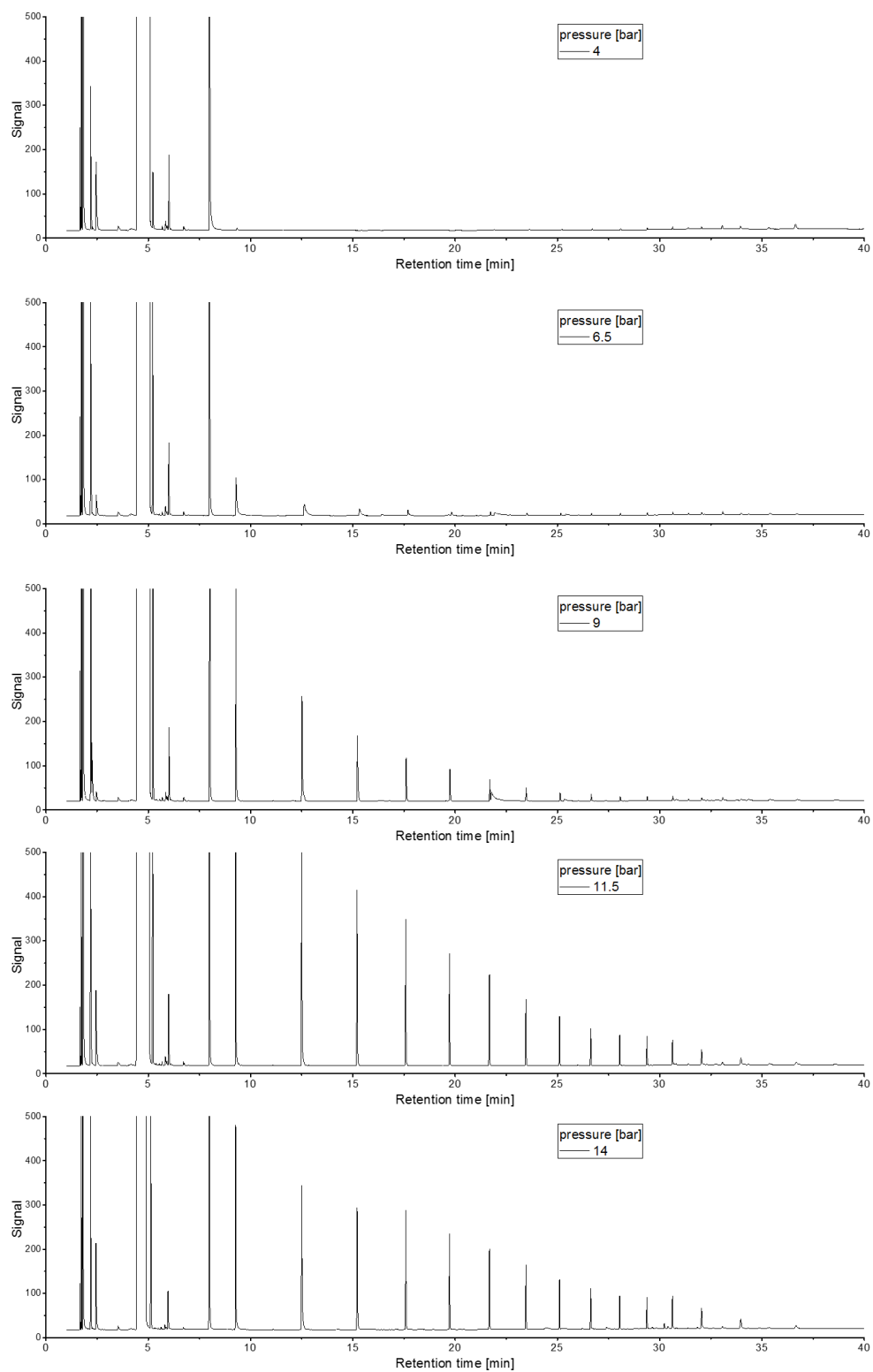
Supplementary Figure 7. Selected gas chromatograms of the products obtained from experiment described in Table 2, (entry 3, 15-18).
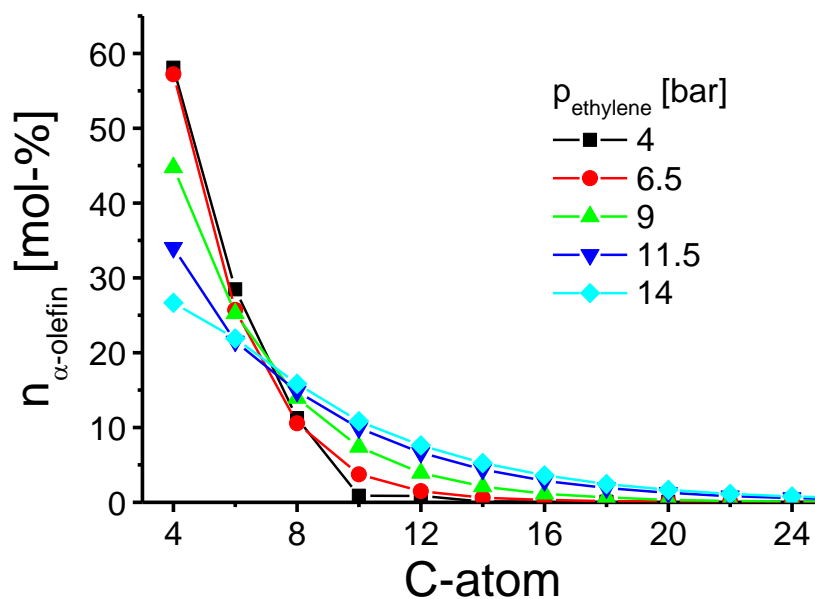
Supplementary Figure 8. Selected product distribution in mol-% obtained from experiments described in Table 2, (entry 3, 15-18).
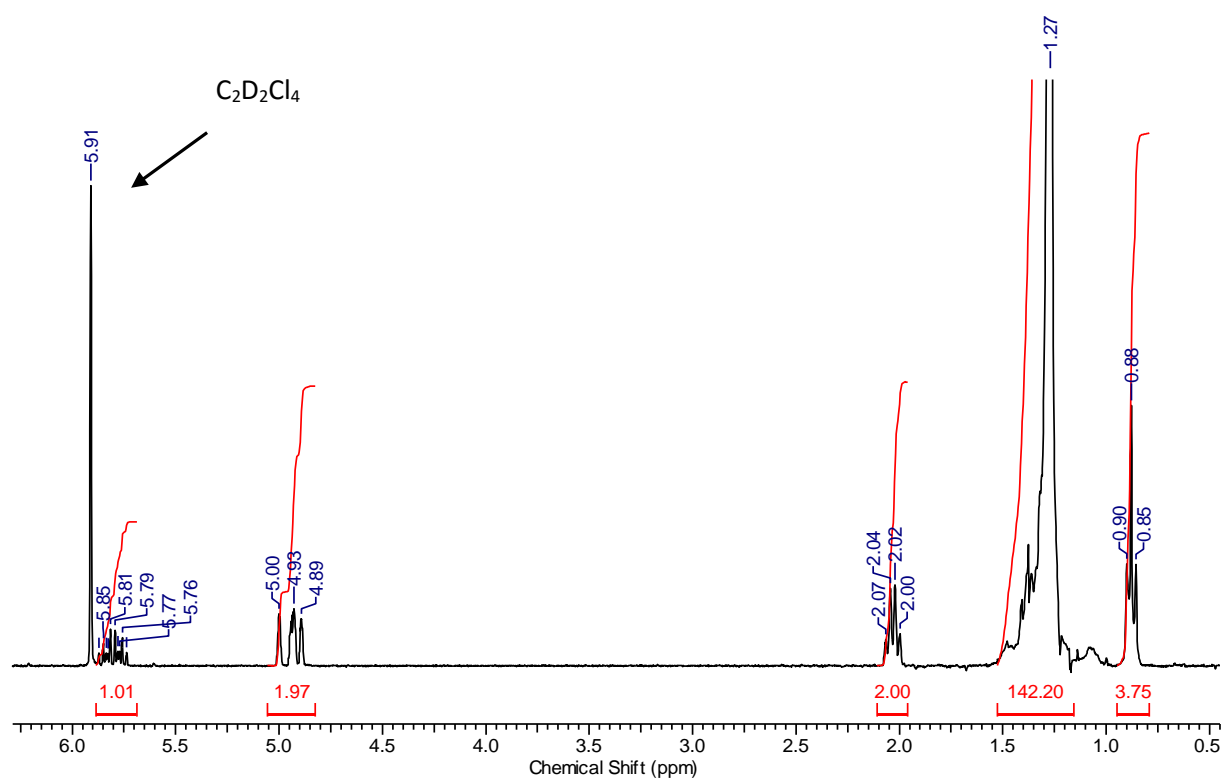
Supplementary Figure 9. ^{1}H NMR spectrum (393 K, $C_2D_2Cl_4$, 300 MHz) obtained from the extreme run with Y/Al/Ni (1/100/0.02) described in Figure 1d, Table 2, (entry 9).
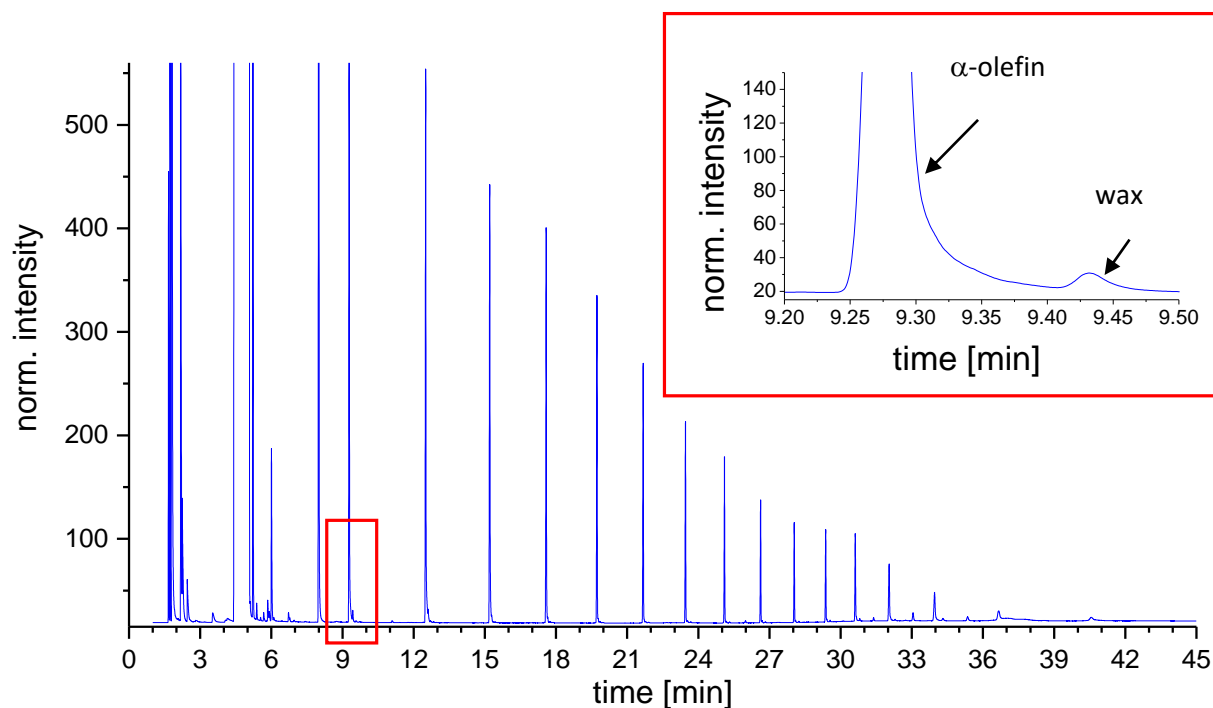
Supplementary Figure 10. A typical gas chromatogram obtained from experiment entry 3 in Table 2. Schulz Flory equation[1] used for fitting calculations (Solver Add-in in Microsoft Excel was used for a least-square fit of the obtained molar distributions): $C_p = c * (1 - \alpha) * \alpha^{(n-1)}$, α = probability of chain propagation, c = total amount (moles) of produced α-olefin, C_p = amount (moles) of α-olefin with n monomer units inserted (n = 1 means the formation of 1-butene, due to an ethyl group is the starting chain length).
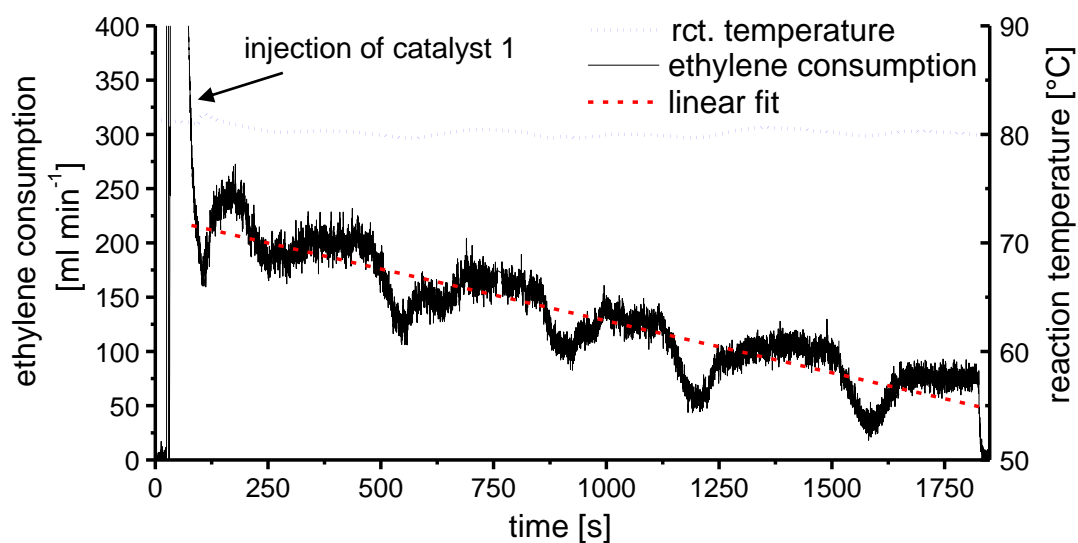
Supplementary Figure 11. Ethylene consumption [ml min^{-1}] (black line, left y-axis) over time and reaction temperature (dotted blue line, right y-axis) [°C] of the CCTP run with catalyst 1, TEA and Ni(cod)$_2$ described in Table 1, Entry 9. Linear fit of the ethylene consumption: y = -0.0956 (± 3.272 10^{-4}) ml min^{-1} s^{-1} * x + 223.8 (± 0.3534) ml min^{-1}. The half life (time after which 50% of the initial ethylene consumption is reached) of the system is approx. 19 minutes.
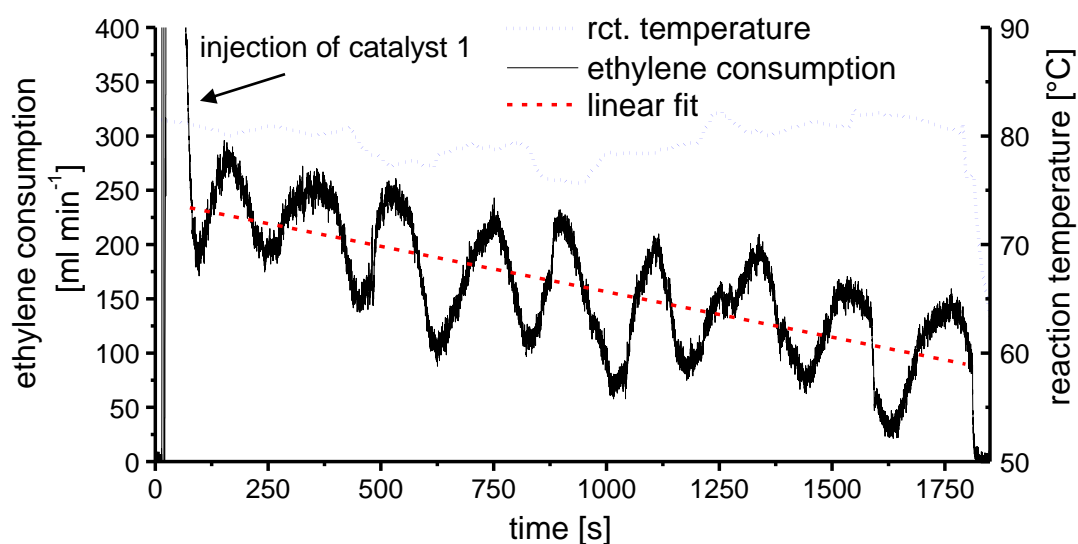
Supplementary Figure 12. Ethylene consumption [ml min^{-1}] (black line, left y-axis) over time of the CCTP run with catalyst 1 and TEA described in Table 1, Entry 6. Linear fit of the ethylene consumption: y = -0.083 (± 6.146 10^{-4}) ml min^{-1} s^{-1} * x + 240.3 (± 0.651) ml min^{-1}. The half life (time after which 50% of the initial ethylene consumption is reached) of the system is approx. 24 minutes.
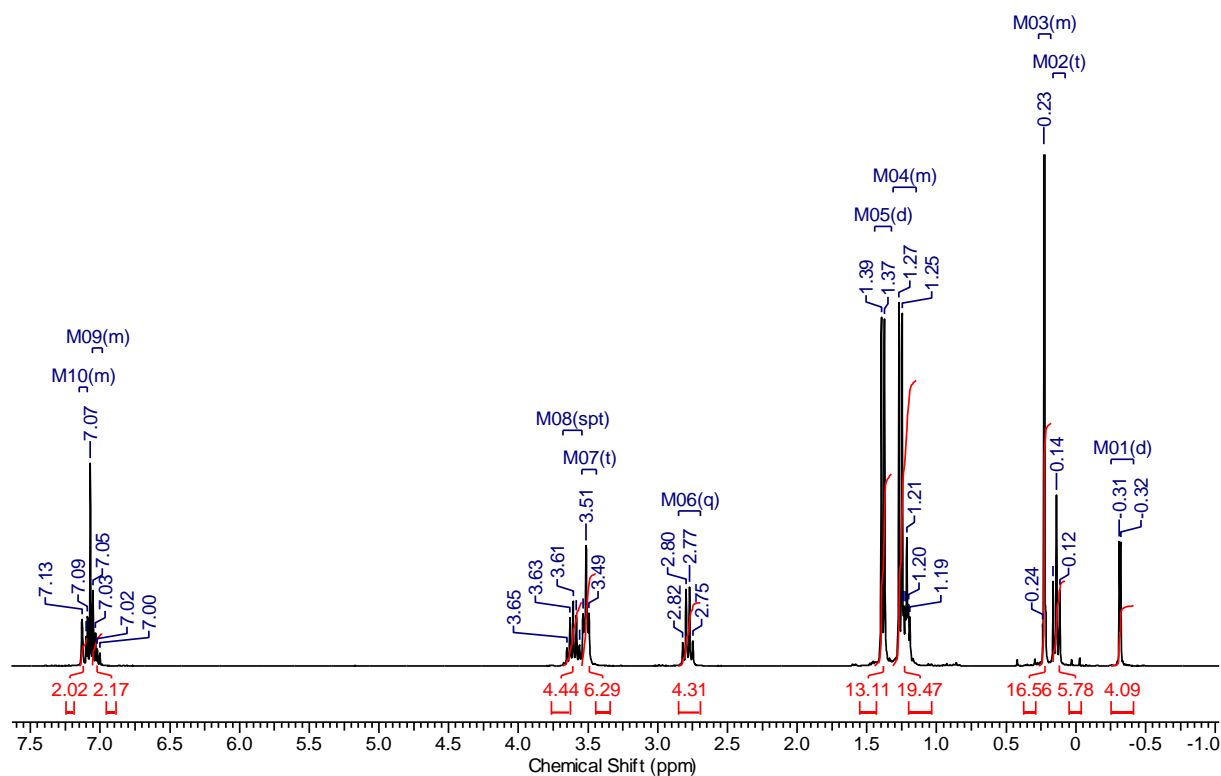
Supplementary Figure 13. ^{1}H NMR spectrum (298 K, C$_6$D$_6$, 300 MHz) of the Yttrium based precatalyst.
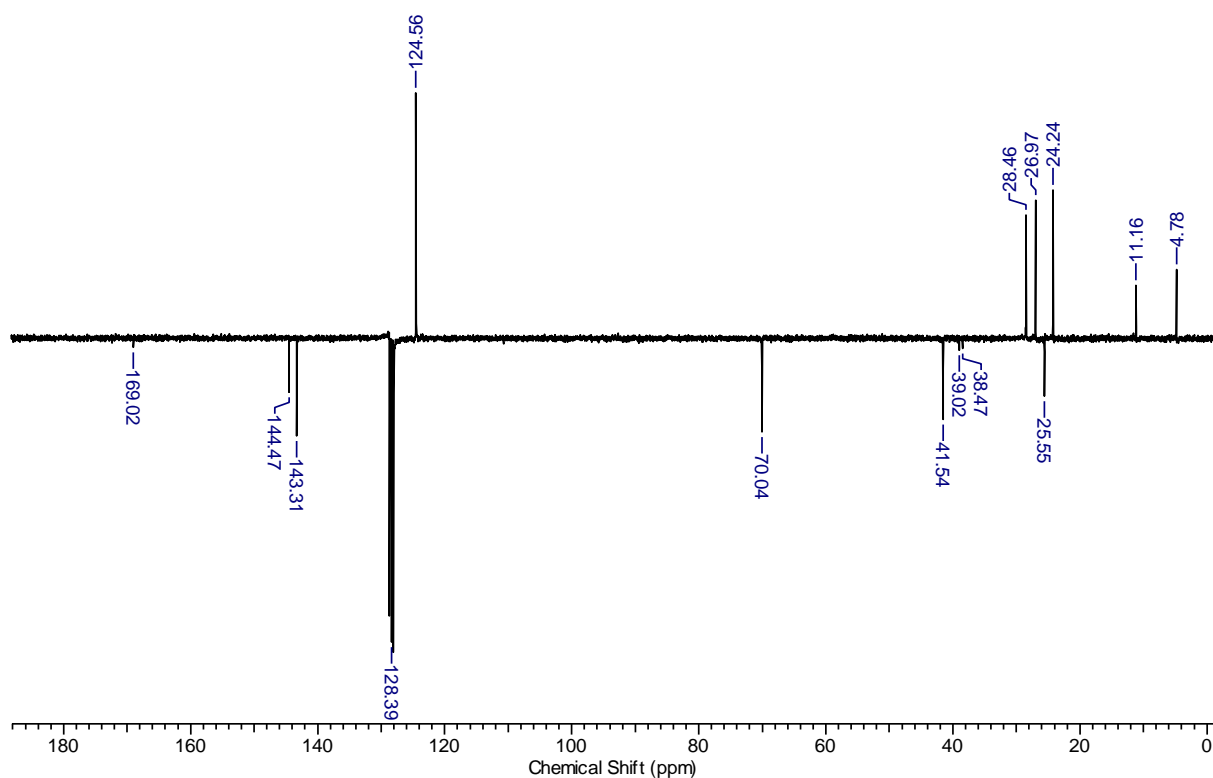
Supplementary Figure 14 . ^{13}C NMR APT spectrum (75 MHz, 298 K, C$_6$D$_6$) of the Yttrium based precatalyst.
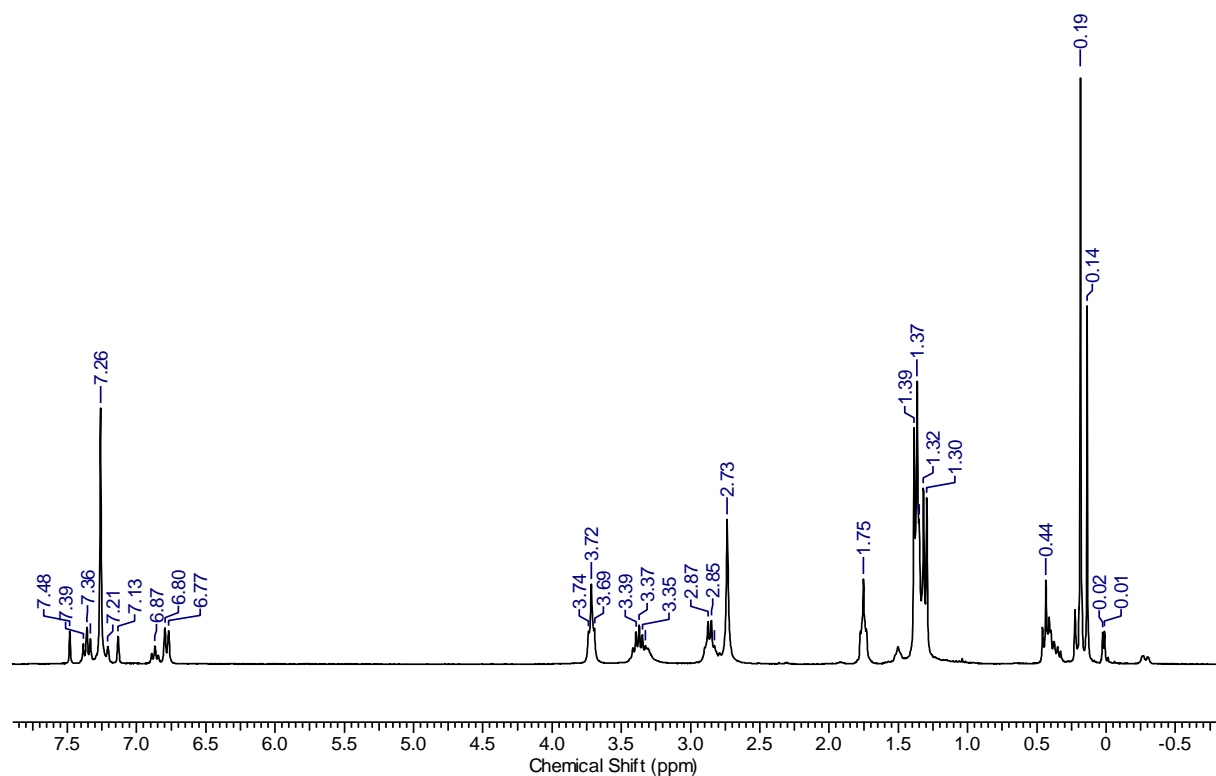
Supplementary Figure 15. ^{1}H NMR spectrum (298 K, C$_6$D$_5$Br, 300 MHz) of the reaction of the catalyst **1**.
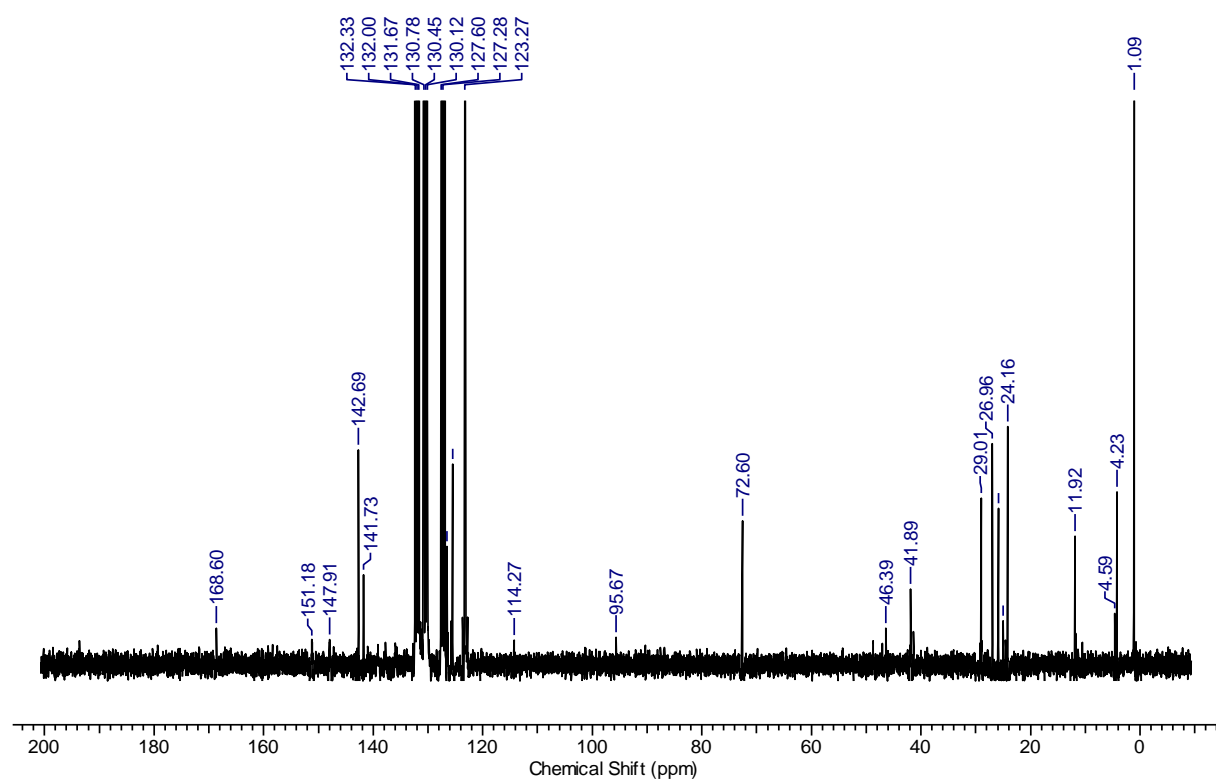
Supplementary Figure 16. ^{13}C NMR spectrum (298K, C$_6$D$_5$Br, 75 MHz) of the catalyst **1** in bromobenzene-d$_5$.

