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Review

Metallocene and related catalysts for olefin, alkyne and silane dimerization and oligomerization

Christoph Janiak *

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany

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Dedicated to Prof. Helmut Alt on the occasion of his 60th birthday

Contents

Abbreviations: ^{n}Bu, *n*-butyl, C_4H_9; ^{i}Bu, *iso*-butyl, $(CH_3)_2CHCH_2$–; ^{t}Bu, tert-butyl, Me_3C–; Cp, cyclopentadienyl, general; Et, ethyl, C_2H_5; Flu′, fluorenyl connected to another ligand or substituent, $C_{13}H_8$; Ind, unsubstituted indenyl, C_9H_7; Ind′, indenyl connected to one other ligand or substituent, C_9H_6, 1-indenyl unless stated otherwise; Ind″, indenyl connected to two other ligands or substituents, C_9H_5; Ind‴, indenyl connected to three other ligands or substituents, C_9H_4; Ind′H_4, tetrahydroindenyl connected to another ligand or substituent, C_9H_{10}; MAO, methylalumoxane; Me, methyl, CH_3–; Ph, phenyl, C_6H_5–; ^{n}Pr, *n*-propyl, C_3H_7; ^{i}Pr, *iso*-propyl, $(CH_3)_2CH$–; THF, tetrahydrofuran

* Tel.: +49 7612036127; fax: +49 7612036147.
E-mail address: janiak@uni-freiburg.de.

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Abstract

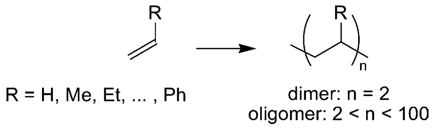
This review summarizes the use of metallocene complexes and related compounds as catalysts in the dimerization or oligomerization of olefins (alkenes) or terminal acetylenes (alkynes) and in the dehydrocoupling/dehydrooligomerization of silanes. Metallocene complexes of group-III metals (scandocenes, yttrocenes, lanthanocenes), lanthanoids (neodymocenes) and group-IV metals (titanocenes, zirconocenes, hafnocenes) have been utilized in the selective (co-/hydro-)oligomerization of ethene, of the α-olefins propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, and 1-octene, of branched olefins, e.g. methyl-butenes, methyl-pentenes and styrene, of cycloolefins, e.g. cyclopentene and norbornene and of α, ω-dienes, e.g. 1,5-hexadiene and 1,7-octadiene. Group-III metallocenes are often active in the C–C coupling without a cocatalyst; group-IV metallocenes require the help of a cocatalyst, such as methylalumoxane, MAO, aluminum alkyls, e.g. $Al^{i}Bu_3$, or perfluorated boranes, e.g. $B(C_6F_5)_3$. The actinoid metallocenes $(C_5M_5)_2AnMe_2$ with An = thorium, uranium allow for the dimerization and oligomerization of terminal acetylenes. The dehydrooligomerization of (hydro)silanes is typically achieved by group-IV metallocene chlorides together with *n*-butyl lithium. Also included in this review are related sandwich and half-sandwich (mono-cyclopentadienyl) complexes used for olefin oligomerization. The related sandwich complexes feature phospholyl, boratabenzene or carboranate ligands. Methods of oligo–olefin analyses by gel permeation chromatography (GPC), ^{1}H NMR spectroscopy, gas chromatography (GC) or viscosity measurements for molecular weight determinations and by ^{1}H and ^{13}C NMR spectroscopy or MALDI–TOF mass spectrometry for end group structure determinations are summarized. Possible applications of olefin oligomers, in particular oligopropenes are presented. The functionality of a double bond at the end of each chain (for further modifications) together with the product homogeneity are the advantages of oligomers from metallocene catalysis. In addition, olefin oligomerization is used to study mechanistic aspects and to obtain a better insight into the reaction mechanism of metallocene polymerization catalysis because of the homogeneity of the reaction mixture and because certain mechanistic aspects are easier to investigate in oligomeric products than in high-molar-mass polymers.

Keywords: Metallocene catalysts; Olefins; Alkynes; Silanes; Oligomerization; Hydrooligomerization

1. Introduction

The use of olefin oligomers as intermediates for specialty chemicals, versatile feedstocks and building blocks drives the interest in the catalytic oligomerization [1,2]. Ethene oligomers, in particular higher linear α-olefins of chain lengths C_4–C_{18} are well established and nickel chelate complexes used in the SHELL-higher-olefin-process (SHOP) feature prominently in their manufacturing [1,3,4]. A variety of metals and methods are available for the oligomerization of α-olefins [4–6], but feasible processes involving well-defined catalysts are rare [7].

The formation of olefin chains is categorized as follows: dimerization when $n = 2$, oligomerization when $2 < n < 100$ and polymerization when $n > 100$ [1].



The term “metallocene catalyst” typically refers to the bent metallocenes of the group-IV transition metals titanium, zirconium and hafnium. In particular, “metallocene catalysts” refer to zirconocene complexes, which are in the center of academic and industrial attention; see reviews in [8–21]. The titanocene catalysts are unstable at conventional polymerization temperatures and the hafnium systems are too expensive. From the beginning of the 1990’s these bis(cyclopentadienyl)group-IV metal complexes (single-site catalysts) were introduced in industry as a new generation of Ziegler-Natta catalysts for the polymerization of olefins [22–30]. Neutral group-III (Sc, Y, La) and lanthanoid metallocene complexes of the general type Cp_2MR and $[Cp_2MH]_2$ are also capable of polymerizing ethene [31–34]. They are polymerization active even in the absence of a cocatalyst. In their monomeric form the group-III and lanthanoid metallocenes are *iso*-d-electronic (d^0, not counting the f-electrons) with the active group-IV metallocene cation $[Cp_2ZrR]^+$. Group-III and lanthanoid metallocene catalysts show the same mechanistic features, such as olefin insertion, β-H and β-Me elimination and M–R bond hydrogenolysis as the zirconocene catalysts. New studies in this direction also involve divalent samarocene, Cp_2Sm [35] as well as *ansa*-$Cp_2Sm(THF)_2$ [36]. A single-component chiral organoyttrium *ansa*-metallocene catalyst $[Me_2Si(C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}{}^tBu)_2YH]_2$ was found to slowly polymerize propene (97% isotactic), 1-butene, 1-pentene, and 1-hexene [37]. Hence, scandocene [38], yttrocene, lanthanocene and lanthanoid metallocene complexes are also efficient catalysts for the (hydro-)dimerization and (hydro-)oligomerization of α-olefins, isobutene and alkynes (see below).

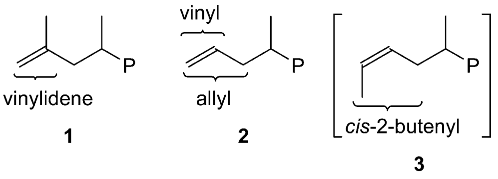
In the beginning of metallocene catalysis the observation of oily, oligomeric or low molar-mass products from propene polymerizations with zirconocene catalysts was generally regarded as unfortunate [39–42] and to some extent still is. It is now more and more recognized that metallocene catalysts can be used effectively for the directed oligomerization of α-olefins [7,43–58] and other monomers. It seems desirable to use the fascinating features of metallocene catalysts in organic synthesis. The key to obtain oligomers is the drastic reduction of the rate of propagation versus the rate of termination. This diverts the catalytic carbon–carbon coupling process from a rapid polymerization to e.g. the synthetically useful dimerization of olefins.

The correlation between the rate constants and the molecular weight of the oligomer can be expressed in mathematical terms [59]: we assume for simplicity only one chain transfer mechanism whose rate is independent of any species concentration other than the active complex (cat*), e.g. β-hydrogen transfer to metal with rate(β-H elim.) = $k_{\beta\text{-H}} c_{\text{cat*}}$. Then the following equations can be derived, using c_M = concentration of monomer; m_M = molecular weight of monomer; $c_{\text{cat*}}$ = concentration of active complex; $k_{\text{(propagation)}}$ = rate constant for chain propagation and, for simplicity here, $k_t = k_{\text{termination}} = k_{\beta\text{-H}}$ = rate constant for β-H elimination.