*Supplementary Table 1. CCTP runs using the catalyst **1** with TEA.*

Entry	$c(AlEt_3)$ [mmol L^{-1}]	Al/Y	V_{eth} [L$_n$]	productivity[a]	M_n [g mol^{-1}]	M_w/M_n
1	16	400	1.4	720	120	1.1
2	8	200	1.9	950	310	1.1
3	4	100	3.1	1600	2160	1.1
4	2	50	5.2	2800	4700	1.2

Reaction conditions: catalyst n = 10 μmol, p_{eth} = 9 bar, T = 80 °C, t = 1800s, $V_{toluene}$ = 250 mL; [a] [kg$_{ehtylene}$ mol^{-1} h^{-1}]

Supplementary Methods

General Methods

All manipulations of air sensitive compounds were performed with exclusion of oxygen and moisture using standard Schlenk techniques or a nitrogen or argon filled glove box (mBraun) with a high capacity circulator (< 0.1 ppm O_2). Deuterated solvents were received from Cambridge Isotope Laboratories. All solvents used for air and moisture sensitive reactions were dried and purified by distillation from Na/benzophenone or CaH_2 (halogenated solvents) under argon atmosphere.

GC, GC-MS, GPC and NMR analysis

The toluene soluble fractions were analyzed with an Agilent 6890N gas chromatograph (GC), equipped with a FID and a 30 m HP-5 column, and with an Agilent 7890A gas chromatograph (GC) combined with an Agilent 5975C mass selective detector (MSD), equipped with a TCD, a 30 m HP-5 column and a Triple-Axis-Detector, using cumene as internal standard.

Gel permeation chromatography (GPC) analyses were carried out on an Agilent (Polymer Laboratories Ltd.) PL-GPC 220 high temperature chromatographic unit equipped with DP and RI detectors and three linear mixed bed columns (PSS POLEFIN Linear XL). GPC analysis was performed at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1 wt-%) 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 (Mw = 518-2,500,000 g mol^{-1}, K = 12.100 and Alpha = 0.707) and were corrected with K and Alpha values for linear PE (K = 40.600 and Alpha = 0.725).

All ^{1}H and ^{13}C spectra were recorded with Varian INOVA 300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced internally by using the residual solvent resonances. Chemical shifts (δ) are reported in ppm.

X-ray Crystallography

X-Ray crystal structure analyses were performed with a STOE IPDS-II and a STOE STADIVARI diffractometer [λ(Mo-Kα)= 0.71073 Å] equipped with an Oxford Cryostream

low temperature unit. Structure solution and refinement were accomplished with SIR97[2], SHELXL-97[3,4] and WinGX[5,6]

Elemental analysis

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

Polymerization

Toluene (Aldrich, anhydrous, 99.8%) and ethylene (Linde AG polymer grade) used for ethylene polymerization was passed over columns of BASF R3–11-supported Cu oxygen scavenger and Al_2O_3 (Fischer Scientific).

Triethyl aluminum ($AlEt_3$, TEA, SASOL Germany GmbH), [Ni(cod)$_2$] (Sigma Aldrich), [Ni(acac)$_2$] (ABCR), [Ni(CO$_2$(CH$_2$)$_{16}$CH$_3$)$_2$] (ABCR), Dimethylanilinium tetrakis (pentafluorophenyl)borate (ABCR) were used without any further purification.

The oligomerization runs were performed in an 1 L stainless steel autoclave (Büchiglasuster) equipped with a mechanical stirrer (at 1000 rpm). It is equipped with a temperature controllable jacket, combining electrical heating and water cooling. Ethylene flow was monitored with a Bronkhorst High-Tech EI-Flow. All catalysts and CTA compounds were applied as stock solutions in toluene.

Synthesis and characterization of the metal complexes

The preparation of the precatalyst was carried out as described in literature.[7,8] The metal precursor Y(CH$_2$SiMe$_3$)$_3$ ∗ 2 THF[9] and the 2,3-bis(2,6-diisopropylphenyl)-1,1-diethylguanidine ligand[10,11,12] were synthesized according to published literature.

Synthesis and characterization of the Yttrium based precatalyst
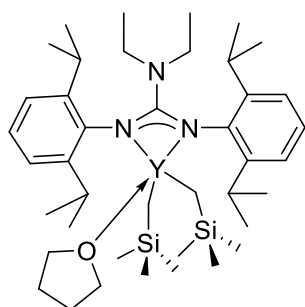
This complex can be obtained with either one or two THF molecules coordinating the Y center.[13] To a solution of Y(CH$_2$SiMe$_3$)$_3$ ∗ 2 THF (2.42 g, 4.90 mmol) in hexane (75 mL) 2,3-bis(2,6-diisopropylphenyl)-1,1-diethylguanidine (2.13 g, 4.90 mmol) was added at rt. and stirred overnight (18 h). After a subsequent filtration and removal of the solvent under reduced pressure to approx. 20 mL, colourless crystals suitable for x-ray were obtained after 2 days at -32 °C. Isolated yield: 3.11 g, 4.04 mmol, 82 %. Elem. Anal. calcd. for C$_{41}$H$_{77}$N$_3$OSi$_2$Y (770.14 gmol^{-1}): C, 63.94; H, 9.69; N, 5.46; found: C, 63.40; H, 9.53; N, 5.44.

^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K) δ ppm -0.32 (d, *J*=3.51 Hz, 4 H) 0.14 (t, *J*=7.03 Hz, 6 H) 0.18 - 0.27 (bs, 18 H) 1.14 - 1.31 (m, 16 H) 1.38 (d, *J*=6.44 Hz, 12 H) 2.78 (q, *J*=7.60 Hz, 4 H) 3.51 (m, *J*=6.44 Hz, 4 H) 3.61 (spt, *J*=6.44 Hz, 4 H) 6.99 - 7.06 (m, 3 H) 7.09 - 7.15 (m, 3 H)

^{13}C NMR (75 MHz, C$_6$D$_6$, 298K): δ = 4.78 (6 C), 11.16(2 C), 24.24 (2 C), 25.55 (4 C), 26.97 (2C), 28.97 (2C), 38.47, 39.02 (2 C), 41.54 (2 C), 70.04 (2 C), 1124.56 (4 C), 143.31 (4 C,), 144.47 (2 C), 169.28 (1 C) ppm.

Synthesis and characterization of 1
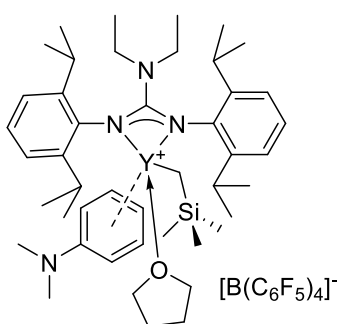
To a solution of the precatalyst (50.0 mg, 0.065 mmol) in 0.5 mL bromobenzene N,N-dimethylaniliniumtetrakis (pentafluorophenyl)borate (52.2 mg, 0.065 mmol) was added, mixed and cooled at -32 °C for 5 days. After addition of a 0.5 mL hexane layered above, suitable crystals for x-ray could be obtained. Isolated yield: 65 mg, 0.043 mmol, 67 %. Anal. calcd. for C$_{69}$H$_{74}$BF$_{20}$N$_4$OSiY (1483.15 gmol^{-1}): C, 55.88; H, 5.03, N, 3.78; found: C, 55.98; H, 4.56; N, 3.71.

^{1}H NMR (300 MHz, C$_6$D$_6$, 298K): δ = 0.02 (d, *J*=3.51 Hz, 2 H), 0.16 (s, 9 H), 0.29 - 0.50 (m, 6 H), 1.27 - 1.43 (m, 24 H), 1.67 - 1.81 (m, 4 H), 2.73 (s, 6 H), 2.86 (q, *J*=7.03 Hz, 4 H), 3.19 - 3.45 (m, 4 H), 3.63 - 3.77 (m, 4 H), 6.78 (d, *J*=8.20 Hz, 2 H), 6.86 (m, 1 H), 7.19 – 7.41 (m, 9H).

^{13}C NMR (75 MHz, C$_6$D$_6$, 298K): δ = 1.09 (3 C), 4.23 (1C), 4.59 (1 C), 11.75 (1 C), 11.92 (2 C), 24.16 (2 C), 25.01 (1 C), 25.89 (2 C), 26.96 (2 C), 29.01 (2C), 41.38 (1 C), 41.89 (2C), 46.39 (1 C), 72.60 (2 C), 95.67 (1 C), 125.51 (2 C), 125.78 (1 C), 126.36 (1 C), 126.54 (2C), 141.73 (1 C), 142.69 (2 C), 147.91 (1 C), 151.24 (1C), 168.60 (1C).