- probability for chain growth: $p = k_p c_M c_{\text{cat*}}/(k_p c_M c_{\text{cat*}} + k_t c_{\text{cat*}}) = k_p c_M/(k_p c_M + k_t)$
- mole fraction of oligomers which have reached the degree of oligomerization i: $x_i = p^{i-1}(1-p)$ thereby assuming a constant growth probability p. The term $(1-p)$ is the probability for chain transfer with $1-p = k_t/(k_p c_M + k_t)$
- number average degree of polymerization $\overline{P}_n = \sum_{i=1}^{n} i x_i = (1-p)\sum_{i=1}^{n} i p^{(i-1)} \approx 1 + p + p^2 + \cdots + p^{n-1}$; $\overline{P}_n = \frac{p^n-1}{p-1} = \frac{1-p^n}{1-p} \approx \frac{1}{1-p}$ for n becoming sufficiently large and $p < 1$ so that $p^n \to 0$.
- $\overline{P}_n = \frac{1}{1-p} = \frac{k_p c_M + k_t}{k_t} = \frac{k_p c_M}{k_t} + 1$
- number average molecular weight $M_n = m_M \sum_{i=1}^{n} i x_i = m_M \overline{P}_n = m_M \left(\frac{k_p c_M}{k_t} + 1\right)$.

Thus the molecular weight M_n is proportional to the rate of propagation, $k_p c_M$ and inversely proportional to the rate of chain transfer, k_t.

With metallocenes the chain-termination reactions can give oligomers with unsaturated, double-bond end groups, predominantly of the vinylidene type (**1**). In special cases also a vinyl/allyl double-bond (**2**) or a 2-butenyl group (**3**) can be formed (for their originating reaction see below). One way to enforce oligomers is to use hydrogenation, that is, hydrogenolysis of the M–R bond as an additional termination reaction. But this has the disadvantage of yielding unfunctionalized, saturated hydro-oligomers.

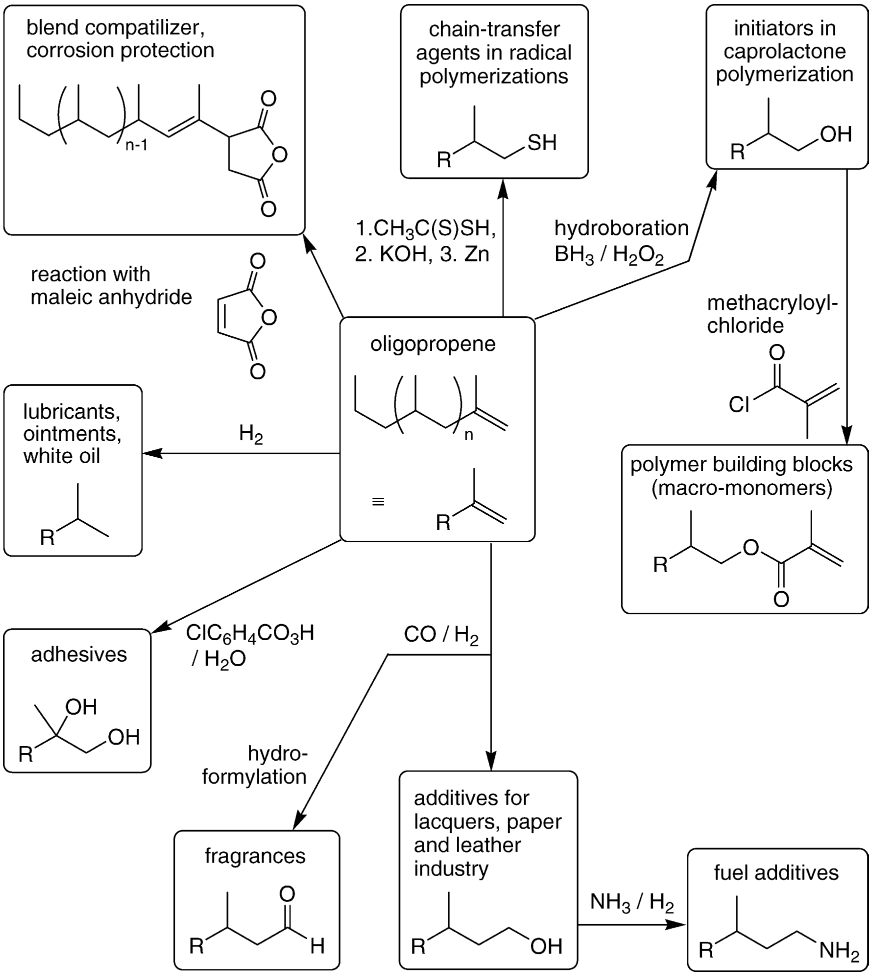


P = continuing polymer / oligomer chain

For oligomers at large, a number of potential applications are possible, such as long chain 1-alkenes for surfactants, clean diesel fuel alkanes [60], octane boosters and new monomers [61–64]. In addition, a variety of functionalization reactions with double-bond end groups in oligomers lead to organic specialities with potential applications as adhesives [65], blend compatilizers [47,48,66], fragrances, synthetic lubricants [55,67,68], additives for fuels [68] or in the paper and leather industry [7,69]. Also, α-olefin oligomers or derivatives thereof can be used as (macro-)monomeric building blocks for novel graft copolymers containing oligo-olefin side chains. The key is the chain end functionalization of the usually vinylidene-terminated oligopropenes via double bond conversion reactions. Succinic anhydride-terminated oligopropenes are obtained by ene-type addition of maleic anhydride. The anhydride-terminated oligopropene reacts with amin-terminated polyamide-6,6 to yield polypropene-b-polyamide-6,6-b-polypropene triblock copolymers which are efficient dispersing agents. Thiol-terminated oligopropenes are chain transfer reagents in radical methylmethacrylate polymerization. Acrylic monomers and styrene are grown onto the thiol end group via a chain transfer reaction, thereby producing a family of block copolymers. Hydroxy-terminated oligopropenes are useful initiators in caprolactone polymerization to form poly(propene-b-caprolactone) block copolymers. Homo- and copolymerization of acrylic oligopropene yield novel classes of graft copolymers with pendant oligopropene chains [46–49] (Scheme 1).

The functionality of a double bond at the end of each chain together with the product homogeneity are the advantages of oligomers from metallocene catalysis. In addition, olefin oligomerization is used to study mechanistic aspects and to obtain a better insight into the reaction mechanism of metallocene polymerization catalysis because of the homogeneity of the reaction mixture (no heterogenation through polymer precipitation) and because in some aspects the oligomeric products are easier to investigate than high-molar-mass polymers [70–84].

sThe average molecular weight of the produced oligo-olefins for a given catalyst system can be controlled by adjustment of reaction temperature and monomer concentration, with the molecular weight being inversely correlated to temperature, while an increase in monomer concentration also increases the molecular weight. The molar masses of poly- (and oligo-)olefins obtained with MAO-activated



Scheme 1. Potential functionalizations and applications for specialty chemicals on the basis of oligopropene (olefin oligomers in general) (adapted from [7,47]). Further details: reaction with maleic anhydride and reaction of the obtained succinic anhydride with diamine-terminated polyamide-6,6 to give triblock copolymer dispersing agents, see [47,48,65]; thiol-terminated oligopropenes as chain transfer agents in radical polymerizations, see [47,49]; hydroxy-terminated oligopropene as initiator for caprolactone polymerization, see [47]; methacrylate-terminated oligopropene, macromonomer for graft copolymers, see [47,49].

zirconocene systems generally decrease with the concentration of the MAO cocatalyst. Addition of $AlMe_3$ also decreases the molecular weight due to the action of TMA as a chain transfer agent [85,86].