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7. Synthesis of Linear α-Olefin Distributions with Flexible Mean Molecular Weight by a Ti-Al-Ni Catalyst System

Authors: Andreas Gollwitzer, Winfried P. Kretschmer, Rhett Kempe*

ORGANOMETALLICS

Synthesis of Linear *α*-Olefin Distributions with Flexible Mean Molecular Weight by a Ti-Al-Ni Catalyst System

Andreas Gollwitzer, Winfried P. Kretschmer, and Rhett Kempe*

Lehrstuhl für Anorganische Chemie II—Katalysatordesign, Universität Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany

S *Supporting Information*

ABSTRACT: The catalytic synthesis of linear *α*-olefins from ethylene is a key reaction in the chemical industry and one of the most important applications of homogeneous catalysis. Thus, novel protocols or concepts for the synthesis of linear *α*-olefins are highly desirable. Herein, we describe a trimetallic catalyst system (Ti-Al-Ni) consisting completely of earth-abundant metals. The titanium catalyst mediates coordinative chain transfer polymerization to the chain transfer agent triethylaluminum with multiple ethylene insertions prior to chain transfer. This Ti catalyst is combined with a simultaneously operating nickel catalyst. The nickel catalyst also undergoes chain transfer, displaces the grown alkyl chains via *β*-hydride elimination/transfer forming linear *α*-olefins, and recycles the chain transfer agent. The catalyst combination permits the highly efficient synthesis of various linear *α*-olefin distributions with flexible mean molecular weight with one catalyst system. Activities of more than 10000 kg_{eth} mol^{-1} bar^{-1} h^{-1} have been observed for most of the runs, and a catalyst half-life of more than 2 h has been monitored. For example, we synthesized distributions with a mean molecular weight (M_n) ranging from 260 to 7000 g mol^{-1}. Such linear *α*-olefin distributions are difficult to synthesize, especially employing a single catalyst system. The reaction can be substoichiometric or formally catalytic regarding Al.
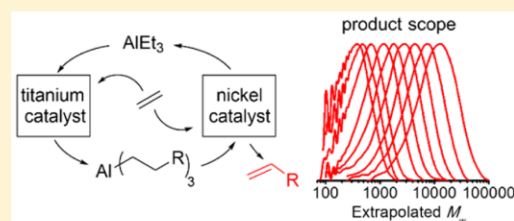
The oligomerization of ethylene to linear *α*-olefins (LAOs) is a highly important chemical reaction and is a key technological application of homogeneous catalysis.[1] It is carried out with an annual worldwide production of multiple megatons and has been intensely investigated in academia and the chemical industry.[2−5] The LAOs produced range from 1-butene, 1-hexene, and 1-octene to various product distributions, mostly Schulz−Flory distributions,[6,7] and are used to produce detergent alcohols, lubricants, plasticizers, and fine and oil field chemicals and are also used as comonomers for polyethylenes.[2−5] Due to the importance of LAOs, novel concepts for their synthesis are highly desirable. We recently introduced a new and highly flexible trimetallic LAO synthesis concept (Figure 1, top).[8] A coordinative chain transfer polymerization (CCTP) catalyst[9−12] is combined with a second catalyst, which formally takes the alkyl chains of the chain transfer agent (CTA) and mediates *β*-hydride elimination/transfer. The *β*-hydride elimination/transfer or displacement step generates olefins and recycles the CTA by forming triethylaluminum (TEA). The key to the formation of various LAO products or selective LAO formation with one catalyst system is the adjustability of the CCTP or *β*-hydride elimination/transfer subprocesses.[8b]

This LAO synthesis concept can also be substoichiometric or formally catalytic regarding Al and, thus, addresses a fundamental problem associated with CCTP: namely, the inverse first-order dependence of the rate of the chain growth from the CTA concentration.[8b,13] Gibson and co-workers described a two-step procedure. Fe-catalyzed CCTP, chain
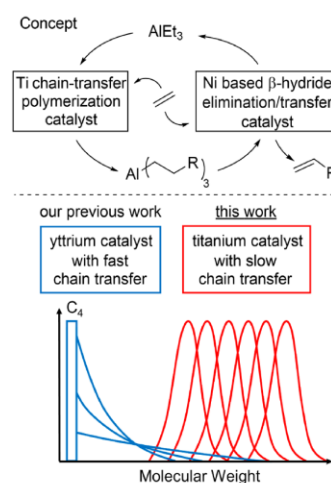
Figure 1. Novel trimetallic linear *α*-olefin (LAO) synthesis concept, our previous work (bottom left, blue LAO products), and the synthesis of various LAO distributions with flexible mean molecular weight reported herein (bottom right, red).

growth at zinc, is followed by a second step, *β*-hydride elimination/transfer of the synthesized zinc alkyls by a nickel

7. Synthesis of Linear α-Olefin Distributions with Flexible Mean Molecular Weight by a Ti-Al-Ni Catalyst System
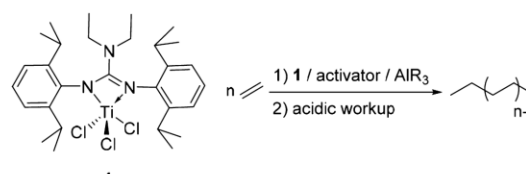
catalyst.[14] If a nickel catalyst is added directly to the CCTP catalyst used by Gibson and co-workers, no displacement reaction is observed.[15] The direct addition of an iron complex as a displacement catalyst permits a very slow β-hydride elimination/transfer reaction. A slow displacement or β-hydride elimination/transfer reaction reduces the applicability and the flexibility of the synthesis drastically. In addition, significant poisoning of the CCTP catalyst by the displacement catalyst has been observed.[15] The Y-Al-Ni catalyst system, introduced by our group very recently,[8b] permits the selective synthesis of 1-butene and various Schulz–Flory distributions (Figure 1, bottom left, blue products). These products can be synthesized or produced by a variety of existing catalyst systems.[2−5] In addition, low activity and a short lifetime of the Y catalyst restricts efficient LAO formation. The product formation in our Y-Al-Ni catalyst system is based on fast and reversible chain transfer.[16] We expected that a CCTP catalyst, which undergoes multiple insertion of ethylene molecules and for which one can easily alter the mean number of inserted ethylene molecules, could give rise to novel LAO product distributions which are also challenging to synthesize (Figure 1, bottom right, red LAO distributions).

Herein, we report on the synthesis of LAOs with an adjustable mean molecular weight employing a single catalyst system. A large range of molecular weights can be addressed, exemplarily demonstrated for M_n from 260 to 7000 g mol^{-1}. The key is a novel trimetallic catalyst system (Ti-Al-Ni) with a Ti-based CCTP catalyst that permits adjustable multiple ethylene insertions prior to polymeryl chain transfer. The Ni catalyst converts the formed Al-alkyl chains highly efficiently into LAO, without poisoning the CCTP process significantly. Our catalyst system is highly active, is resistant to decomposition over a long time, and consists completely of earth-abundant metals. The reaction can be substoichiometric or formally catalytic in Al.

First, we looked for a suitable CCTP catalyst which is highly active and undergoes multiple insertions prior to polymeryl chain transfer toward Al. A Ti catalyst (Table 1, top left), we introduced recently,[17] unfortunately, showed moderate activity and a fast decomposition when it was activated with anilinium borate and aluminum alkyls. Thus, it was investigated

regarding different activation protocols to address the activity issue (Table 1).

A very high activity has been observed if **1** is activated with dry methylaluminoxane (d-MAO). Polymerization experiments with TEA and trimethylaluminum (TMA) confirmed the chain transfer ability after such an activation (Table 1, entries 3 and 4). All reactions (except entry 5, Table 3) were stopped after a consumption of 3 L of ethylene, and the activity was calculated on the basis of the time needed. In order to obtain information on the entire product spectrum, we directly analyzed the toluene fraction of the polymerization runs via high-temperature gel permeation chromatography (HT GPC). A M_w/M_n value of about 2 for the products obtained from the CCTP runs indicate multiple monomer insertion in combination with irreversible CCTP behavior, as expected for this Ti catalyst.[17] ^{1}H NMR analysis of the dried products showed no olefinic end groups.

We next used the conditions of the CCTP run given in Table 1, entry 3, and added Ni(cod)$_2$ (cod = (1Z,5Z)-cycloocta-1,5-diene) in various concentrations to it (Table 2,

Table 2. Influence of the Ti and Ni Catalyst Concentrations on the Molecular Weight Distribution and α-Olefin Content of the LAOs Produced[a]

entry	n_{Ti}[b]	n_{Ni}[b]	time[c]	M_n[d]	olefin[e]	M_w/M_n	activity[f]
1	0.2	1	13.5	1220	68	2.4	15000
2	0.2	5	15.5	1180	94	2.2	13000
3	0.2	10	16.8	1200	98	1.9	12000
4	0.2	20	20.2	1200	99	2.0	10000
5	0.05	10	101	1220	99	2.1	8000
6	0.1	10	33.7	1190	98	2.0	12000
7	0.4	10	9.2	1210	96	2.1	11000

[a]Conditions: T = 60 °C, V_{tol} = 75 mL, V_{eth} = 3.0 L, $n_{d\text{-}MAO}$ = 0.5 mmol, n_{TEA} = 5 mmol, p_{eth} = 5 bar. [b]In μmol. [c]In min. [d]In g mol^{-1}. [e]α-olefin content in mol %. [f]In kg$_{eth}$ mol^{-1} bar^{-1} h^{-1}.

entries 1−4). ^{1}H NMR analysis of the products of the Ti-Al-Ni runs indicate that the olefin content increases with increasing Ni catalyst concentration up to quantitative olefin formation (Table 2, entries 1−4). HT GPC analysis of the products of all runs revealed a molecular weight of M_n = 1200 g mol^{-1} (see the Supporting Information), which matches the M_n observed for the Ni-free run (Table 1, entry 3). In addition, the same polydispersities (M_w/M_n) have been observed (Table 1, entry 3, and Table 2, entries 1−4). Interestingly, altering the Ni catalyst concentration does not change the molecular weight of the products. The observation is well in accordance with a CCTP catalyst that undergoes multiple ethylene insertion and irreversible chain transfer to Al, which means that the Ti catalyst preferentially extends ethyl chains.[17] With increasing time, we do not see an increase in chain length (only more chains are extended) in nickel-free runs or classic CCTP runs.[17] Chain transfer from Ti to Al seems to be slower than from Al to Ti since we see multiple ethylene insertions. The chain displacement or β-H elimination/transfer is first order in nickel.[8b] Here a variation of the nickel concentration has no effect on the molecular weight since the nickel catalyst can only displace an ethyl chain or a once-extended ethyl chain. Other alkyl chains are not available since CCTP is essentially irreversible. To ensure a complete displacement of all chains,

Table 1. Selection of a Suitable CCTP Catalyst: Structure of the Ti Precatalyst 1 and Its Activation and Chain Transfer Behavior toward Trimethylaluminum (TMA) and Triethylaluminum (TEA)[a]

entry	activator	AlR$_3$	time[b]	M_n[c]	M_w/M_n	activity[d]
1	d-MAO		5.2	73700	3.1	38500
2	borate	TEA	25.1	1900	1.9	8000
3	d-MAO	TEA	9.1	1200	2.0	22000
4	d-MAO	TMA	7.5	1600	2.1	26000

[a]Conditions: T = 60 °C, V_{tol} = 75 mL, n_{Ti} = 0.2 μmol, V_{eth} = 3.0 L, n_{CTA} = 5 mmol, $n_{d\text{-}MAO}$ = 0.5 mmol, borate ([HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]) 0.22 μmol. [b]In min. [c]In g mol^{-1}. [d]In kg$_{eth}$ mol^{-1} bar^{-1} h^{-1}.

we have to add enough nickel catalyst. Under the conditions investigated, altering the concentration of the Ti catalyst does not influence the molecular weight of the products (Table 2, entries 5−7). Again, this is expected if only ethyl chain extension and multiple monomer insertion are operating in the CCTP subprocess. In comparison to the experiments without Ni, a decrease of activity of the trimetallic catalyst system is observed. The activity also decreases with an increasing amount of Ni catalyst. We still observed a very high overall activity of 12000 kg_{eth} mol^{-1} bar^{-1} h^{-1} at nickel catalyst concentrations needed for quantitative olefin formation. At this stage, we have no other explanation than a slight poisoning of the Ti catalyst by the Ni catalyst or its ligands.

We next became interested in altering the average molecular weight of the LAOs and studied the influence of the TEA concentration first (Table 3 and Figure 3). A clear decrease of

Table 3. Influence of the TEA Concentration on the Molecular Weight Distribution[a]

entry	n_{TEA}[b]	time[c]	M_n[d]	M_w/M_n	activity[e]
1	0.5	33.6	7000	2.0	6000
2	1	25.1	4000	1.9	8000
3	2	20.0	2400	1.9	10000
4	2.5	18.3	2000	2.1	11000
5[f]	2.5	20.2	2000	2.0	10000
6	5	16.7	1200	1.9	12000
7	10	15.5	780	2.0	13000
8	20	13.4	620	1.9	15000

[a]Conditions unless specified otherwise: V_{tol} = 75 mL, T = 60 °C, V_{eth} = 3.0 L, $n_{d\text{-}MAO}$ = 0.5 mmol, n_{Ti} = 0.2 μmol, n_{Ni} = 10 μmol, p_{eth} = 5 bar. [b]In mmol. [c]In min. [d]In g mol^{-1}. [e]In kg_{eth} mol^{-1} bar^{-1} h^{-1}. [f]V_{eth} = 19 L, TON Al = 4.2, n_{Ti} = 0.5 μmol.

the molecular weight of the LAO obtained with increasing TEA concentration is observed (Table 3 and Figures 2 and 3).
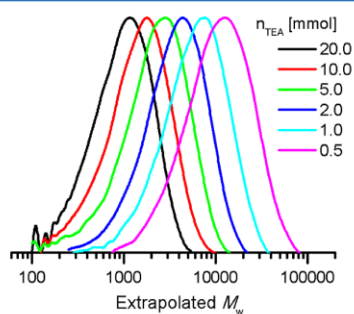
Figure 2. Normalized molecular weight distributions of the LAOs obtained from the experiments described in Table 3.

HT GPC analysis revealed that the average molecular weight can be altered over a large range (M_n from 7000 to 620 g mol^{-1}). ^{1}H NMR analysis of the products indicates quantitative olefin formation in all runs. The TEA concentration influences the chain transfer rate and, thus, the ethylene insertions prior to chain transfer. A plot of the mean number of ethylene insertions or M_n of the LAO obtained versus the inverse Al concentration is strictly linear for all experiments given in Table 3 or Figure 2. See the Supporting Information for details. Due to the Ti-Al-Ni system being resistant to decomposition, a high-yield polymerization run was conducted
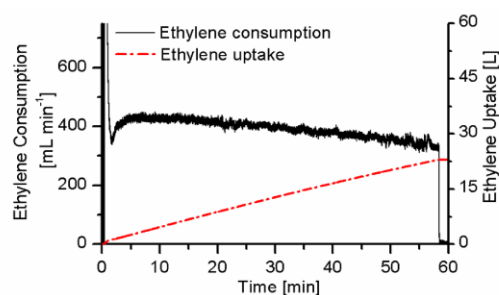
Figure 3. Ethylene consumption for the high-yield synthesis of LAOs with the Ti-Al-Ni catalyst system. The polymerization procedure is described in Table 3, entry 5. The half-life of the catalyst system, assuming a linear decay, is 126 min.

(see Table 3, entry 5, and Figure 3). The half-life of the catalyst system is 126 min, assuming a linear decay. We were able to produce up to 21 g of LAOs with an average chain length of 2000 g mol^{-1}, which displays a TON Al of 1.4 or 4.2 per alkyl chain (Figure 3).

As expected, the ethylene pressure can influence the insertion rate. We varied the pressure applied from 3.0 to 10 bar (Supporting Information) to demonstrate this dependence. Furthermore, the temperature is affecting the chain transfer rate, and we examined the influence of the temperature at constant ethylene concentrations (Supporting Information). A lowering of molecular weight of the LAOs is observed with increasing temperatures. To ensure a constant polymerization temperature, very low Ti catalyst loadings of 0.2 μmol were applied. Finally, we became interested how far we could push the system toward products with a low molecular weight, since such LOA products are difficult to synthesize.[18] Therefore, we combined high aluminum concentrations with low ethylene pressures at high temperature (see Table 4). By applying 2 bar of ethylene pressure and an Al/Ti ratio of 60000, M_n can be reduced to 260 g mol^{-1}, which displays an average polymerization degree of nine ethylene monomers.

Table 4. Combination of a High TEA Concentration and Low Ethylene Pressures To Produce Low-Molecular-Weight LAOs[a]

entry	p_{eth}[b]	time[c]	M_n[d]	M_w/M_n	activity[e]
1	5	18.4	520	1.6	11000
2	4	25.3	390	1.7	10000
3	3	35.4	310	1.6	9500
4	2	63.1	260	1.5	8000

[a]Conditions: V_{tol} = 50 mL, T = 60 °C, V_{eth} = 3.0 L, $n_{d\text{-}MAO}$ = 0.5 mmol, n_{Ti} = 0.5 μmol, n_{Ni} = 10 μmol, n_{TEA} = 30 mmol. [b]In bar. [c]In min. [d]In g mol^{-1}. [e]In kg_{eth} mol^{-1} bar^{-1} h^{-1}.

Our Ti catalyst incorporates the formed LOA very rarely, as concluded from copolymerizations experiments with 1-hexene. ^{13}C NMR analysis of the product showed a very poor incorporation of 1-hexene (see the Supporting Information).

In summary, we report the highly flexible synthesis of LAO with an adjustable average molecular weight ranging from 260 to 7000 g mol^{-1} employing a single catalyst system. This system is highly active, is resistant to decomposition over a long time, and consists completely of earth-abundant metals. Such LAO product distributions, especially in the low-

molecular-weight range, are difficult to synthesize by applying existing polymerization catalyst systems.[18]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00428.

General methods, screening experiments, and characterization data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for R.K.: kempe@uni-bayreuth.de.

ORCID ⊙

Rhett Kempe: 0000-0002-9138-4155

Notes

The authors declare the following competing financial interest(s): A.G., W.P.K., and R.K. are inventors of patent applications WO2016180539 and WO2016180538, filed May 13, 2015, published May 16, 2016.

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Supporting Information for

Synthesis of linear α-olefin distributions with flexible mean molecular weight by a Ti-Al-Ni catalyst system

Andreas Gollwitzer, Winfried P. Kretschmer and Rhett Kempe*

Lehrstuhl für Anorganische Chemie II—Katalysatordesign, Universitätsstr. 30, Universität Bayreuth, 95440 Bayreuth, Germany.

1. General Methods

1.1 General

All reactions of air sensitive compounds were performed with exclusion of oxygen and moisture using standard Schlenk techniques or a nitrogen or argon filled glove box (mBraun) with a high capacity circulator (< 0.1 ppm O_2). Deuterated solvents were received from Euriso-Top. All solvents used for air and moisture sensitive reactions were dried and purified by distillation from Na/benzophenone or CaH_2 (halogenated solvents) under argon atmosphere.

1.2 GPC and NMR analysis

Gel permeation chromatography (GPC) analyses were carried out on an Agilent (Polymer Laboratories Ltd.) PL-GPC 220 high temperature chromatographic unit equipped with DP and RI detectors and three linear mixed bed columns (Mixed-D). GPC analysis was performed at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer or the toluene solvated sample (0.1-2.0 wt-%) 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 polyethylene standards (M_w = 110-470,000 g mol^{-1}, K = 40.600 and Alpha = 0.725).

All ^{1}H and ^{13}C spectra were recorded with Varian INOVA 300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced internally by using the residual solvent resonances. Chemical shifts (δ) are reported in ppm.

1.3 Catalyst synthesis

The synthesis of the titanium catalyst was done according to published procedures.[1]

1.4 Polymerization procedure

Toluene (Aldrich, anhydrous, 99.8%) and ethylene (Linde AG polymer grade) used for ethylene polymerization was passed over columns of BASF R3–11-supported Cu oxygen scavenger and Al_2O_3 (Fischer Scientific).

Triethyl aluminum (AlEt$_3$, TEA, SASOL Germany GmbH), [Ni(cod)$_2$] (Sigma Aldrich), Dimethylanilinium tetrakis (pentafluorophenyl)borate (ABCR) were used without any further purification. "TMA-depleted" MAO (d-MAO) was obtained by removal of all volatiles under reduced pressure from commercially available MAO (Eurecen Al 5100-10-Toluene, Chemtura Europe Limited)

The oligomerization runs were performed in a 300 mL stainless steel autoclave (Büchiglasuster) equipped with a mechanical stirrer (at 1000 rpm). The temperature was adjusted with an external water bath. Ethylene flow was monitored with a Bronkhorst High-Tech EI-Flow and is given in litres (L) at normal conditions. The pre-catalysts solutions and the TEA solution were applied as stock solutions in toluene.

A typical oligomerization run was carried out as followed:

The autoclave was evacuated ($1*10^{-3}$ mbar) and heated at 60°C for 30 min. Afterwards, the polymerization temperature was adjusted and the autoclave was charged with the desired amount toluene (typically 50 to 75 mL) and pressurized with ethylene. Subsequently the activator, CTA and the nickel solution were added via a syringe. Afterwards the catalysts stock solution was added. The ethylene flow was measured over the course of the polymerization procedure and is given as V_{eth} under normal conditions. After the poly-/oligomerization the reaction mixture was washed with acidified deionized water. The toluene phase containing the products was used for the HT GPC analysis. For ^{1}H NMR analysis, the toluene phase was dried in vacuo and measured at 120 °C in $C_2D_2Cl_4$.

2. Screening Experiments

Table S 2. Influence of the Ti and Ni catalyst concentrations on the molecular weight distribution and α-olefin content of the LAOs produced

$$n \diagup\diagup \xrightarrow[\text{2) acidic workup}]{\text{1) }\mathbf{1}\text{ / activator / AlEt}_3\text{ / Ni}} \diagup\diagup \overset{}{\underset{n-1}{(\ \ )}} R$$
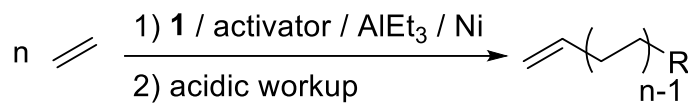
Entry	n_{Ti} [μmol]	n_{Ni} [μmol]	Time [min]	M_n [g mol^{-1}]	α-olefin [mol- %]	M_w/M_n	Activity[a]
1	0.2	1	13.5	1220	68	2.4	15000
2	0.2	5	15.5	1180	94	2.2	13000
3	0.2	10	16.8	1200	98	1.9	12000
4	0.2	20	20.2	1200	99	2.0	10000
5	0.05	10	101	1220	99	2.1	8000
6	0.1	10	33.7	1190	98	2.0	12000
7	0.4	10	9.2	1210	96	2.1	11000

Conditions: T= 60 °C, V_{tol} = 75 mL, V_{eth} = 3.0 L, $n_{d\text{-}MAO}$ = 0.5 mmol, n_{TEA} = 5 mmol, p_{eth} = 5 bar. [a] kg$_{eth}$ mol^{-1} bar^{-1} h^{-1}

2.1 GPC Traces
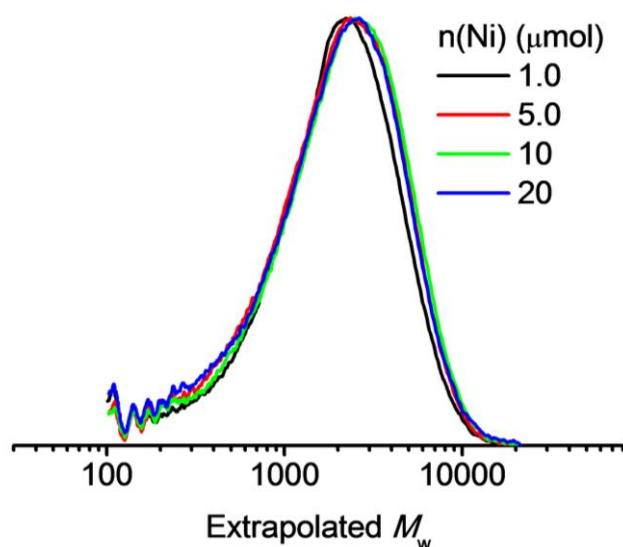
Figure S 17. Normalized molecular weight distribution plots of the obtained linear α-olefins obtained from the experiments described in Table S1, Entry 1-4.
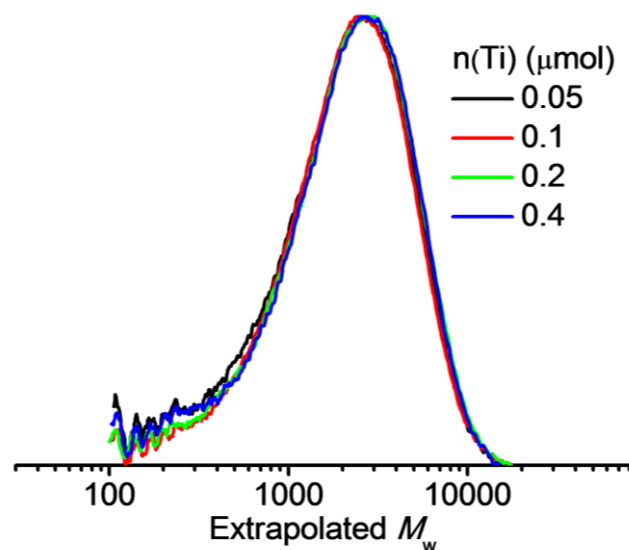
Figure S 18. Normalized molecular weight distribution plots of the obtained linear α-olefins obtained from the experiments described in Table S1, Entry 3, 5-7.
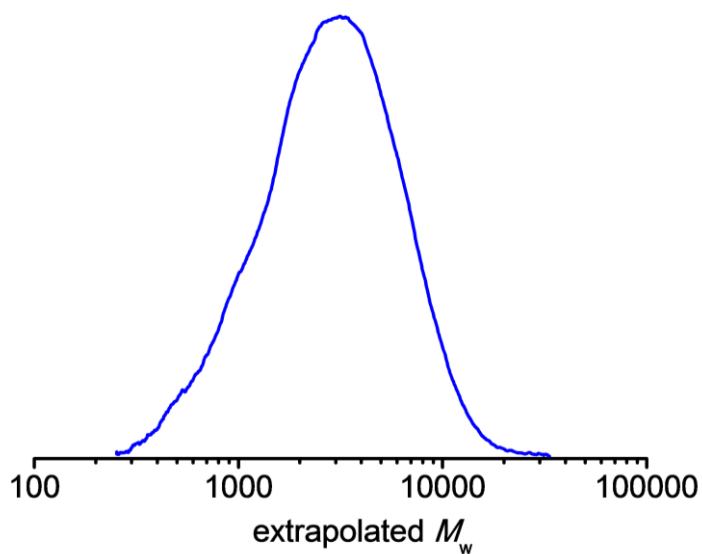
Figure S 19. Molecular weight distribution plots of the obtained linear α-olefins obtained from the experiment described in Table 3, Entry 5.
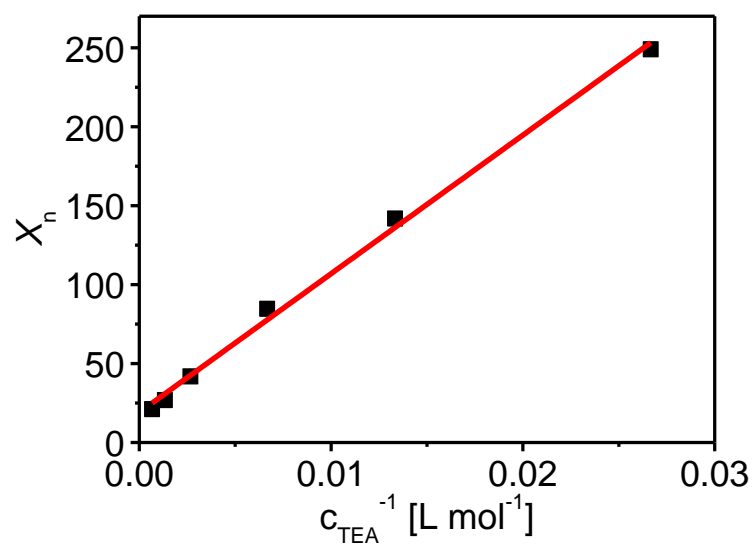
Figure S 20. Plot of the average degree of polymerization (X_n) over the inverse TEA concentration.

Table S 2. Influence of the Temperature on the molecular weight distribution of the produced linear alpha olefins.

Entry	Temp	Time	M_n	M_w/M_n	Activity[a]
	[°C]	[min]	[g mol^{-1}]		
1	30	59.0	3000	2.1	5200
2	40	35.4	2100	2.0	8000
3	50	23.2	1500	2.1	11000
4	60	16.8	1200	2.0	12000
5	70	20.8	850	2.0	9000
6	80	84.3	760	2.0	2000

rct. conditions: V_{tol} = 75 mL, $c_{ethylene}$ = 0.015 mol L^{-1} ethylene pressure was adjusted, to keep the ethylene concentration constant with different toluene temperatures[2], n(Ti) = 0.2 μmol, V_{eth} = 3.0 L, n(Al) = 5 mmol, n(d-MAO) = 2 mmol, n(Ni) = 10 μmol.
[a] kg$_{eth}$ mol^{-1} bar^{-1} h^{-1}
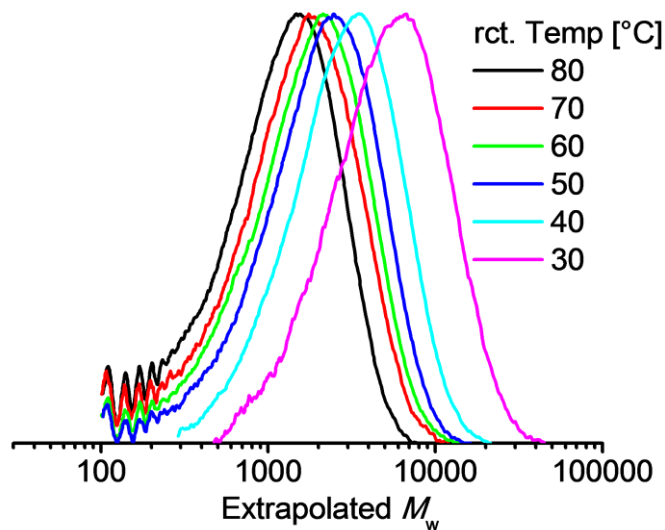
Figure S 21. Normalized molecular weight distribution plots of the obtained linear α-olefins obtained from the experiments described in Table S 2.

Table S 3. Influence of the ethylene pressure on the molecular weight distribution of the produced LAO.

Entry	p_{eth}	Time	M_n	M_w/M_n	Activity[a]
	[bar]	[min]	[g mol^{-1}]		
1	3.0	50	850	1.8	6700
2	5.0	16.8	1200	2.0	12000
3	7.0	11.1	1450	2.2	13000
4	10	7.8	1710	1.7	13000

Conditions: V_{tol} = 75 mL, T = 60 °C. n_{Ti} = 0.2 µmol, V_{eth} = 3.0 L, n_{TEA} = 5 mmol, n_{d-MAO} = 0.5 mmol, n_{Ni} = 10 µmol,

[a] kg_{eth} mol^{-1} bar^{-1} h^{-1}
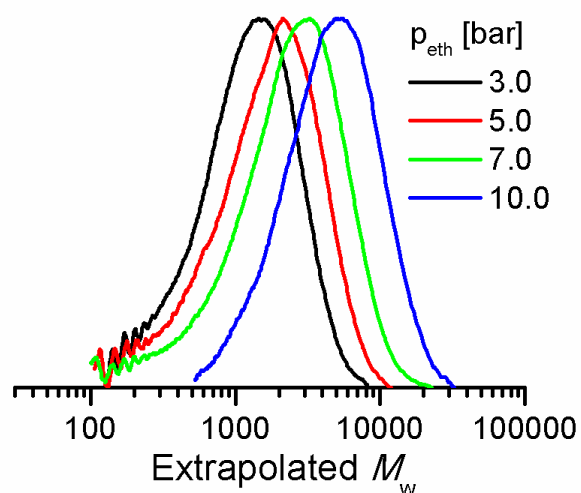
Figure S 22. Normalized molecular weight distribution plots of the obtained linear α-olefins obtained from the experiments described in Table S 3.