2. Oligomer analyses

A presentation of methods on oligo-olefin analyses is helpful as the results from these analyses form the basis of many mechanistic conclusions drawn from the oligomer syntheses by metallocene and related catalysts which will subsequently be presented in Sections 3 and 4.

2.1. Molecular weight determinations

Molecular weight determinations of olefin oligomers are typically based on either gel permeation/size exclusion chromatography (GPC/SEC), ^{1}H NMR spectroscopy, gas chromatography (GC), viscosity and/or cryoscopy measurements.

2.1.1. Gel permeation/size exclusion chromatography

GPC/SEC is widely used for determining the molar mass and distribution of polymer samples. Recent work has, however, shown the use of GPC together with the universal calibration method to be problematic when molar masses are small ($<5000\,g\,mol^{-1}$) and particular in the oligomer range, because of the asphericity of individual oligomer configurations [87]. Also, for methyl methacrylate oligomers a non-linear response to ultraviolet (UV) and differential refractive index (DRI) detection was demonstrated, i.e. the extinction coefficient and relative index of refraction was found to be chain length-dependent. This resulted in systematic errors in detection, such that without extensive calibration for chain length, the content of the low molar mass oligomers was determined too low. As the role of end groups becomes increasingly important with lower molar mass, this caveat may be general to other oligomeric systems [88]. To avoid the potential pitfalls of GPC measurements it may be advisable to employ a variety of methods for the molar mass determination. The oligomer dispersity $Q = M_w/M_n$ can, however, only be determined by GPC.

2.1.2. ^{1}H NMR spectroscopy

Assuming that each oligomer possesses a double-bond end group, the ratio of olefinic protons to alkyl protons can be determined by integration of the ^{1}H NMR spectrum. From this an average chain length is derived which translates into the number average molar mass, M_n [89]. Furthermore, the relative content of different types of double bonds (if present) can be determined. Among the methods described here, NMR spectroscopy is one of the fastest and simplest procedure, requiring only a small amount of sample.

2.1.3. Gas chromatography, GC and GC/mass spectrometry, GC/MS

For oligomeric fractions which are sufficiently volatile and can be evaporated without decomposition at elevated temperatures, a GC (with flame ionization detection, FID) or GC/MS analysis is often used to separate the different oligomers, to determine their individual molecular weight (by MS) and, hence, the degree of oligomerization, and to establish their identity. The latter is either done by MS analysis or by comparison with separately synthesized or otherwise available reference compounds. GC or GC/MS analysis is often applied to low oligomeric products, that is, oligomers formed at early reaction stages (dimers, trimers, tetramers, etc.). Typically, long (>25 m) capillary columns with silicone stationary phases are used for the GC separation of the unpolar oligomers. If complete evaporation can be ensured integration of the GC peaks provides a quantitative measure to the relative content of the different oligomers [45,54,63,73,75,79,85,90–92]. The number average oligomerization degree $\overline{\mathrm{P}}_n$ can be approximated from GC oligomer distributions [77].

2.1.4. Viscosity

The intrinsic viscosity (η in dL g^{-1}) of oligomer solutions in decalin (decahydronaphthalene) or tetralin (tetrahydronaphthalene) at 135 °C can be obtained from measurements with a Ubbelhode type viscometer and converted to the viscosity average molecular weight, M_η [93] or to the weight average molecular mass, M_w. The latter is calculated by using, for example, the Mark–Houwing–Sakurada parameters for atactic polypropene shown in the following equation $[\eta] = 1.85 \times 10^{-4}\ M_w{}^{0.73}$ dL g^{-1} [94,100] or $[\eta] = 1.10 \times 10^{-4}\ M_w{}^{0.80}$ dL g^{-1} [95].

2.1.5. Cryoscopy and vapor pressure osmometry

The molar mass obtained through the melting point or vapor pressure depression corresponds to the number average molar mass, M_n. With the help of molecular standards, a considerable deviation to lower mass values was seen starting above 500 g/mol. Hence, the experimental values of the oligomers had to be corrected according to this calibration [81]. In addition, the high amount of sample required (300–500 mg) and the lower solubility of the higher molar mass oligomers proves disadvantageously. Cryoscopy can be carried out in benzene, vapor pressure osmometry in chloroform (at 25 °C) or in methylcyclohexane (at 50 °C) [96].

2.1.6. Raman spectroscopy

For 1-decene oligomers the relative content of double bonds could be determined by the integrated intensities of the C=C vibrational bands around 1660 cm^{-1} when referenced to the intensity of ν(C=C) of trans-4-decene [97]. Assuming that each oligomer chain contains a double bond, the relative intensity of the C=C vibration can be compared to an external standard and is then inversely proportional to the average chain length from which M_n can be obtained. For the vinylidene-terminated propene and 1-hexene oligomers, 2-ethyl-1-butene, $H_2C{=}C(Et)CH_2CH_3$, was used as a reference whose molar mass corresponds to a dimer or monomer unit, respectively. The C=C stretch lies at 1650 cm^{-1} for the vinylidene (**1**) and at 1642 cm^{-1} for the vinyl group (**2**). Alternatively, IR spectroscopy could be applied for the same purpose by using the peaks at 888 cm^{-1} (vinylidene) and 910, 992 cm^{-1} (vinyl) [98]. The error in the reproducibility of the peak integral was found to be 3% for the standard material and up to 10% for the oligomers, depending on the peak area [81].

2.2. End group analyses

2.2.1. ^{1}H and ^{13}C NMR spectroscopy

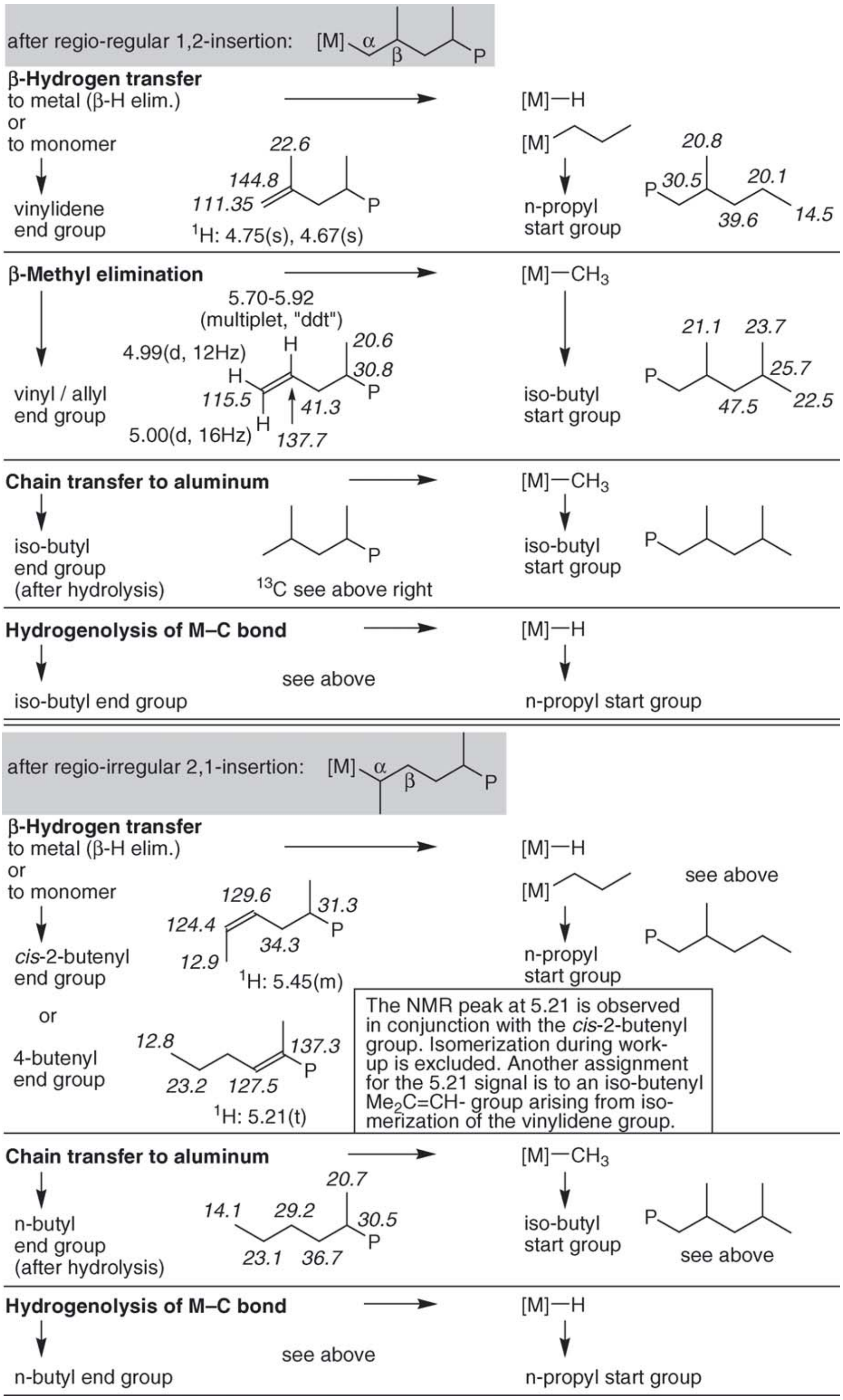
The (start and) end group structure is of uttermost importance in elucidating the chain transfer mechanism. Assignment of the end group functionality is typically based on ^{1}H, occasionally also on ^{13}C NMR. Scheme 2 collects the different possible end groups for oligopropenes together with their originating chain transfer reaction or chain start species and gives the NMR chemical shifts. Fig. 1 illustrates the ^{1}H NMR spectra in the olefinic region of a mainly vinylidene- and allyl-terminated oligopropene.