3. Characterization Data

3.1 ^{1}H NMR Spectra
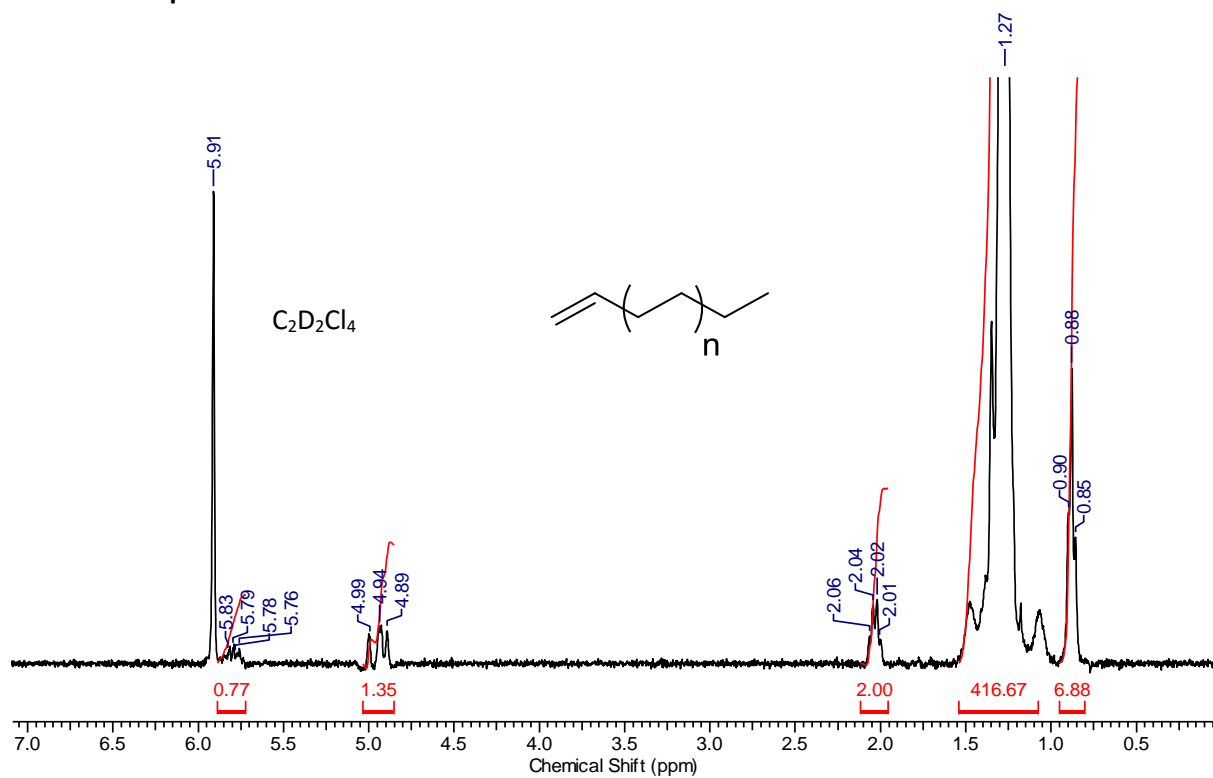
Figure S 23. ^{1}H NMR spectrum ($C_2Cl_4D_2$, 300 MHz, 120°C) of the products obtained from experiment described in Table 2 Entry 1, α-olefin content: 68 mol-%.
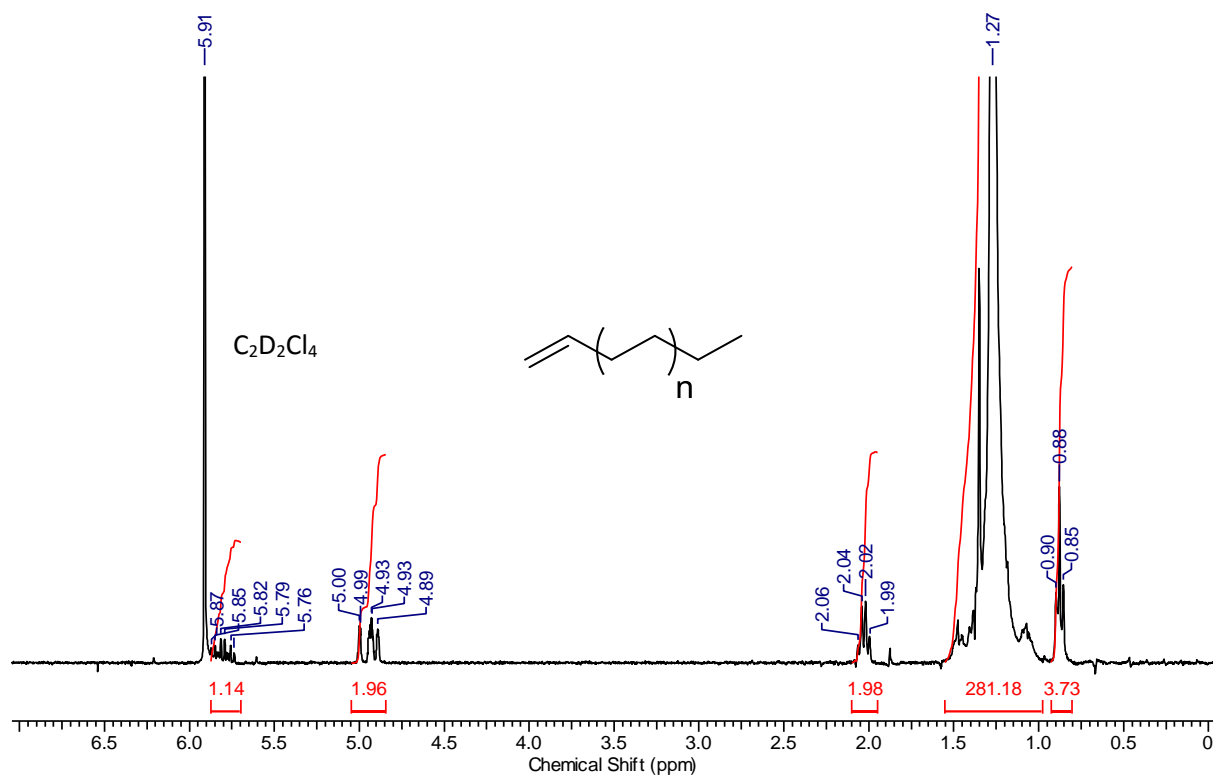
Figure S 24. ^{1}H NMR spectrum (C$_2$Cl$_4$D$_2$, 300 MHz, 120°C) of the products obtained from experiment described in Table 2 Entry 2.
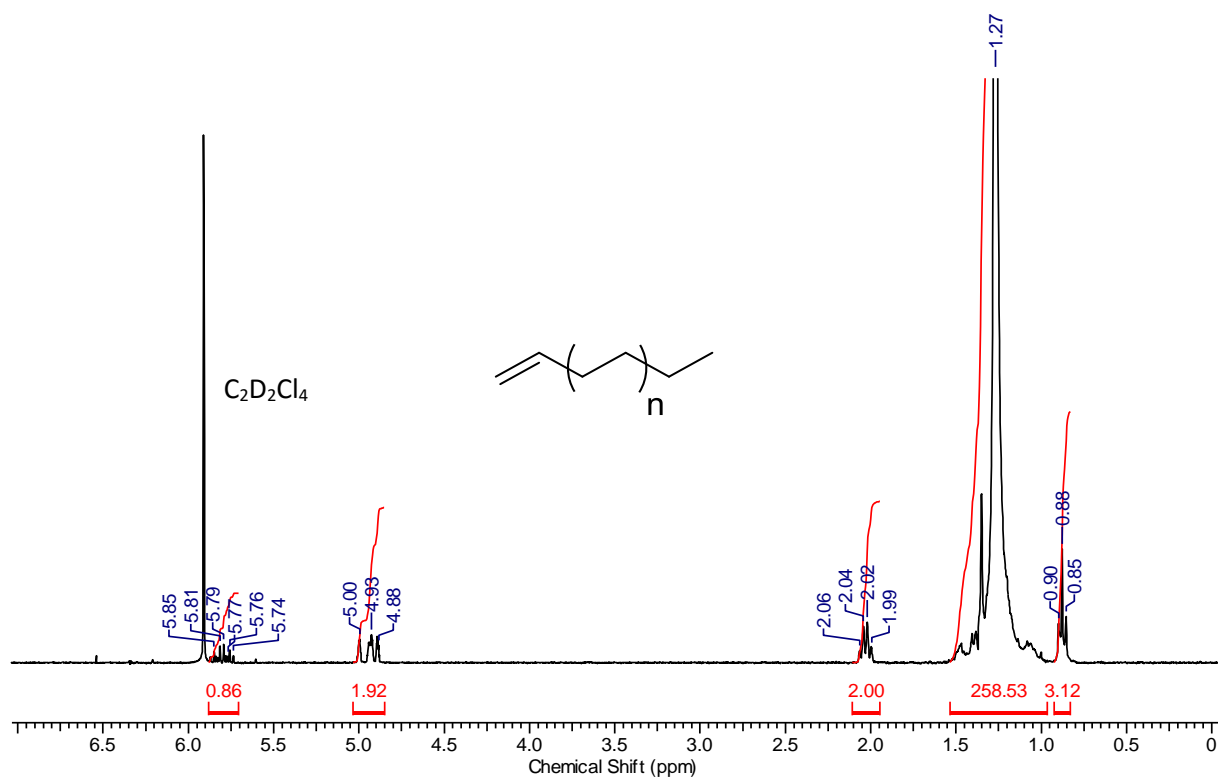
Figure S 25. ^{1}H NMR spectrum (C$_2$Cl$_4$D$_2$, 300 MHz, 120°C) of the products obtained from experiment described in Table 2 Entry 3.
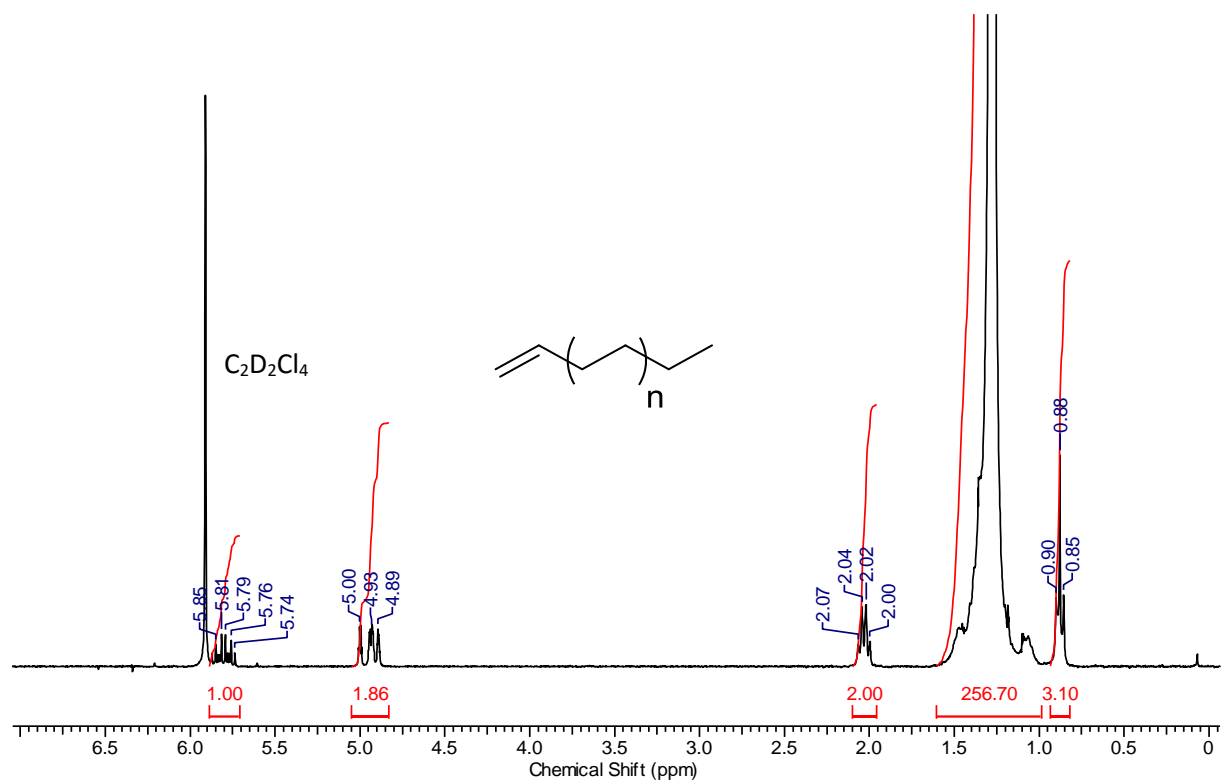
Figure S 26. ^{1}H NMR spectrum (C$_2$Cl$_4$D$_2$, 300 MHz, 120°C) of the products obtained from experiment described in Table 2 Entry 4.
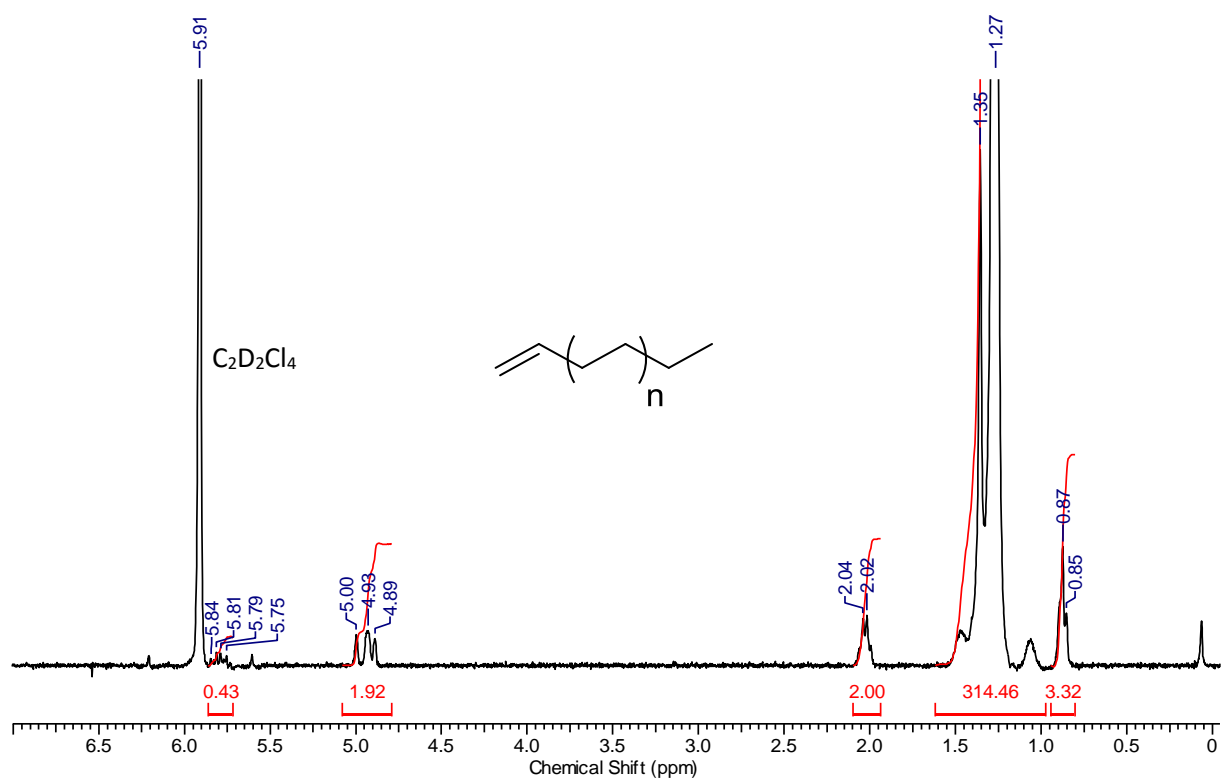
Figure S 11. ^{1}H NMR spectrum (C$_2$Cl$_4$D$_2$, 300 MHz, 120°C) of the products obtained from experiment described in Table 3 Entry 5.
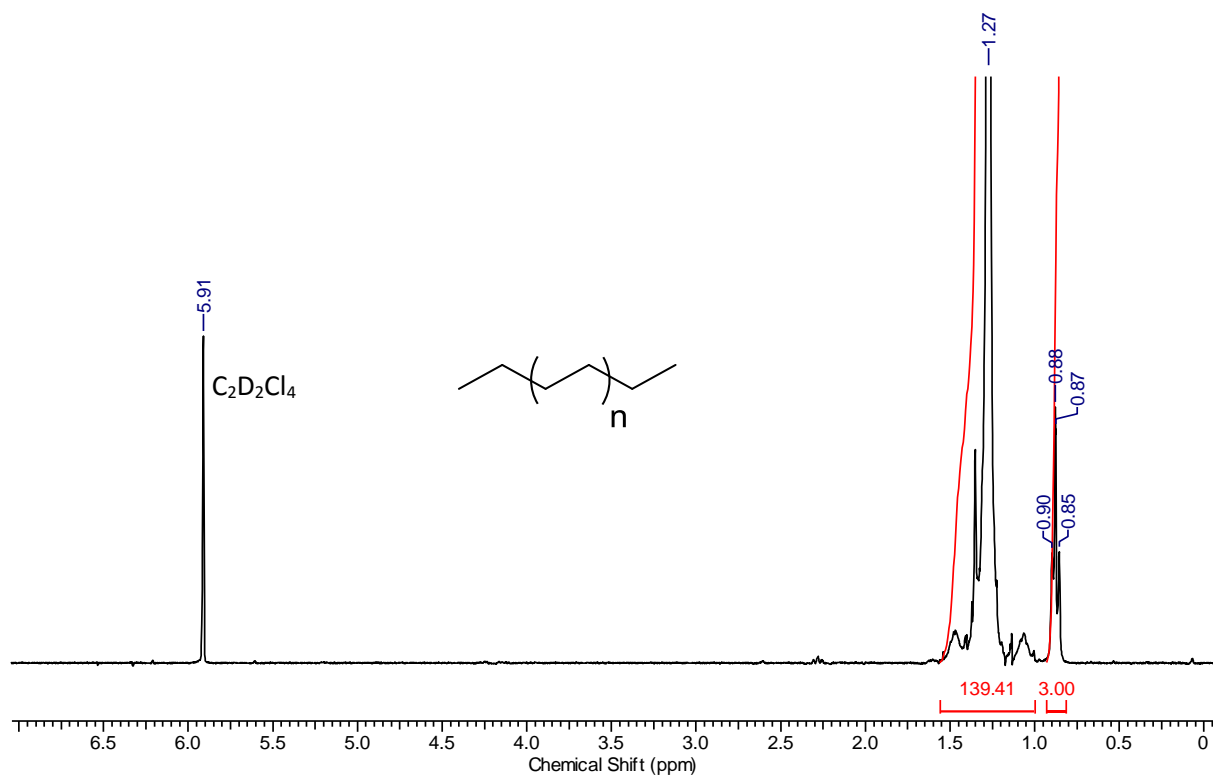
Figure S 12. ^{1}H NMR spectrum (C$_2$Cl$_4$D$_2$, 300 MHz, 120°C) of the products obtained from experiment described in Table 1 Entry 3.
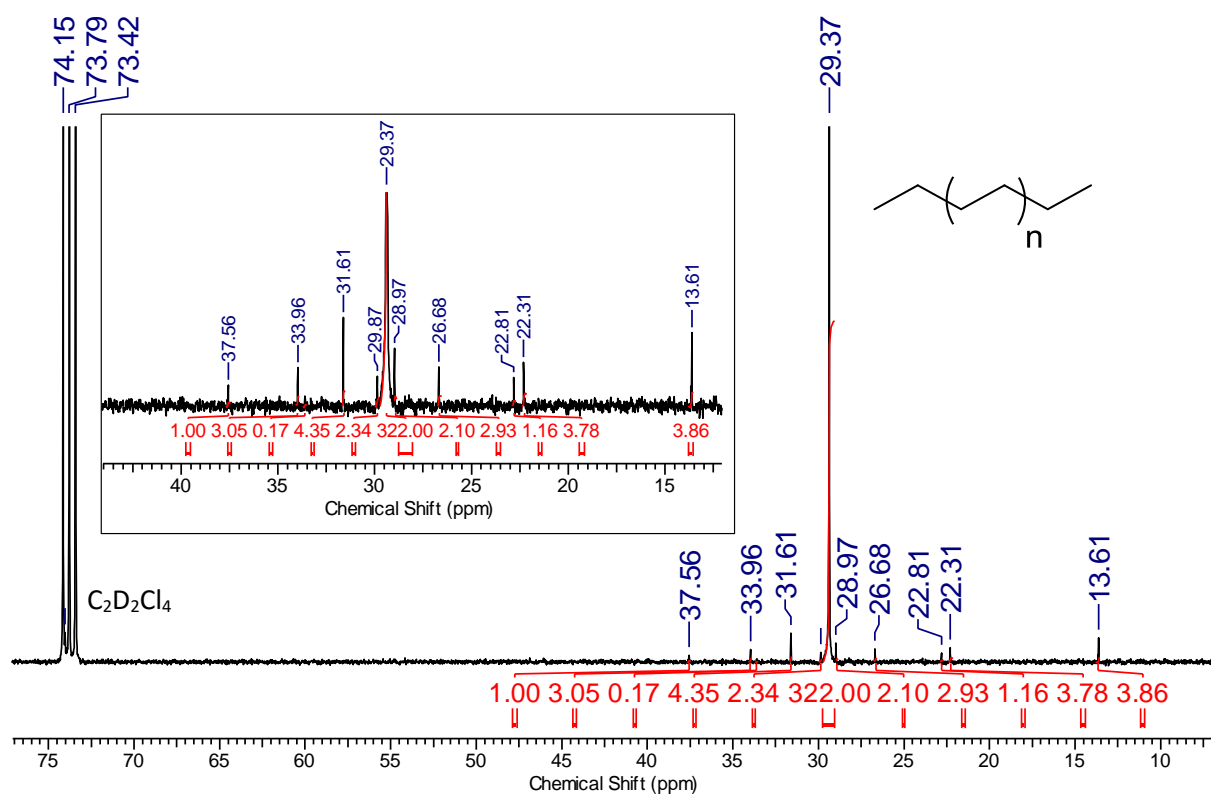
Figure S 13. ^{13}C NMR spectra of the products obtained in the experiment described in Table 1 Entry 3 with additionally 10 mL of 1-hexene. The calculated incorporation of 1-hexene is <1 %.[3]

4. References

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8. Tailor-made α-Olefins by Coordinative Chain Transfer Polymerisation, Displacement Reaction and Two Chain Transfer Agents

Authors: Andreas Gollwitzer, Winfried P. Kretschmer, Rhett Kempe*

Journal Name

COMMUNICATION

Tailor-made α-Olefins by Coordinative Chain Transfer Polymerisation, Displacement Reaction and Two Chain Transfer Agents

Andreas Gollwitzer, Winfried P. Kretschmer and Rhett Kempe*[a]

A highly flexible synthesis of linear α-olefins by the combination of a Zr based coordinative chain transfer polymerization catalyst and a Ni based chain displacement catalyst in the presence of triethylaluminum and diethylzinc as chain transfer agent is described. Linear α-olefins as Schulz-Flory distributions with flexible α-values ranging from C_4 to C_{40} and C_{40+} can be obtained specifically.

The oligomerization of olefins and especially of ethylene by homogenous catalysts is one of the most important industrial processes with an increasing total world production of multiple megatons annually. The produced linear α-olefins are used as co-monomers to produce polyethylene, detergent alcohols, lubricants, plasticizers and oil field chemicals.[1] A novel and highly flexible trimetallic catalyst system for the synthesis of linear α-olefins (LAO) has been introduced recently.[2] The trimetallic Y–Al–Ni catalyst system consists of an Y based coordinative chain transfer polymerization (CCTP) catalyst which undergoes fast and reversible chain transfer to triethylaluminum (TEA) and a Ni based β-hydride elimination/transfer catalyst (Scheme 1). The concept allows the flexible production of LAO matching to a Schulz Flory[3] distribution. The products can be adjusted from selective 1-butene formation to distributions centered at 850 gmol^{-1}.[4] The key to the synthesis of this vast product spectrum and product distributions with a single catalyst system is the alteration of the rates of the CCTP and/or the β-hydride elimination/transfer sub-process independently of each other. We also introduced a second trimetallic Ti-Al-Ni based catalyst system which is able to produce LAO with a distinctly higher molecular weight ranging from 260 g mol^{-1} up to 7000 g mol^{-1}.[5] Here, the Ti CCTP catalyst mediates slow and irreversible chain transfer to Al.[6] These novel catalytic syntheses concepts can be sub-

stoichiometric or formally catalytic in the aluminum based chain transfer agent (CTA) and, thus, address a fundamental problem associated with high amounts of CTA in CCTP namely the inverse first order dependence of the chain growing rate from the CTA concentration.[7] A conceptually similar approach, namely the combination of the Gibson[8] Fe/Zn based CCTP system and Fe based displacement catalysts was described by Cariou and Shabaker.[9] Unfortunately, strong catalyst poisoning and a very slow displacement rate restricts the applicability of this bimetallic catalyst system.
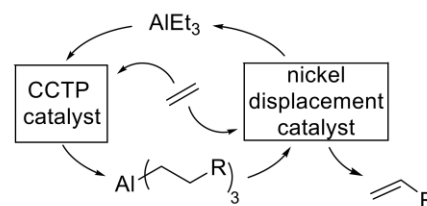
Scheme 1. Concept for the trimetallic ethylene oligomerization using a CCTP catalyst in combination with a nickel based displacement catalyst to produce linear alpha olefins.

Herein we describe a highly flexible synthesis of linear α-olefins from ethylene by a combination of a novel Zr based CCTP catalyst and a Ni based chain displacement catalyst in the presence of TEA and diethylzinc (DEZ) as CTAs. The Zr catalyst is inactive in the presence of solely diethylzinc and undergoes slow chain transfer in the exclusive presence of TEA. The Zr catalyst mediates faster and reversible chain transfer in the presence of a mixture of both CTAs. Furthermore, the displacement rates of both CTAs were investigated. Results showed that Al alkyls are displaced almost 70 times faster than zinc alkyls. The observed rate scenario permits the synthesis of short chain linear α-olefins as Schulz-Flory distributions with flexible α-values applying the Zr-Al-Zn-Ni catalyst system and long chain (C_{40+}) α-olefins using only Al as the CTA.

Cyclopentadienyl-aminopyridinato group 4 metal complexes are able to mediate chain transfer towards aluminium and tolerate a high Al to catalyst ratio.[10] To improve the stability, a

Lehrstuhl für Anorganische Chemie II—Katalysatordesign, Universitätsstr. 30, Universität Bayreuth, 95440 Bayreuth, Germany.

8. Tailor-made α-Olefins by Coordinative Chain Transfer Polymerisation, Displacement Reaction and Two Chain Transfer Agents

limitation observed so far of this type of catalyst, we introduced the bulky di(t-butyl)cyclopentadienyl ligand. The synthesis of the Zr pre-catalysts IIa-c and the molecular structure is shown in the SI. (for details see SI) and the molecular structure of IIc is shown in Figure 1. The introduction of the aminopyridinato ligands via methane elimination is quantitative by ^{1}H NMR. Three pre-catalysts could be synthesized by this method. To quantify the chain transfer behaviour of the Zr based catalysts to Al and/or Zn alkyls CCTP runs were performed first.
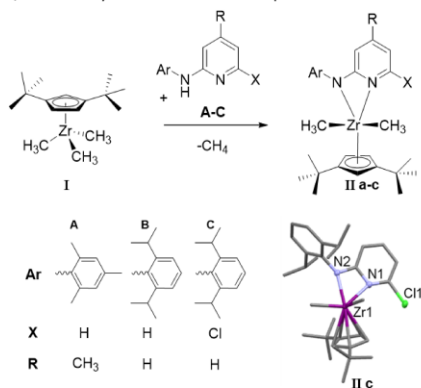
Figure 1. Synthesis of the pre-catalysts IIa-c and molecular structure of IIc.

A comparison of IIa-c in CCTP towards TEA revealed the highest activity (3900 kg$_{PE}$mol$_{cat}^{-1}$h^{-1}bar^{-1}) for IIb (Table 1). Furthermore, a high and [TEA] dependent M_n of the products is observed (Table 1, Entry 4-6). The rather broad dispersity indicates a relatively slow chain transfer behaviour of IIb. ^{1}H NMR measurements of the products after acidic workup confirmed the absence of olefinic end groups. In time dependent experiments, almost no growth of molecular weight of the polymers is observed (SI). This indicates a relatively slow chain transfer (relative to monomer insertion) from the Zr based catalyst to Al, leading to multiple ethylene insertions prior to chain transfer back to Al.

Table 1. CCTP experiment results with I and IIa-c, applying TEA and/or DEZ as CTA.^{a}

En.	Precat.	Al/Zr^b	Zn/Zr^b	Yield^c	Act^d	M_n^e	M_w/M_n
1	I	300	-	-	-	-	-
2	IIa	300	-	0.92	900	2.68	2.6
3	IIc	300	-	2.86	1400	2.85	1.9
4	IIb	1000	-	3.90	3900	3.00	1.6
5	IIb	500	-	3.19	3200	3.80	1.6
6	IIb	100	-	3.10	3100	7.20	1.7
7	IIb	-	1000	n.d.	n.d.	n.d.	n.d.
8	IIb	-	10	n.d.	n.d.	n.d.	n.d.
9	IIb	600	400	2.31	2200	1.14	1.3
10	IIb	800	200	2.62	2450	1.21	1.4

^{a}Conditions: n(pre-catalysts) = 2 μmol; ammonium borate [R$_2$N(CH$_3$)H] [B(C$_6$F$_5$)$_4$] (R = C$_{16}$H$_{33}$ - C$_{18}$H$_{37}$), Zr/B = 1/1.5; V$_{tol}$ = 150 mL, T = 50 °C, p$_{eth.}$ = 2 bar; t = 15 min. ^{b} in equivalents. ^{c} in g. ^{d} in kg$_{PE}$mol$_{cat}^{-1}$h^{-1}bar^{-1}. ^{e} in kg mol^{-1}.

An increase in molecular weight by time indicates reversible CCTP with different mixtures of TEA and DEZ (SI). A lower Mn

and dispersity of the products is obtained compared to the runs with TEA (Table 1, Entry 9-10). No polymerization activity could be observed by solely applying Zn alkyls. The results indicate chain transfer to Al is slow and irreversible, the chain transfer to Zn and Al is faster and reversible. Next, we investigated the differences of the rate of the Ni catalyzed displacement reaction rate between aluminum and zinc alkyls.
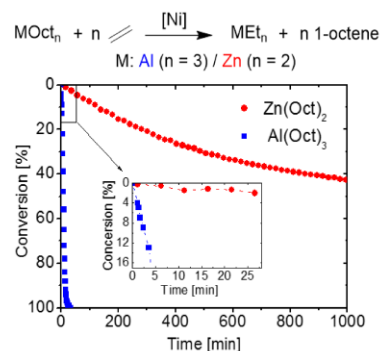

Figure 2. ^{1}H NMR monitored displacement reaction of dioctylzinc and trioctylaluminum, catalyzed by a nickel based displacement catalyst.

Therefore, we conducted ^{1}H NMR monitored kinetic studies on the nickel catalyzed displacement reaction. [Ni(cod)$_2$] was placed in a NMR tube equipped with a Young valve, followed by the addition of either trioctylaluminum or dioctylzinc dissolved in benzene-d6. The solutions were cooled with liquid nitrogen and ethylene was condensed into the NMR tubes. After warming to room temperature, the reaction was monitored by ^{1}H NMR (Figure 2, for more details see SI). For Al(Oct)$_3$, full conversion to TEA and 1-octene was observed after 25 minutes while initial rate for the displacement reaction of corresponding Zn(Oct)$_2$ was 70 times slower under equivalent conditions. A tandem CCTP with Zn alkyls and a Ni displacement catalyst would demand high amounts of Ni and therefore, not be very efficient. Furthermore, decomposition of the Ni catalyst in the presence of Zn alkyls was observed.

Table 2. Influence of DEZ and/or TEA on the tandem catalysis using IIb and [Ni(cod)$_2$] to produce Schulz-Flory distributed α-olefins.^{a}

En.	Zn/Zr^b	Al/Zr^b	Act^c	α-olefin^d	Σn_{olefin}^e	M_n^f	M_w/M_n	α-value
1	50	300	1500	97	9.1	-	-	0.87
2	100	300	1300	97	9.8	-	-	0.84
3	200	300	1500	96	11.8	-	-	0.79
4	300	300	1500	96	12.7	-	-	0.77
5	500	300	1600	96	14.0	-	-	0.72
6	1000	300	2200	85	14.5	-	-	0.67
7	-	1000	3300	98	0.84	3.00	1.7	-
8	-	500	3200	99	0.65	3.80	1.7	-
9	-	100	2900	98	0.34	7.20	1.8	-

^{a}Conditions: n$_{IIb}$ = 2 μmol; ammonium borate, [R$_2$N(CH$_3$)H][B(C$_6$F$_5$)$_4$] (R = C$_{16}$H$_{33}$ - C$_{18}$H$_{37}$), Zr/B = 1/1.5; V$_{tol}$ = 150 mL, T = 50 °C; p$_{eth}$ = 2 bar; V$_{eth}$ = 2 L, n$_{Ni}$ = 3 μmol. ^{b} in equivalents. ^{c} Based on the time required until 2 L ethylene were consumed; in kg$_{PE}$mol$_{cat}^{-1}$h^{-1} bar^{-1}. ^{d} in mol-%. ^{e} in mmol, ^{f} in kg mol^{-1}.

Next, the reaction of the combined catalysts, IIb and [Ni(cod)$_2$] and the influence of CTA composition and its concentration on product distribution was investigated (Table 2).

The alteration of the Zn-to-Zr ratio between 100 and 500 maintaining a constant Al-to-Zr ratio of 300 allows the synthesis of low molecular weight α-olefins (Table 2, Entries 2-6) with a selectivity higher than 95% and adjustable α-values ranging from 0.72 to 0.87. A Zn-to-Zr ratio of 1000 give rise to a selectivity of 85 % and an α-value of 0.67, while aliphatic byproducts were observed after hydrolysis. The high Zn concentration and the relatively slow displacement reaction of Zn alkyls[8] by Ni complexes reduces the α-olefin selectivity. A decreasing α-value was observed with increasing Zn alkyl concentrations. The obtained distribution of products matches a Schulz-Flory distribution (Entries 1-6, Table 2) and are shown in Figure 3a.
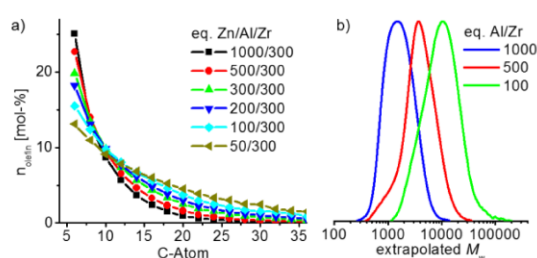
Figure 2. a) LAO distributions obtained from experiments described in Table 2, Entry 1-6. b) normalized LAO distribution obtained from experiments described in Table 2, Entry 7-9.

Both metals can be applied substochiometrically compared to the applied amounts of Zn and Al. A maximum of 5 mmol of alkyl chains was applied and a minimum of 9.9 mmol of LAO was observed. α-Olefins with high molecular weight are obtained if solely Al alkyls are applied. A decreasing M_n with increasing Al alkyl concentration and a product range from 3.00 to 7.20 kg mol^{-1} could be obtained (Table 2, Entry 7-9, Figure 3b).

Conclusions

In conclusion, we introduced a highly flexible synthesis of linear α-olefins by a combination of a CCTP catalyst based on Zr and Ni catalyzed chain displacement in the presence of TEA and DEZ as CTA. The Zr catalyst does not show any polymerization activity in the presence of Zn alone, mediates a slow chain transfer to Al and conducts faster and reversible chain transfer in the presence of an Al/Zn mixture. In addition, the displacement reaction rates of both CTA were investigated and remarkable differences were observed. The initial rate of the chain displacement of Al alkyls is 70 times higher compared to Zn alkyls. Based on the observed transfer and displacement rates, we were able to synthesize short chain linear α-olefins as Schulz-Flory distributions with flexible α-values, applying a Zr-Al-Zn-Ni catalyst system and long chain (C$_{40+}$) α-olefins using only Al as the chain transfer agent.

Conflicts of interest

The authors declare the following competing financial interest(s): A.G., W.P.K. and R.K. are inventors of patent applications WO2016180539 and WO2016180538, filed: May 13, 2015, published: May 16, 2016.

Notes and references

‡Crystallographic data CCDC 1861182 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the cambridge crystallographic data centre via www.ccdc.cam.ac.uk/structures.

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<p style="text-align:center">Supporting Information for</p>

Tailor-made α-Olefins by Coordinative Chain Transfer Polymerisation, Displacement Reaction and Two Chain Transfer Agents

Andreas Gollwitzer, Winfried P. Kretschmer and Rhett Kempe*

*Lehrstuhl für Anorganische Chemie II—Katalysatordesign, Universitätsstr. 30, Universität Bayreuth, 95440 Bayreuth, Germany.

1. Experimental

1.1 General

All manipulations of air sensitive compounds were performed with exclusion of oxygen and moisture using standard Schlenk techniques or a nitrogen or argon filled glove box (mBraun) with a high capacity circulator (< 0.1 ppm O_2). Deuterated solvents were purchased by Deutero and Eurisotop. All ^1H and ^{13}C spectra were recorded with Varian INOVA 300 (^1H: 300 MHz, ^{13}C: 75.4 MHz) spectrometer at 298 K. The ^1H and ^{13}C NMR spectra 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. All solvents used for air and moisture sensitive reactions were dried and purified by distillation from Na/benzophenone under argon atmosphere.

Toluene (Aldrich, anhydrous, 99.8%) used for ethylene polymerization was passed over columns of BASF R3–11-supported Cu oxygen scavenger and Al_2O_3 (Fischer Scientific). Ethylene (AGA polymer grade) was passed over BASF R3-11-supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å).

Triethyl aluminum ($AlEt_3$, TEAL, 25 wt-% in toluene, Aldrich), Diethyl zinc ($ZnEt_2$, DEZ, 15 wt-% in toluene, Aldrich), $Ni(cod)_2$ (Aldrich) *N,N,N*-trialkylammonium tetrakis-(pentafluorophenyl)borate ([R_2NMeH] [$B(C_6F_5)_4$], R = $C_{16}H_{33}$-$C_{18}H_{37}$ 6.2 wt-% $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals) were used as received.

1.1 Oligo-/Polymerization procedure

The oligomerization runs were performed either in a 300 mL glass or in a 1 L stainless steel autoclave (Büchiglasuster). Both are equipped with mechanical stirrers and stirred at 800 or 1000 rpm, respectively. The former was heated with an external water bath, while the latter one is equipped with a temperature controllable jacket, combining electrical heating and water cooling. Ethylene flow was monitored with a Bronkhorst High-Tech EI-Flow.

The autoclaves were evacuated and heated at 50 and 120°C for 1 h respectively. Afterwards, the oligo-/polymerization temperature was adjusted and the autoclaves were charged with the desired amount toluene, ethylene, *N,N,N*-trialkylammonium tetrakis(pentafluorophenyl)borate (2.2 µmol, 24.5 mg, 11% stock solution in Isopar) as activator, cumene, CTA- (and nickel-) solutions (added via a syringe). After saturation with ethylene the pre-catalyst solution was added. The ethylene flow was measured over the course of the polymerization procedure and is given as V_{eth} under normal conditions. After the procedure the reaction mixture was quenched with acidified ethanol and the obtained products were analyzed.

1.2 GC, GC-MS and GPC analysis

The toluene soluble fractions were analyzed with an Agilent 6890N gas chromatograph (GC), equipped with a FID and a 30 m HP-5 column, and on an Agilent 7890A gas chromatograph (GC) combined with an Agilent 5975C mass selective detector (MSD), equipped with a TCD, a 30 m HP-5 column and a Triple-Axis-Detector, using cumene as internal standard.

Gel permeation chromatography (GPC) analyses were carried out on an Agilent (Polymer Laboratories Ltd.) PL-GPC 220 high temperature chromatographic unit equipped with DP and detectors and three linear mixed bed columns (Polyolefin Linear M). GPC analysis was performed at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1 wt-%) 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 = 518-2,500,000 g mol^{-1}, K = 12.100 and Alpha = 0.707) and were corrected with K and Alpha values for linear PE (K = 40.600 and Alpha = 0.725).

1.3 X-ray Crystallography

X-Ray crystal structure analyses were performed with a Stoe IPDS-II diffractometer and a STOE STADIVARI [λ(Mo-Kα) = 0.71073 Å] equipped with an Oxford Cryostream low temperature unit. Structure solution and refinement were accomplished with SIR97[1],SHELXL-97[2] and WinGX[3].

1.4 Elemental analysis

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

2. Preparation of pre-catalysts

(1,3-Di-*tert*-butylcyclopentadienyl)-trimethanidozirconium(IV) (I, Cp''ZrMe$_3$, η^5-(1,3-^{t}Bu$_2$C$_5$H$_3$)Zr(CH$_3$)$_3$] was synthesized according to published literature.[4]

The ligands N-mesityl-4-methylpyridine-2-amine (A, Ap^{Me}H)[5], N-(2,6-diisopropylphenyl)-pyridine-2-amine (B, Ap^{H}H)[6], 6-Chloro-N-(2,6-diisopropyl-phenyl)-pyridine-2-amine (C, Ap^{Cl}H) were synthesized as reported.[7]
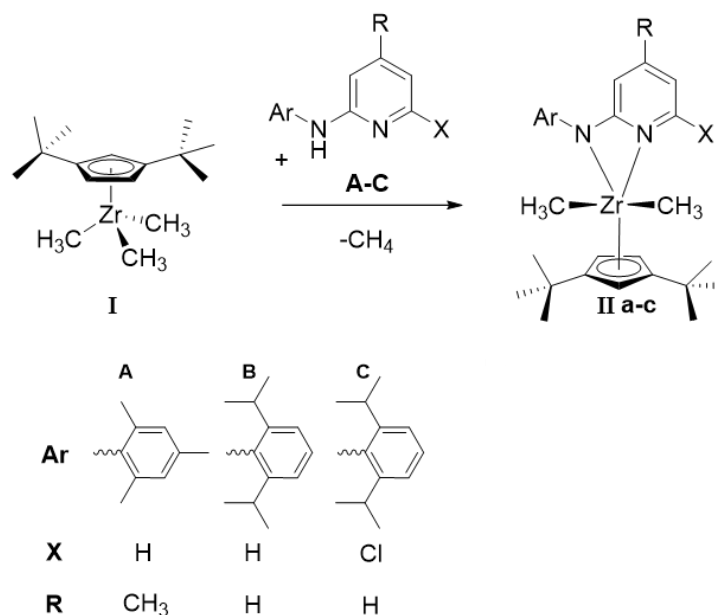
Scheme S1. Synthesis of the Cp''-Ap-stabilized dimethanido Zr(IV) pre-catalysts IIa-c.