To assess the origin of, for example, an *iso*-butyl group (either as a start group from β-Me elimination or as an end group from chain transfer to Al) one can check for the presence of and the correlated intensity to the signals of the vinyl end group (from β-Me elimination). For the correlation of intensity in ^{13}C NMR it is appropriate to compare correlated intensities between spectra of different oligomers.

2.2.2. MALDI–TOF MS (matrix assisted laser desorption ionization–time of flight mass spectrometry)

This method has proven quite successful for the characterization of large biopolymers and synthetic polymers [103,104]. It offers the possibility to determine the accurate molecular mass and the molar mass distribution. The ionization technique allows for the investigation of very large and/or thermolabile molecules without fragmentation of the molecular ions. A prerequisite for the application of MALDI is the presence of functional groups in the polymer which are necessary for the adduct formation with silver (sodium or potassium) ions used for the ionization. Hence, polyolefins are in principle not susceptible to the MALDI technique. The reason that MALDI–TOF MS also promises a potential for analysis of olefin oligomers is because of their double-bond end-group functionality. MALDI–TOF MS investigations of such unpolar samples are quite rare, so far [53,81,82].

Fig. 2 shows a typical MALDI–TOF mass spectrum for an oligopropene and an oligo-1-hexene material. The peak separation corresponds to the monomer mass. From



Scheme 2. ^{1}H and ^{13}C NMR chemical shifts (relative to TMS; ^{1}H olefinic region only; ^{13}C assignments in italics) for common poly-/oligo-propene end groups together with their originating chain transfer reaction (P = continuing polymer/oligomer chain). NMR chemical shifts from Ref. [11,79,81,82,99,100–102]. The *iso*-butyl group is sometimes also referred to as *iso*-propyl.

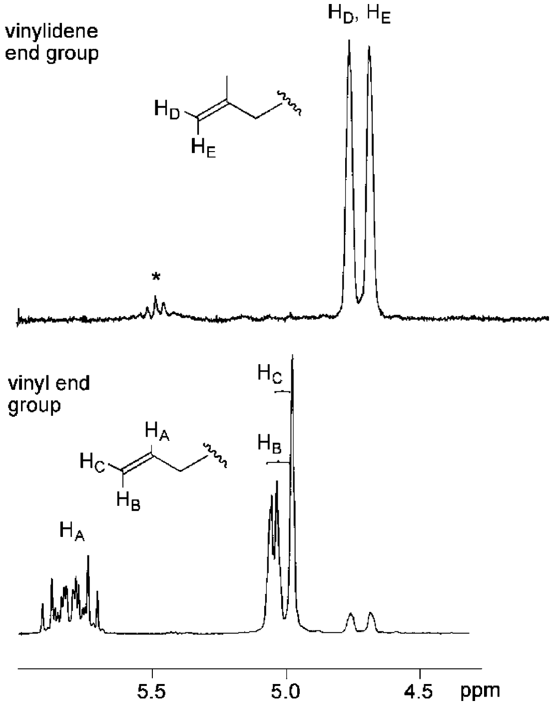


Fig. 1. ^{1}H NMR spectra of the olefinic region of a mainly vinylidene-terminated (top) and vinyl/allyl-terminated (bottom) oligopropene (200 MHz, $CDCl_3$). The protons of the vinylidene double bond appear as broad singlets at 4.67 and 4.75 ppm. The weak multiplet at 5.45 ppm (*) in the top spectrum is assigned to a *cis*-2-butenyl group arising from β-H elimination after a secondary, 2,1-insertion. The allyl group protons feature two overlapping doublets at 4.95–5.05 ppm and a multiplet (ddt) at 5.70–5.92 ppm. The vinyl/allyl-terminated oligopropene was obtained with catalyst $(C_5Me_5)_2ZrCl_2$/MAO [81,82,102].

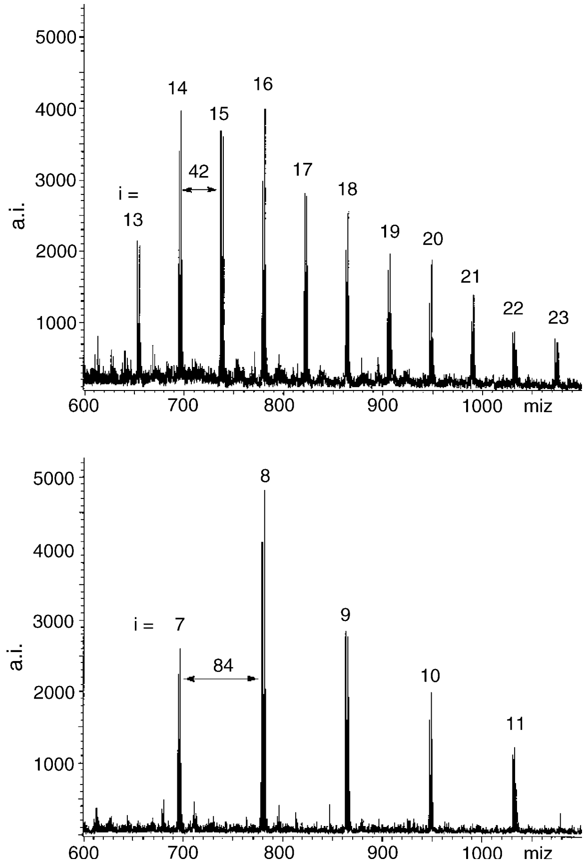


Fig. 2. MALDI–TOF mass spectra for samples of oligopropene (top) and oligo-1-hexene (bottom). Peaks correspond to the silver adduct of M_i (i = degree of oligomerization, number of monomer units) (a.i.: arbitrary intensity) [81,82].

the mass/charge minus a whole-numbered multiple of the monomer mass, the residual mass is obtained which corresponds to the start group. Normally the intensity of mass peaks in mixtures is proportional to the molar amount of each species and therefore the mass spectra should yield M_n and M_w/M_n (Q). Indeed the mass spectra in Fig. 2 represent a mass distribution curve. However, it is apparent that the method and the apparative conditions impose severe limitations with respect to interpreting the olefin oligomer spectra in this direction. The vacuum which is applied before ionization already removes the very low molar mass content from the sample, which is rather critical here. At the same time, the high molar mass end of the sample is also not well reproduced because of the single double-bond functionality together with the detection of the molecular ion as a metal adduct. Thus, olefin oligomers investigated with MALDI–TOF MS give a too small dispersion Q which does not reflect the real molar mass distribution. Still, MALDI–TOF is able to provide valuable information concerning the start and end group of the oligomers and the mechanism of chain transfer as is illustrated in Fig. 3 together with Scheme 3 [81,82].

Evidence for the β-methyl elimination is obtained in the MALDI–TOF mass spectra by an $M_i - 14$ and $M_i + 14$ peak around M_i in Fig. 3 (M_i = multiples of 42 for propene). The $M_i - 14$ peak originates from an oligomer with a [Zr]–H start group and chain termination by β-CH_3 elimination (Scheme 3b). Since the latter gives rise to Zr–CH_3 start groups an $M_i + 14$ peak is seen for those oligomers which are then terminated by β-H elimination (Scheme 3c). The oligomers which start with [Zr]–CH_3 and end with β-CH_3 elimination feature the M_i peak (just like those with a [Zr]–H start group and β-H elimination) (Scheme 3a and d).

MALDI–TOF MS can also support the formulation of a chain-transfer to aluminum. Fig. 3, bottom displays a sample spectrum of an oligo-1-hexene which features $M_i + 14$ peaks in addition to M_i peaks. Chain-transfer to aluminum will give rise to saturated end groups which do not show as peaks in the MALDI–TOF MS due to lack of the double-bond functionality (Scheme 3f and h). The M_i and $M_i + 14$ peaks correspond to oligomers from [Zr]–H and [Zr]–CH_3 start groups, respectively, which are terminated by β-hydrogen elimination (Scheme 3e and g). The relative intensities of the M_i and $M_i + 14$ peaks are a direct measure of the probability or percentage of the chain-termination pathway.

It is, however, difficult to assess the importance of chain transfer to aluminum with MALDI–TOF MS if β-methyl elimination is operating simultaneously. The ratio of the $M_i - 14$ and $M_i + 14$ peak might be used as a measure.

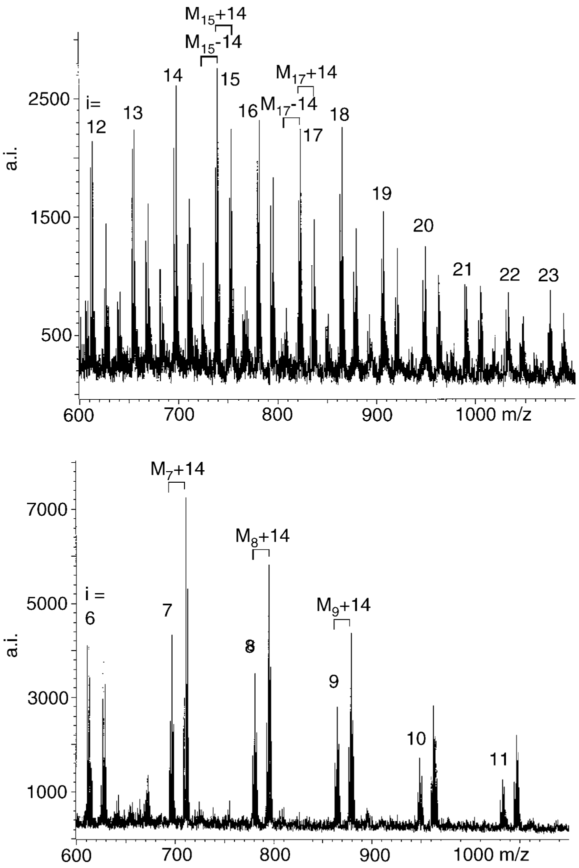


Fig. 3. MALDI–TOF mass spectra for samples of an oligopropene with β-methyl elimination (top, note the $M_i + 14$ and $M_i - 14$ peaks) and an oligo-1-hexene with chain transfer to aluminum (bottom, note the $M_i + 14$ peak); see also Scheme 3. Peaks correspond to the silver adduct of M_i (i = degree of oligomerization, number of monomer units) (a.i.: arbitrary intensity) [81,82].

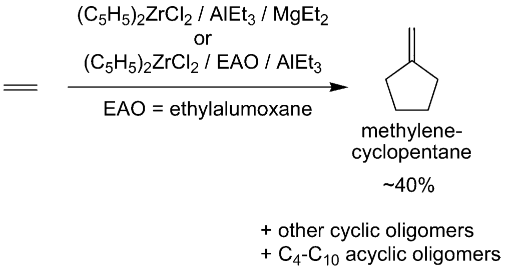
However, both peaks possess a different double-bond (vinyl/allyl versus vinylidene) which may not have the same ion-coordination and, thus, ionization probability [81,82].

3. Metallocene complexes for olefin, alkyne and silane oligomerization

3.1. Ethene oligomerization

Wang et al. described the catalytic cyclo-oligomerization of ethene by $(C_5H_5)_2ZrCl_2/AlEt_3/MgEt_2$ (ratio 1:100:10; 150 °C, $p_{C_2H_4} = 1.4$ MPa) to give 51% of the cyclic oligomers exo-methylenecyclopentane (41%), methylcyclopentane (3%), 1-methyl-1-ethylcyclopentane (4%) and vinylcyclohexane (3%) together with open-chain alkenes [Eq. (1)]. With $(C_5Me_5)_2ZrCl_2$, $(Ind)_2ZrCl_2$ or $(C_5H_5)_2TiCl_2$ in place of $(C_5H_5)_2ZrCl_2$ the selectivity for exo-methylenecyclopentane dropped to 1–8% [105]. Also ethylalumoxane/Al^iBu_3 could be used as a cocatalyst for $(C_5H_5)_2ZrCl_2$ [Eq. (1)]. With ethylalumoxane/$AlEt_3$ as cocatalyst under optimal conditions, the oligomerization of ethene gave methylenecyclopentane and C_4–C_{10} chain olefins in a ratio of 45/55 [106].

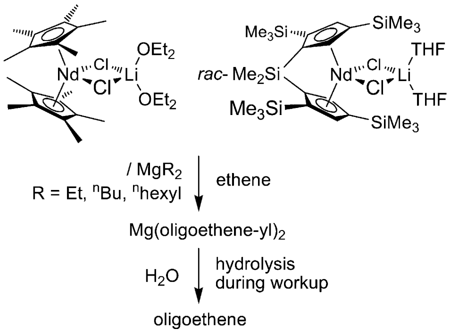
The oligomerization of ethene by $(C_5H_5)_2ZrL_2$ (L = Cl, Me, OC_6H_4-*p*-Me)/ethylalumoxane/$AlEt_3$ (Al:Zr = 100, 150 °C, $p_{C_2H_4} = 1.4$ MPa) gave methylenecyclopentane in 39% selectivity which could be further improved to 43% under optimal conditions by addition of C_5H_5N to $(C_5H_5)_2ZrCl_2/AlEt_3$ [107,108].



(1)

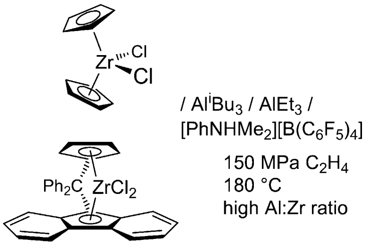
Sun described a mixed 8-aminoquinoline nickel dichloride/$(C_5H_5)_2ZrCl_2$ catalyst supported on silica to produce branched polyethylene with oligomer chains remaining in the final solution. With decreasing amount of Ni catalyst in the supported catalyst, the molecular chains of oligomers in the resulting solution became shorter, while α-olefin selectivity increased [109].