2.1 Preparation of IIa
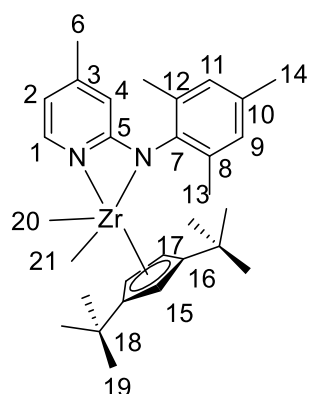
23 mg (0.103 mmol) **A** were added to a toluene solution (5 mL) of 32 mg (0.103 mmol) **I** at room temperature and stirred overnight. All volatiles were removed under reduced pressure and the product was washed twice with toluene. Isolated yield: 41 mg, 76 %. Anal. Cal. for $C_{30}H_{44}N_2Zr$ (523.92): C, 68.78, H, 8.47; N 5.35. Found: C, 68.30; H, 8.09; N, 5.39.

^{1}H NMR (300 MHz, C_6D_6): δ = 7.83 (d, ^3J = 6 Hz, 1H, H^1), 7.00 (m, 2H, $H^{9,11}$), 6.63 (t, ^4J = 2.5 Hz, 1H, H^{15}), 6.57 (d, ^4J = 2.5 Hz, 2H, H^{17}), 5.90 (s, 1H, H^2) 5.56 (s, 1H, H^4), 2.23 (s, 6H, H^{13}), 2,20 (s, 3H, H^{14}), 1.58 (s, 3H, H^6), 1.21 (s, 18H, H^{19}), 0.65 (s, 6H, $H^{20,21}$).

^{13}C NMR (75.4 MHz, C_6D_6): δ = 169.2 (s, 1C, C^5), 153.2 (s, 1C, C^1), 143.5 (s, 1C, C^3), 142.7 (s, 1C, C^7), 139.4 (s, 1C, C^{16}), 133.4 (s, 2C, $C^{8,12}$), 133.2 (s, 1C, C^{10}), 129.6 (s, 2C, $C^{9,11}$), 110.45 (s, 1C, C^{15}), 111.8 (s, 1C, C^4), 106.55 (s, 2C, C^{17}), 104.8 (s, 1C, C^2), 40.9 (s, 2C, $C^{20,21}$), 32.50 (s, 2C, C^{18}), 31.3 (s, 6C, C^{19}), 21.1 (s, 1C, C^6), 20.5 (s, 1C, C^{14}), 19.1 (s, 2C, C^{13}).

2.2 Preparation of IIb
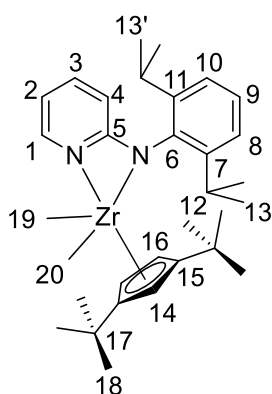
To a solution in toluene (10 mL) of 88 mg (0.346 mmol) of **B** were added 108 mg (0.346 mmol) **I** and stirred over night. All volatiles were removed under reduced pressure and the product was washed twice with toluene. Isolated yield: 140 mg, 77 %. Anal. Cal. for $C_{30}H_{44}N_2Zr$ (523.92): C, 69.63; H, 8.77; N, 5.08; Found: C, 69.13; H, 8.63; N, 4.78.

^1H NMR (300 MHz, C_6D_6): δ = 7.48 (d, ^3J = 5 Hz, 1H, H^1), 6.98 – 7.31 (m, 3H, $H^{2,3,4}$), 6.67 (t, ^3J = 7.3 Hz, 1H, H^9), 6.45 (t, ^3J = 2.3 Hz, 1H, H^{14}), 5.99 (d, ^3J = 2.2 Hz, 2H, H^{16}), 5.82 (m, 1H, H^{10}), 5.56 (d, ^3J = 8.8 Hz, 1H, H^8), 3.44 (sept, ^3J = 6.6 Hz, 2H, H^{12}), 1.32 (d, ^3J = 6.6 Hz, 6H, $H^{13'}$), 1.13 (s, 18H, H^{18}), 1.07 (d, J = 6.6 Hz, 6 H, H^{13}), 0.47 (s, 6H, $H^{19,20}$).

^{13}C NMR (75.4 MHz, C_6D_6): δ = 173.2 (s, 1C, C^5), 144.9 (s, 2C, $C^{7,11}$), 144.1 (s, 1C, C^{10}), 143.3 (s, 1C, C^1), 141.6 (s, 1C, C^6), 140.2 (s, 1C, C^{14}), 126.3 (s, 1C, C^3), 124.9 (s, 2C, $C^{8,10}$), 109.7 (s, 2C, C^{16}), 110.45 (s, 1C, C^4), 108.4 (s, 2C, C^{15}), 107.5 (s, 1C, C^2), 42.6 (s, 2C, $C^{19,20}$), 33.24 (s, 2C, C^{18}), 32. 111.8 (s, 1C, C^4), 106.55 (s, 2C, C^{17}), 104.8 (s, 1C, C^2), 40.9 (s, 2C, $C^{20,21}$), 32.50 (s, 2C, C^{17}), 32.00 (s, 6C, C^{18}), 28.7 (s, 2C, C^{13}), 26.0 (s, 2C, $C^{13'}$), 24.67 (s, 2C, C^{12}).

## 2.3 Preparation of IIc
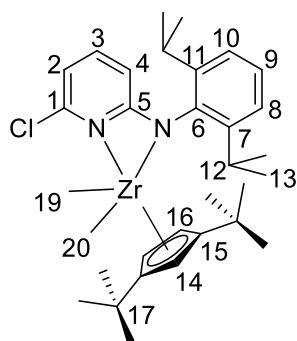
To a solution of 106 mg (0.337 mmol) **I** in toluene (5 mL) 97.6 mg (0.337 mmol) **C** were given and stirred at rt. overnight. All volatiles were removed under reduced pressure and the product was washed twice with toluene. Isolated yield: 185 mg, 92 %. Anal. Cal. for $C_{32}H_{47}ClN_2Zr$ (586.42): C, 65.54; H, 8.08; Cl, 6.05; N, 4.78;. Found: C, 65.94, H, 8.21, N, 4.45.

^{1}H NMR (300 MHz, C_6D_6): δ = 7,19 – 6.95 (m, 3H, H^{2,3,4}), 6.62 (t, ^4J = 2.6 Hz, 1H, H^{14}), 6.30 (t, ^3J = 8.2 Hz, 1H ,H^9), 6.29 (d, ^4J = 2.9 Hz, 2H, H^{16}), 5.88 (d, ^3J = 6.3 Hz, 1H, H^{10}), 5.33 (d, ^3J = 8.2 Hz, 1H, H^8), 3.46 (sept, ^3J = 6.5 Hz, 2H, H^{12}), 1.29 (d, ^3J = 7.0 Hz, 6H, H$^{13'}$), 1.17 (s, 18H, H$^{18)}$, 1.01 (d, ^3J = 6.4 Hz, 6H, H^{13}), 0.60 (s, 6H, H^{20,21}).

^{13}C NMR (75.4 MHz, C_6D_6): δ = 171.87 (s, 1C, C^5), 146.7 (s, 1C, C^6) 143.9 (s, 2C, C^{7,11}), 142.6 (s, 1C, C^1), 141.7 (s, 2C, C^{16}), 140.63 (s, 1C, C^9), 128.9 (s, 1C, C^4), 125.9 (s,1C, C^3), 124.27 (s, 1C, C^2), 110.20 (s, 1C, C^4), 109.5 (s, 1C, C^{14}), 108,51 (s, 2C, C^{15}), 105.58 (s, 1C, C^{8,10}), 45.58 (s, 2C, C^{19,20}), 32.6 (s, 2C, C^{17}), 31.45 (s, 6C, C^{18}), 28.80 (s, 2C, C^{12}), 26.04 (s, 2C, C$^{13'}$), 24.48 (s, 2C, C^{13}).
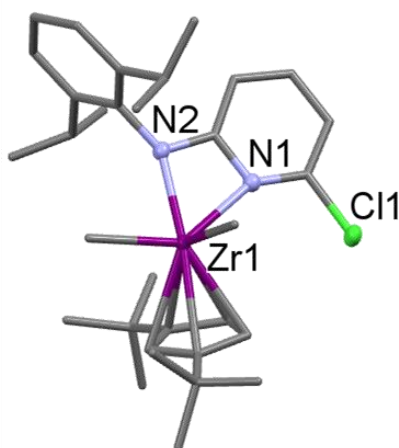
Figure S 127. Molecular structure of **IIc** with 50% probability of thermal ellipsoids; Hydrogen atoms, disordered isopropyl carbons and the solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1-Zr1 2.388(2); N2-Zr1 2.251(2); C32-Zr1 2.227(2); C31-Zr1 2.261(2); N1-C5 1.371(3); C5-N2 1.350(2); N2-C6 1.436(3); C31-Zr1-C32 102.48(8); Zr1-N1-C5 92.3(1); Zr1-N2-C5 99.1(1); N1-Zr1-N2 57.48(6); C5-N2-C6 117.39(2).

3. Polymerization runs

Table S 3*. Time dependent CCTP with pre-catalyst **IIb** in presence of 2 mmol TEAL[a].*

Entry	Time [min]	V_{eth} [L]	Activity[b]	M_n [kg/mol]	M_w/M_n
1	10	2.4	4500	3.45	1.8
2	15	3.1	3900	3.50	1.7
3	20	3.5	3300	3.55	1.7
4	25	3.9	2100	3.60	1.7

[a] Conditions: pre-catalyst **IIb**, n = 2 μmol; ammonium borate, $[R_2N(CH_3)H][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$ - $C_{18}H_{37}$), Zr/B = 1/1.5; 250 mL of toluene; p_{eth} = 2 bar; n_{TEAL} = 2 mmol (c = 8.0·10^{-3} M, Zr/Al = 1/1000). [b] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$].
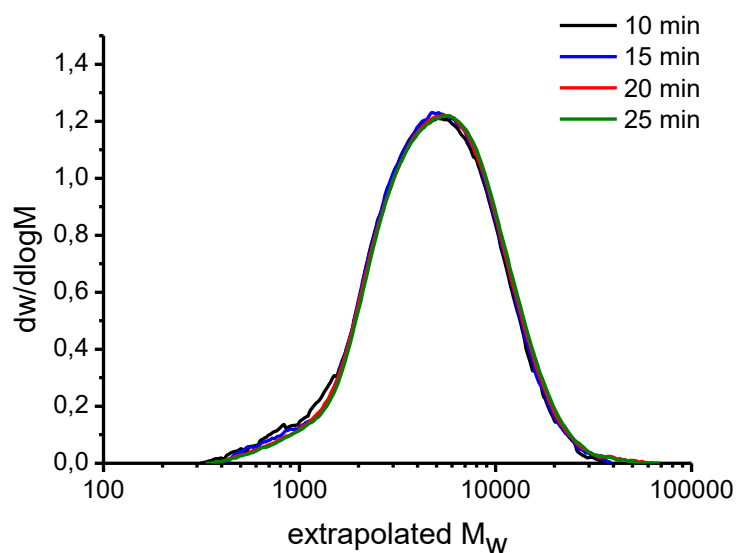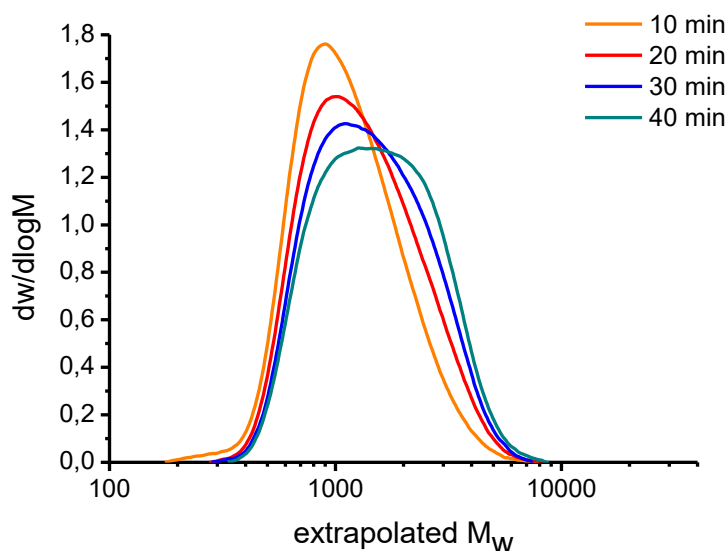

Figure S 2. Molecular-weight distribution plot of polymerization experiments described in **Table S 3**.

Table S 4. Time dependent CCTP with pre-catalyst **IIb** in presence of 1.6 mmol TEAL and 0.4 mmol DEZ[a].

Entry	Time [min]	V_{eth} [L]	Activity[b]	M_n [kg/mol]	M_w/M_n
1	10	1.7	3300	0.94	1.4
2	20	2.6	2450	1.14	1.5
3	30	3.4	2300	1.31	1.7

[a] Conditions: pre-catalyst **IIb**, n = 2 μmol; ammonium borate, $[R_2N(CH_3)][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$ - $C_{18}H_{37}$), Zr/B = 1/1.5; 250 mL of toluene; p_{eth} =2 bar; n_{TEAL} = 1.6 mmol (c_{TEAL} = 6.4·10^{-3} M, Zr/Al = 1/800); n_{DEZ} = 0.4 mmol, (c_{DEZ} =1.6·10^{-3} M, Zr/Zn = 1/200). [b] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$].
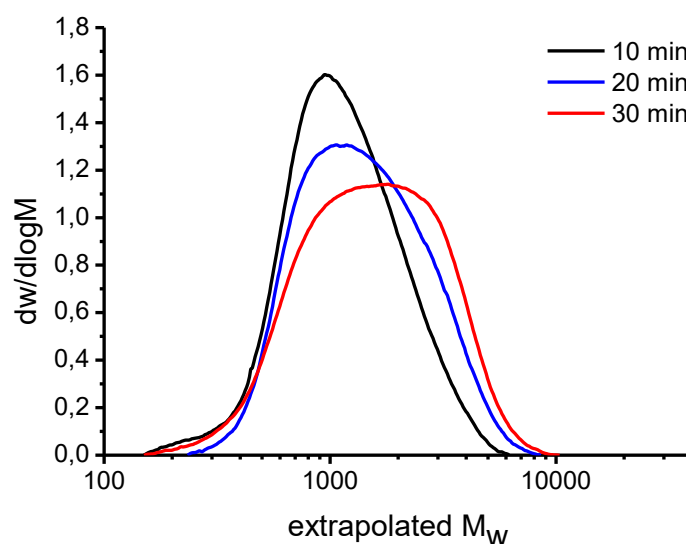
Figure S 3. Molecular-weight distribution plot of polymerization experiments described in **Table S 4**.

Table S 5. Time dependent CCTP with pre-catalyst **IIb** in presence of 1.2 mmol TEAL and 0.8 mmol DEZ[a].

Entry	Time [min]	V_{eth} [L]	Activity[c]	M_n [kg/mol]	M_w/M_n
1	10	1.5	2900	0.98	1.3
2	20	2.3	2200	1.12	1.3
3	30	3.0	1800	1.21	1.3
4	40	3.3	1600	1.29	1.3

[a] Conditions: pre-catalyst **IIb**, n = 2 μmol; ammonium borate, $[R_2N(CH_3)][B(C_6F_5)_4]$ (R = $C_{16}H_{33}$ - $C_{18}H_{37}$); Zr/B = 1/1.5; 250 mL of toluene; pressure, 2 bar; n_{TEAL} = 1.2 mmol (c_{TEAL} = 4.8·10^{-3} M, Zr/Al = 1/600); n_{DEZ} = 0.8 mmol, (c_{DEZ} =3.2·10^{-3} M, Zr/Zn = 1/400). [b] [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$].

Figure S 4. Molecular-weight distribution plot of polymerization experiments described in **Table S 5**.

4. ^{1}H NMR Experiments

4.1 Displacement reaction of Al alkyls
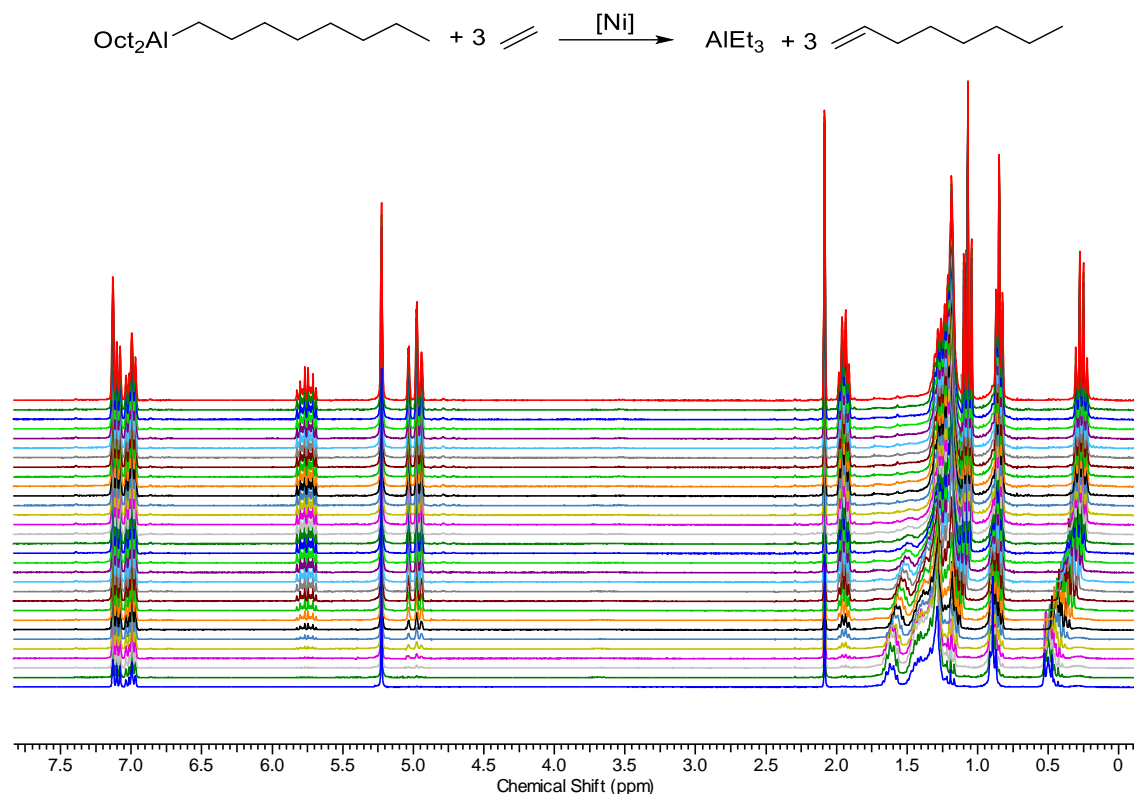
Figure S 5. ^{1}H NMR monitored displacement reaction of AlOct$_3$ with ethylene catalyzed by Ni with toluene as internal standard; c[Ni(cod)$_2$] = 1.27 10^{-4} mol/L, c(AlOct$_3$) = 0.0926 mol/L.
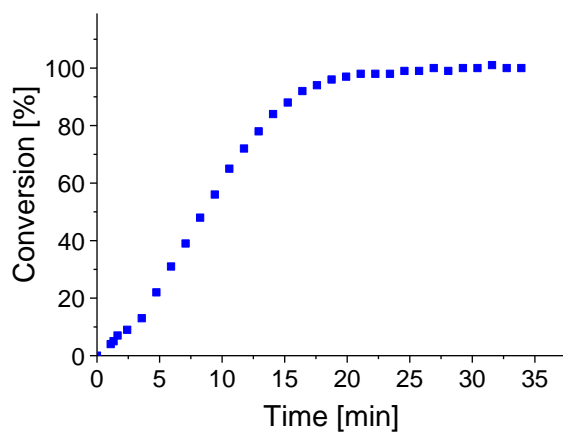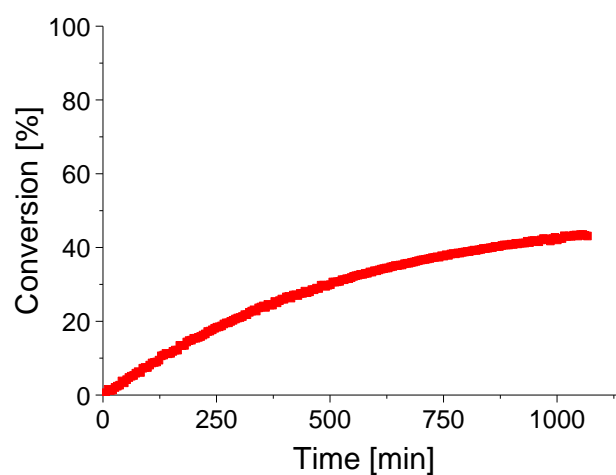

Figure S 6. Conversion over time plot of the displacement reaction of AlOct$_3$ with ethylene catalyzed by Ni.