Carpentier et al. used in situ combinations of $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(OEt_2)_2$ and $Mg(Et)(^nBu)$ or $Mg(^nhexyl)_2$ to obtain oligoethylenes with M up to 2500 and narrow dispersion $M_w/M_n < 1.10$ in moderate activity (79×10^3 g mol_{Nd}^{-1} h^{-1} atm^{-1} at 80 °C, 1 atm). Combinations of *rac*-$Me_2Si(C_5H_2\text{-}3\text{-}SiMe_3\text{-}4\text{-}^tBu)_2Nd(\mu\text{-}Cl)_2Li(THF)_2/Mg(Et)(^nBu)$ or $Mg(^nhexyl)_2$ showed decreased activity compared to the C_5Me_5-Nd analog but the oligoethylenes had also a narrow dispersion $M_w/M_n < 1.2$ and higher contents of vinyl terminations [110]. The trivalent neodymium complexes when combined in situ with a dialkylmagnesium cocatalyst, initiated the oligomerization of ethene (and 1-octene) to yield di(oligoalkyl)magnesium species which were finally hydrolyzed to oligomers [Eq. (2)]. Ethylene oligomerization (M_n = 400–5000) was best achieved with the complexes *rac*-$Me_2Si(C_5H_2\text{-}2,4\text{-}\{SiMe_3\}_2)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$ and $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(OEt_2)_2$ as significant catalyst decay occurred with the also investigated complexes *rac*-$Me_2Si(C_5H_2\text{-}3\text{-}SiMe_3\text{-}4\text{-}^tBu)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$ and $Me_2Si(C_5H_2\text{-}2,4\text{-}\{SiMe_3\}_2)(C_5H_2\text{-}3,4\text{-}\{SiMe_3\}_2)Nd(\mu\text{-}Cl)_2Li(THF)_2$ [111].



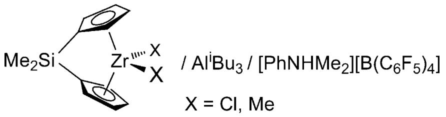
(2)

Gotz et al. obtained small amount of waxes due to ethylene oligomerization during high pressure polymerization of ethylene at 150 MPa, 180 °C and higher Al concentrations with $(C_5H_5)_2ZrCl_2$ or $Ph_2C(C_5H_4)(Flu')ZrCl_2/Al^iBu_3$ (=TIBA)/$AlEt_3/[PhNHMe_2][B(C_6F_5)_4]$ (4) [112].



4

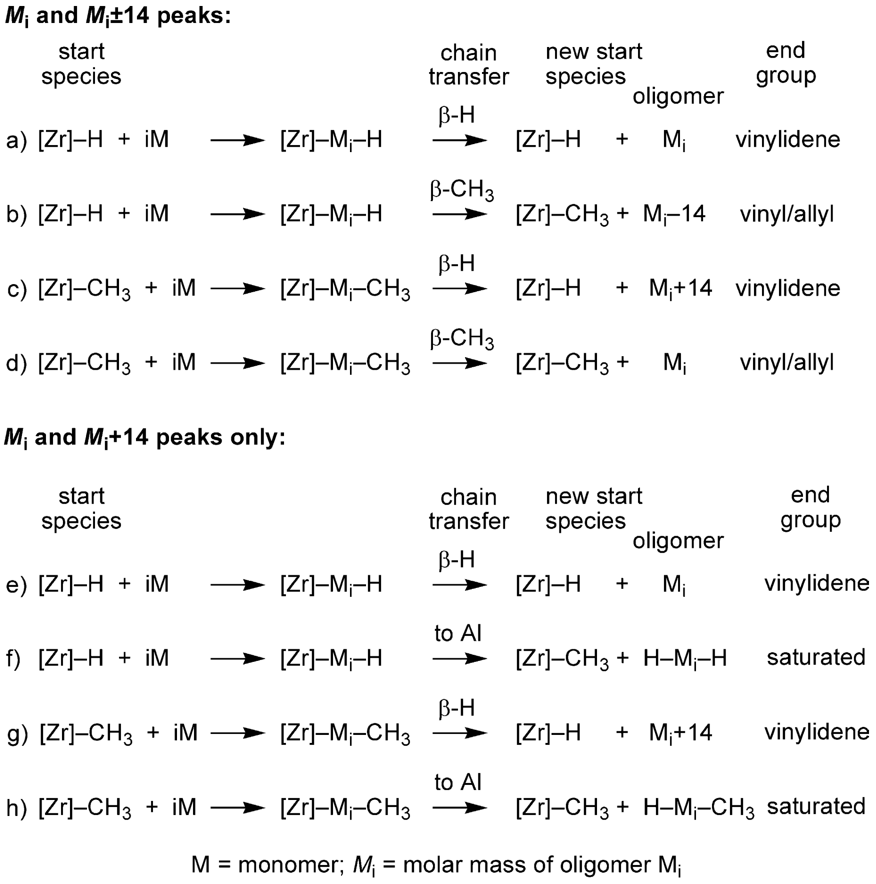
Bravaya et al. described low-molecular weight polyethylene from $Me_2Si(C_5H_4)_2ZrMe_2/Al^iBu_3/[Ph_3C]$- or $[PhNHMe_2]$-$[B(C_6F_5)_4]$ and from $Me_2Si(C_5H_4)_2ZrCl_2/Al^iBu_3/[PhNHMe_2][B(C_6F_5)_4]$ (**5**). Analysis of the polymer products by ^1H NMR, IR, GPC and kinetics of the polymerization suggested that the active site contains Al^iBu_3 as a heteronuclear Zr–Al bridged cationic complex and that the growing polymer chain is intensely transferred to the monomer with $k_p/k_t = 350$–500 for the above dimethyl-complex catalytic system [113,114].



5

He et al. studied the ethylene oligomerization activities and selectivities of $(Ind)_2Zr(O\text{-}C_6H_4\text{-}p\text{-}Me)_2/AlEt_nCl_{3-n}$ ($n = 1$, 1.5, 2) at different reaction and aging temperatures as well as at various reaction times. The activity increased with the ethyl amount (n) in the cocatalyst to a maximum of 1666 g g_{Zr}^{-1} h^{-1}. The selectivity for C_4–C_{10} olefins was 92.7%, the selectivity for linear α-C_4–C_{10} olefins was 86% [115].

Siedle et al. carried out a mechanistic study on the homogeneous catalyst formed from $(C_5H_5)_2ZrMe_2$/MAO in toluene. They relied on ethene oligomerization to investigate the chain termination which predominantly involved transfer to Al in exchange with the Al–Me group together with a concomitant chain transfer by σ-bond metathesis of the Zr-bound growing chain with ethene. From the former, the terminal Al-chain bonds of the Al-bound oligomer are finally cleaved on hydrolytic workup to produce saturated end groups. The latter σ-bond metathesis yields the new initiating species $[(C_5H_5)_2Zr\text{-}CH{=}CH_2]^+$ from which mono-unsaturated C_n



Scheme 3. Correlation between start and end group for the different chain transfer reactions. Only oligomers with vinylidine or vinyl/allyl end groups can be seen in MALDI–TOF MS. Saturated oligomers do not give an MS peak with this method [81,82].

(n = even) alkenes are obtained. Chain transfer by β-H elimination was detectable but relatively insignificant under the conditions employed. For propene and 1-hexene β-H elimination was the predominant chain transfer step, however. Chain transfer was fast relative to propagation so that the products were low molecular weight oligomers [80].

Conti et al. described the formation of ethene oligomers ($M_n = 4000\ \mathrm{g\,mol^{-1}}$, $M_w/M_n = 4.25$, sample constituted of solid PE and oligomers of C_6–C_{30} distribution) with $(C_5HPh_4)_2ZrCl_2$/MAO in lower activity ($75 \times 10^3\ \mathrm{g\,mol_{Zr}^{-1}\,h^{-1}}$) than in the case of unsubstituted or methyl-substituted ligands (186 or $372 \times 10^3\ \mathrm{g\,mol_{Zr}^{-1}\,h^{-1}}$, respectively). Steric and electronic effects by the phenyl substituents of this "bulky" cyclopentadienyl ligand [116] were seen responsible for this catalytic behavior [117].

Fink and Schnell obtained polymerization rates and developed mechanistic suggestions for Ti alkylation, activation equilibria, Ti-olefin π complex formation, chain growth at titanium and Ti → Al chain transfer processes based on kinetic studies and the analysis of ethene oligomer distributions from short reaction times with $(C_5H_5)_2Ti(R)Cl/AlEtCl_2$ (R = Et, ^{n}Pr, ^{n}Bu, n-pentyl, n-hexyl) [84]. Reichert and Meyer had carried out similar short time ethene polymerizations with $(C_5H_5)_2Ti(Et)Cl/AlEtCl_2$ to arrive at ethene oligomers whose analyses yielded rate constants for the first insertion steps of the monomer [83].

3.2. Ethene/α-olefin co-oligomerization

Van Looveren et al. used the in situ synthesis of MAO (from $AlMe_3$) on the crystalline structure of phosphotungstate heteropoly acids to generate a highly active and weakly coordinating compound for the ansa-metallocene pre-catalyst $C_2H_4(Ind')_2ZrCl_2$, $Me_2Si(Ind')_2ZrMe_2$ or $(C_5H_5)_2ZrMe_2$. The combination of the alumoxo-heteropoly compound and the metallocene gave a highly active catalyst ($\sim$2–$4 \times 10^6\ \mathrm{g\,mol_{Zr}^{-1}\,h^{-1}}$) for the co-oligomerization of ethene and propene ($M_n = 660$–$1300\ \mathrm{g\,mol^{-1}}$, $M_w/M_n \approx 2$, 53–58 mol.% propene) [67,118].

Ciardelli et al. tested the capacity of the nonbridged zirconocene complexes $(C_5H_5)_2ZrMe_2$, $(Ind)_2ZrCl_2$ and $(C_5Me_5)_2ZrCl_2$ activated with MAO to produce structurally controlled oligomers from ethene/α-olefin mixtures (propene and higher olefins) by varying the different reaction parameters (temperature, pressure, Al:Zr ratio). The chain transfer reaction is most probably induced by the propene monomer when the propagating chain end is a propene unit [56].

3.3. Propene oligomerization

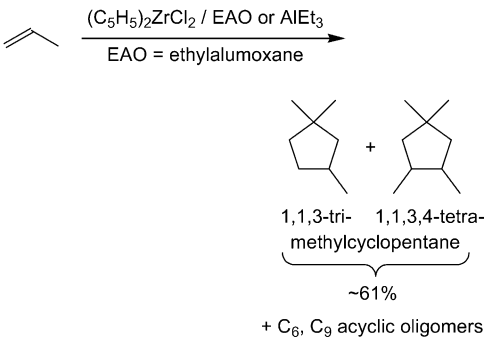
The achiral prototypical metallocene catalyst $(C_5H_5)_2ZrCl_2$/MAO appears to be one of the most employed systems for propene oligomerization leading to exclusively vinylidene-terminated oligopropenes [43,47–49,78,79,119–121]. Actually all members of the methyl-substituted series $(C_5H_{5-n}Me_n)_2ZrCl_2$ up to $(C_5Me_5)_2ZrCl_2$ as well as the mixed methyl-substituted zirconocenes $(C_5H_5)(C_5HMe_4)ZrCl_2$ and $(C_5H_5)(C_5Me_5)ZrCl_2$ give atactic propene oligomers in combination with MAO [41,79,102].

Mülhaupt et al. showed that addition of the Lewis-acids trimethyl- or triphenylboroxine, $(BOMe)_3$ or $(BOPh)_3$, respectively, or phenylboronic acid, $PhB(OH)_2$ to $(C_5H_5)_2ZrCl_2$/MAO could substantially enhance catalyst activities and affect molecular weight. From an activity of $3.68 \times 10^5\ \mathrm{g\,mol_{Zr}^{-1}\,atm^{-1}\,h^{-1}}$ an increase to 11.12×10^5 with $(BOMe)_3$, 5.56×10^5 with $(BOPh)_3$ and $4.95 \times 10^5\ \mathrm{g\,mol_{Zr}^{-1}\,atm^{-1}\,h^{-1}}$ with $PhB(OH)_2$ was found under otherwise identical conditions (temperature = 40 °C, propene pressure 2 bar, $[Zr] = 50 \times 10^{-6}\ \mathrm{mol\,l^{-1}}$, Al:Zr = 500) and with a molar $B_{modifier}$:Zr ratio of 25. In the same order the molecular weight M_n increased from $300\ \mathrm{g\,mol^{-1}}$ without modifier to 570, 830 and $420\ \mathrm{g\,mol^{-1}}$ [119].

Jacobs et al. described the immobilization of $(C_5H_5)_2ZrMe_2$ on zeolite MCM-41 whose silanol groups were pre-reacted with $B(C_6F_5)_3/PhNMe_2$ to result in the heterogeneous catalyst $[\{MCM\text{-}41\text{-}O\}\text{-}B(C_6F_5)_3]^-[(C_5H_5)_2ZrMe]^+$. Activities of this heterogeneous propene oligomerization catalyst were comparable to homogeneous $(C_5H_5)_2ZrCl_2/\{AlMe_3$, MAO, $B(C_6F_5)_4^-$ or $B(C_6F_5)_3\}$ systems ($\sim 10^5\ \mathrm{g\,mol_{Zr}^{-1}\,h^{-1}}$) and over 90% 1-alkenes with Schulz-Flory carbon number distribution [122].

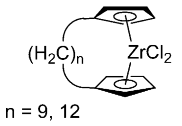
Van Looveren et al. similarly anchored MAO by the in situ hydrolysis of $AlMe_3$ on the internal pore walls of a mesoporous MCM-41 support to generate a highly active host for $(C_5H_5)_2ZrMe_2$ in the oligomerization of propene with a typical Schulz-Flory distribution of the propene oligomers [57,58].

Wang et al. catalyzed the oligomerization of propylene by $(C_5H_5)_2ZrCl_2$/ethylalumoxane or $AlEt_3$ at low Al/Zr ratios and high temperature to afford the trimeric carbocyclic products 1,1,3-trimethylcyclopentane and 1,1,3,4-tetramethylcyclopentane (combined optimized selectivity 61%), along with C_6 and C_9 chain olefins [Eq. (3)]. The product distribution was affected by the reaction temperature, propylene pressure, Al/Zr ratio and reaction time [123].



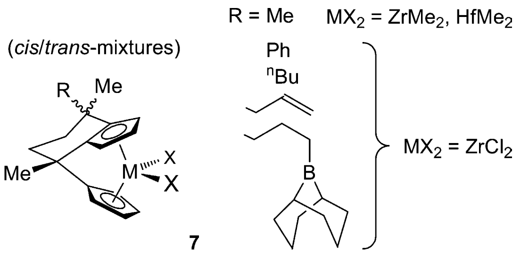
(3)

Erker et al. described *ansa*-metallocenes with long $-(CH_2)_n-$ chains, namely $(CH_2)_n(C_5H_4)_2ZrCl_2$ (**6**)/MAO with $n = 9$, 12 for the oligomerization of propene with activities of 4.56 and 3.32×10^5 g mol_{Zr}^{-1} h^{-1} bar^{-1} [124].



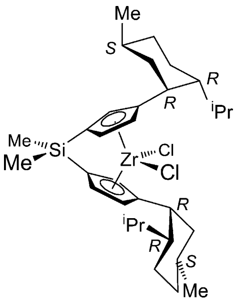
6

The very rigid compounds (4-cyclopentdienylidene-7-R-4,7-dimethyl-4,5,6,7-tetrahydroindenyl)MX_2 (R = Me, MX_2 = Zr- or $HfMe_2$; R = Ph, ^{n}Bu, allyl, -$(CH_2)_3$-9-BBN, $MX_2 = ZrCl_2$) (**7**) exhibit a large opening angle in front of the metal (gap aperture) and produce low molecular weight propene oligomers (M_η = 830–1900 g mol^{-1}) when activated with MAO between −20 and 0 °C; activities between 0.15–11 × 10^3 g g_{Zr}^{-1} h^{-1} (Al:Zr = 550–860) [50,125].