4.2 Displacement reaction of Zn alkyls

OctZn $\diagup\diagdown\diagup\diagdown\diagup\diagdown$ + 2 $\diagup\!\!\!\diagup$ $\xrightarrow{\text{[Ni]}}$ ZnEt$_2$ + 2 $\diagup\diagdown\diagup\diagdown\diagup$
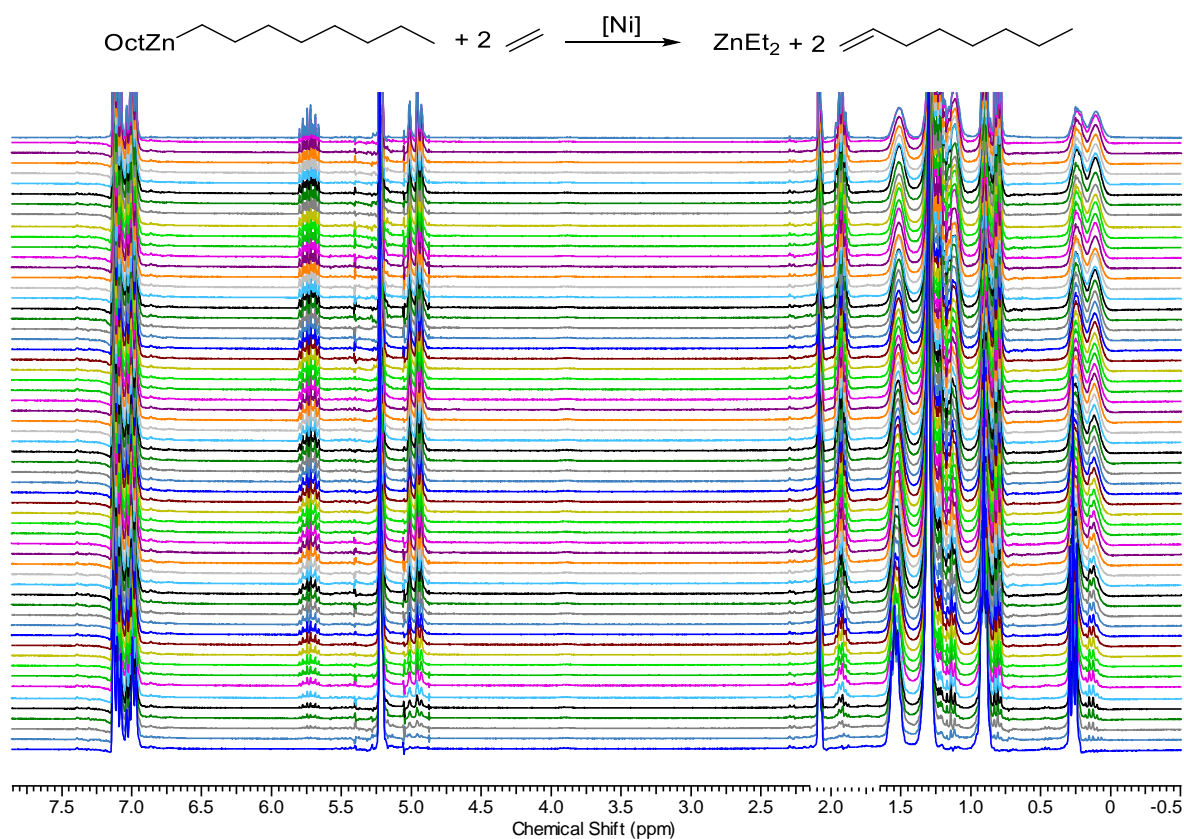
Figure S 7. ^{1}H NMR monitored displacement reaction of ZnOct$_2$ with ethylene catalyzed by Ni with toluene as internal standard; c[Ni(cod)$_2$] = 1.27 10^{-4} mol/L, c(ZnOct$_2$) = 0.0926 mol/L.

Figure S 8. Conversion over time plot of the displacement reaction of ZnOct$_2$ with ethylene catalyzed by Ni.

5. Schulz-Flory curve fitting analysis

Table S4. Influence of DEZ and/or TEA on the tandem catalysis using IIb and [Ni(cod)₂] to produce Schulz-Flory distributed α-olefins.[a]

En.	Zn/Zr [eq.]	Al/Zr [eq.]	Act[b]	α-olefin [mol-%]	Σ[n_{olefin}][c]	α-Value
1	50	300	1500	97	9.1	0.87
2	100	300	1300	97	9.8	0.84
3	200	300	1500	96	11.8	0.79
4	300	300	1500	96	12.7	0.77
5	500	300	1600	96	14.0	0.72
6	1000	300	2200	85	14.5	0.67

[a] Conditions: nIIb = 2 µmol; ammonium borate, [$R_2N(CH_3)H$][$B(C_6F_5)_4$] (R = $C_{16}H_{33}$ - $C_{18}H_{37}$), Zr/B = 1/1.5; V_{tol} = 150 mL, T = 50 °C; p_{eth} = 2 bar; V_{eth} = 2 L, n_{Ni} =3 µmol;[b] Based on the time required until 2 L ethylene were consumed; [$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$], [c] in mmol

Experimentally obtained oligomer distributions were analyzed using the Solver add-in for Microsoft Excel which enables a least-square fit of the experimentally obtained molar distributions to the Schulz-Flory formula:

$$C_p = c * (1 - k) * a^{(p-1)}$$

α = α-Value
C_p = amount of oligomer in moles (having p units of monomer inserted)
c = total amount of product in moles
p = number of monomer units inserted in the metal-carbon bond
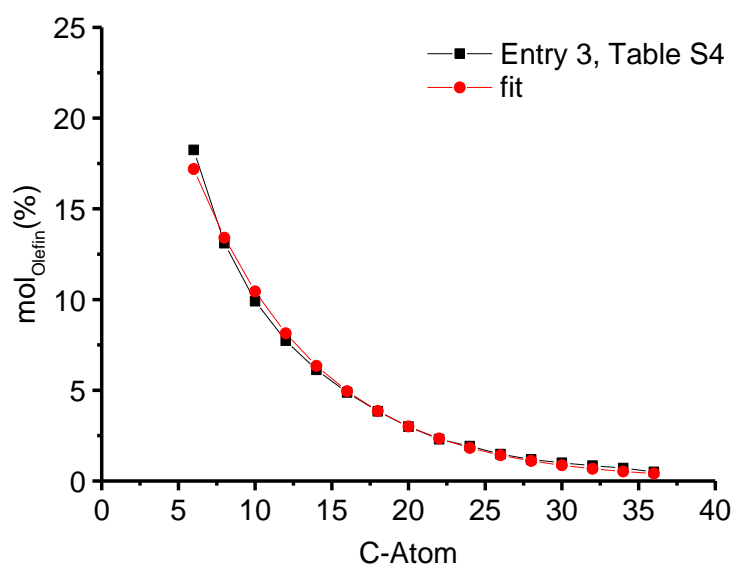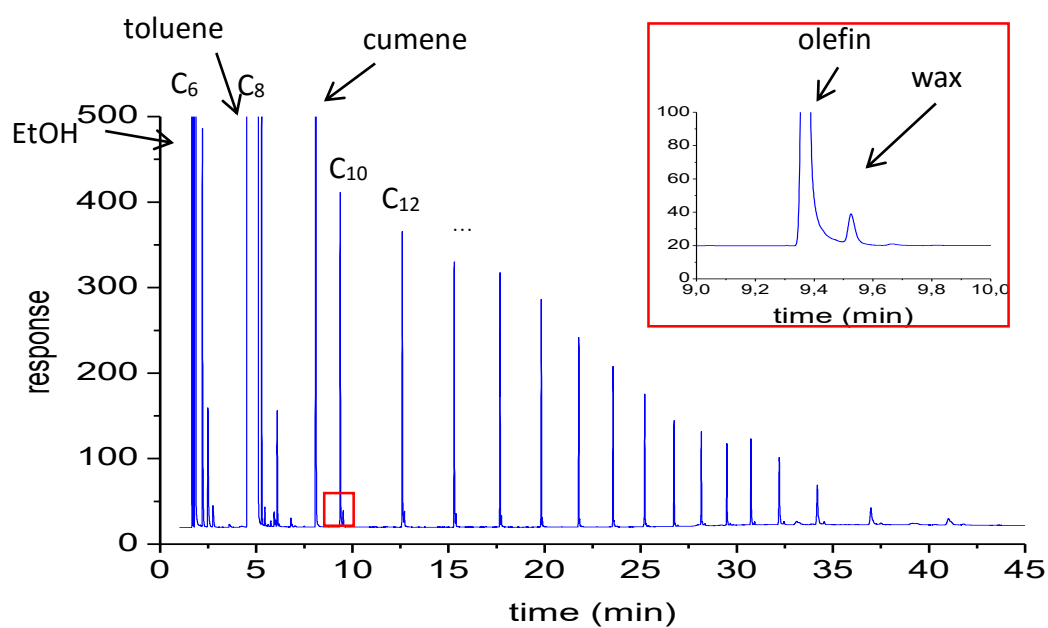R^2 = sum of square errors

Figure S 9. Fit and experimental distribution of α-olefins obtained from Entry 3, Table S4.

Figure S 10. GC-Chromatogram obtained from Entry 1, Table S4. Excerpt shows wax-byproduct due to the acidic workup.
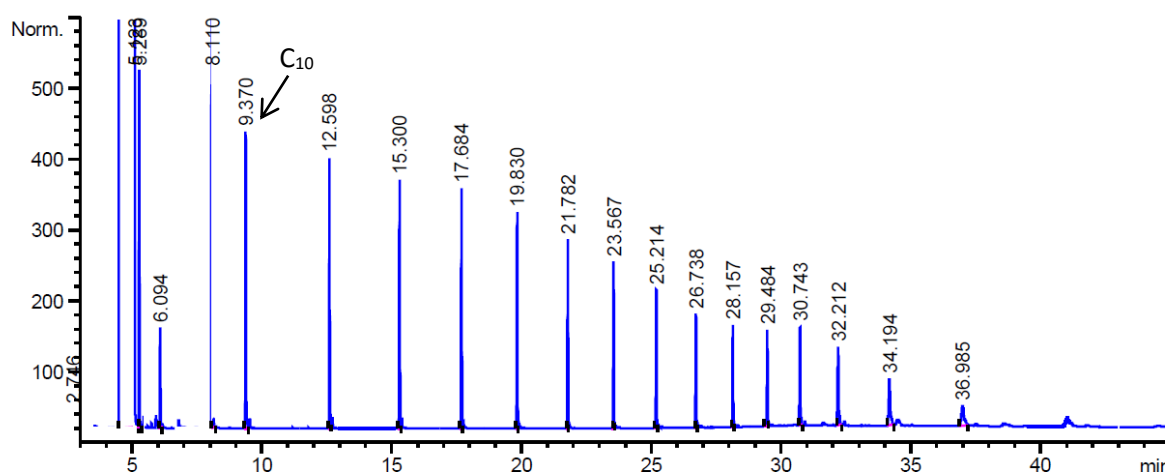
5. Screening experiments

Figure S 11. GC Chromatogram of the toluene fraction, obtained from Entry 1 in Table S4.
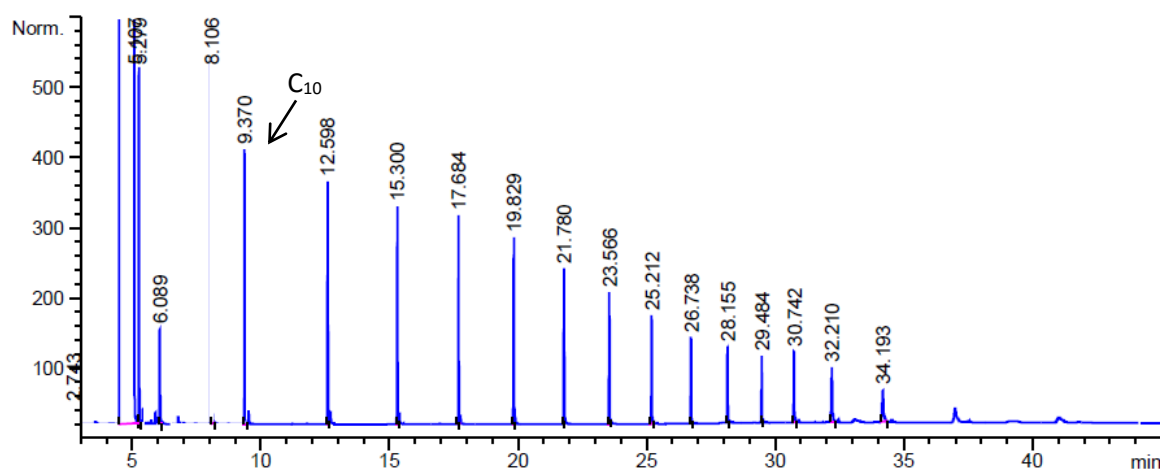

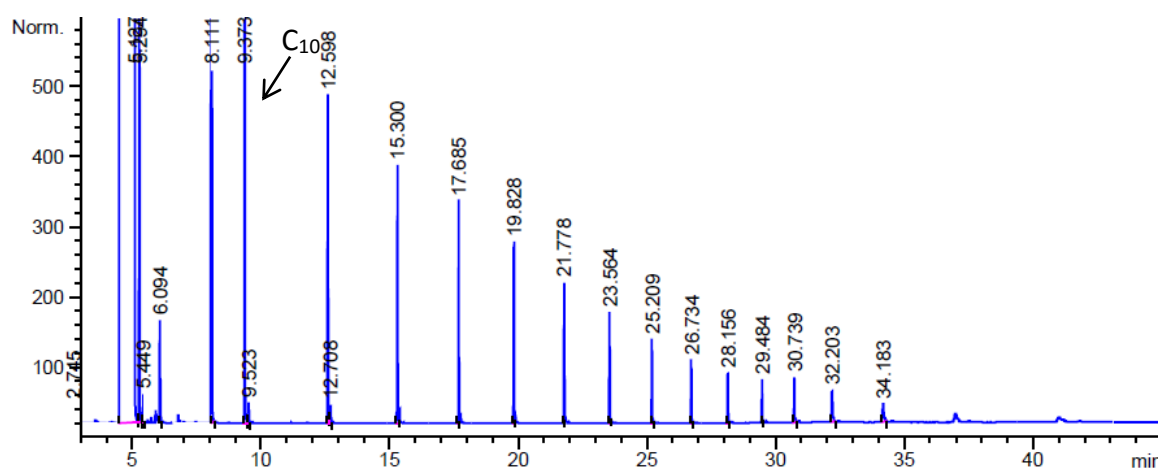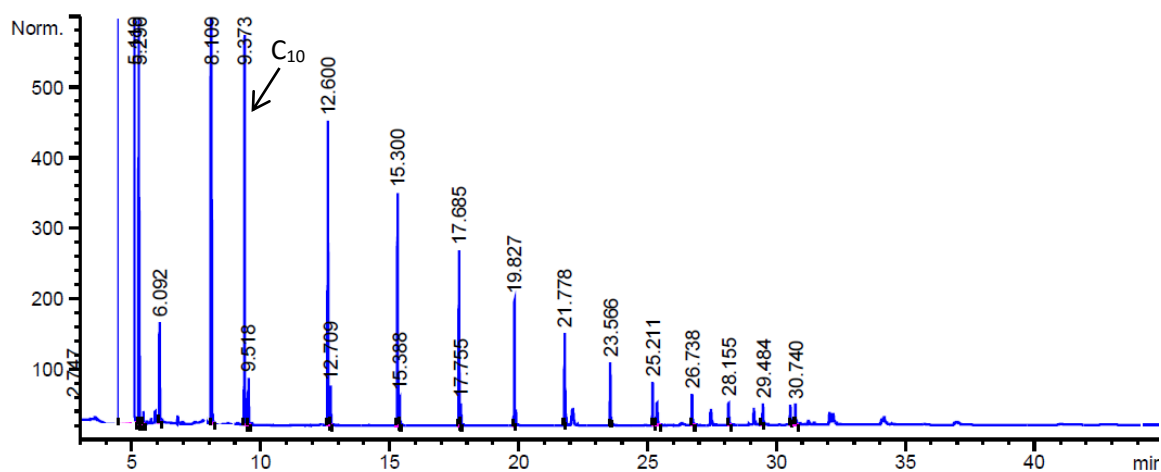**Figure S 12**. GC Chromatogram of the toluene fraction, obtained from Entry 2 in Table S4.

Figure S 13. GC Chromatogram of toluene the fraction, obtained from Entry 3 in Table S4.

Figure S 14. GC Chromatogram of the toluene fraction, obtained from Entry 4 in Table S4.

6. References

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