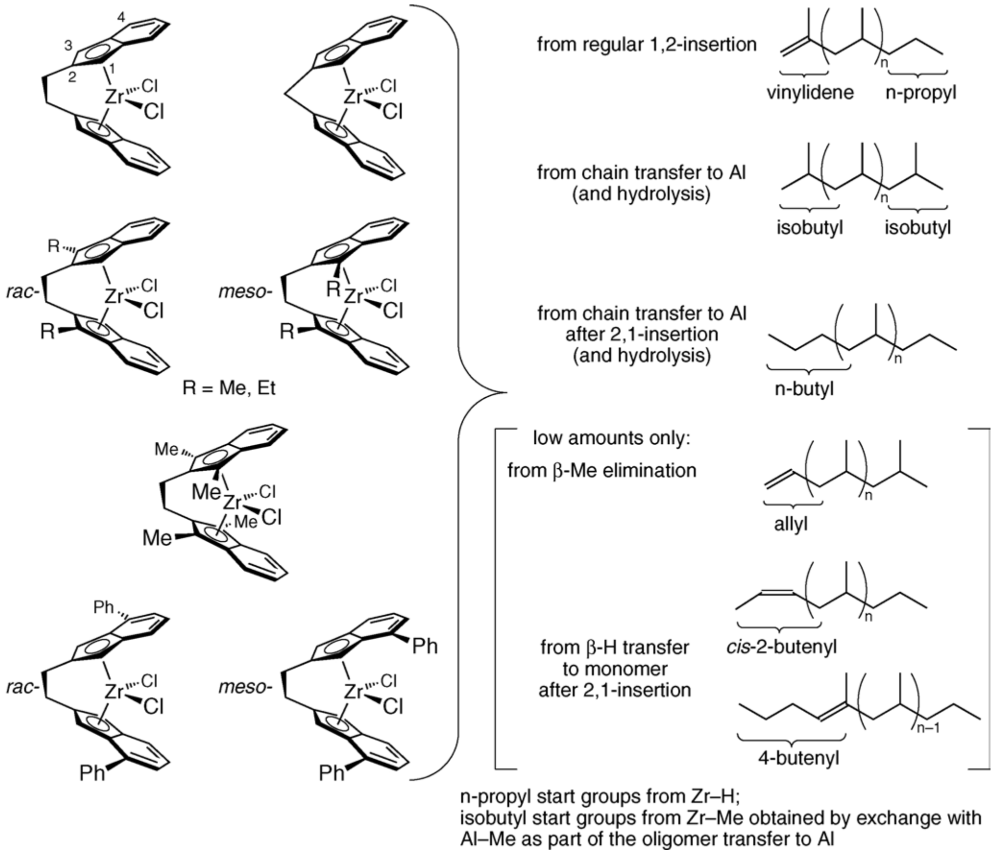
7

The chiral, meso-like ansa-zirconocene complex **8**/MAO produces oligopropenes (M_η = 4400 – 380 g mol^{-1}) between 0 and 80 °C ($p_{C_3H_6}$ = 2–20 bar, Al:Zr = 1100–2000) with activities between 0.34 and 1.2×10^3 g g_{Zr}^{-1} h^{-1} bar^{-1}, respectively [44].



8

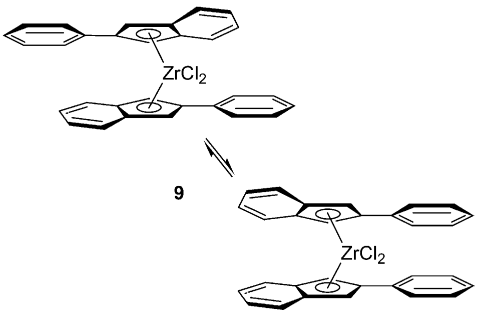
Schaverien et al. reported on the class of ethylene-bis(2-indenyl)zirconocenes, $(C_2H_4)(2\text{-Ind}')_2ZrCl_2$ with various methyl substitution patterns in the 1- and 3-position and phenyl-substitution in the 4-position (Scheme 4). When activated with MAO (Al:Zr between 1000 and 40,000) these compounds oligomerized propene (M_n from ^{1}H NMR between 400 and 5500 g mol^{-1}) with activities between ∼2 × 10^3 and 6.0×10^4 g g_{Zr}^{-1} h^{-1}. Addition of 2–3 mol% H_2 drastically increased the activities by a factor of >100 for the same catalyst and up to 6.2×10^6 g g_{Zr}^{-1} h^{-1}. The formation of oligopropenes was exploited for a comprehensive identification of



Scheme 4. End group analysis of oligopropenes by NMR based on (mostly ethylene) bridged bis(2-indenyl)zirconocenes [126].

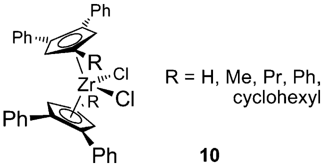
the end groups, thereby providing information on the chain transfer mechanism. In the absence of H_2 *n*-propyl (start) and vinylidene end groups characteristic of 1,2-insertion into Zr–H and β-H elimination to the metal or β-H transfer to monomer are found. Strong signals were also observed for isobutyl end groups, indicating chain transfer to Al (and eventual hydrolysis) as a major termination pathway, commensurate with the high Al:Zr ratio and the low activity (isobutyl start groups then also arise from obtaining Zr–Me start species by this transfer route). A significant percentage of 2,1-regioerrors with some of the complexes gave *n*-butyl end groups after transfer to Al. Furthermore small amounts of allyl end groups (from β-Me elimination) were observed throughout. Relatively high levels of *cis*- or *trans*-2-butenyl and 4-butenyl end groups were also formed by β-H transfer to monomer after a 2,1-insertion. Addition of H_2 reduced the 2,1-insertions and increased the saturated propene oligomers due to chain transfer to H_2 [126].

Bravaya et al. found that an increase in the Al:Zr ratio in the catalytic system (2-PhInd′)$_2$ZrMe$_2$ (**9**)/Al^{i}Bu$_3$ from 50 to 300 led to an enhancement of the molecular weight of the polypropene samples from oligomeric products to a viscosity average molecular weight of 220,000 g mol^{-1} [127].



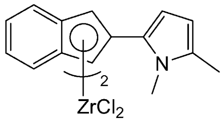
9

Mu et al. noted that the unbridged zirconocene complexes (C_5H_3-1,2-Ph_2)$_2$ZrCl$_2$, (C_5H_2-1,2-Ph_2-4-Me)$_2$ZrCl$_2$, (C_5H_2-1,2-Ph_2-4-Pr)$_2$ZrCl$_2$, (C_5H_2-1,2,4-Ph_3)$_2$ZrCl$_2$, and (C_5H_2-1,2-Ph_2-4-cyclohexyl)$_2$ZrCl$_2$ (**10**), despite their racemic-like, near C_2 symmetrical conformation in the solid state, when activated with MAO gave only atactic, oily propene oligomers (M_n = 1000 g mol^{-1}), albeit at high activities (1.8–4.2 × 10^6 g mol$_{zr}{}^{-1}$ h^{-1}, Al:Zr = 1500) [128–130].



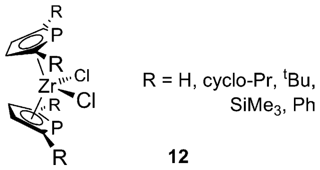
10

Similarly, Erker et al. found that the catalyst derived from the 2-(5′-methyl-2′-*N*-methylpyrrolyl)-substituted complex (Ind′)$_2$ZrCl$_2$ (**11**) yielded only propene oligomers (M_w = 3600 g mol^{-1}, Al:Zr = 991, temperature −20 °C, activity 5.9 × 10^4 g mol$_{zr}{}^{-1}$ bar^{-1} h^{-1}) although similar bis(2-arylindenyl)- and bis(2-hetarylindenyl)ZrCl$_2$/MAO catalysts showed a C_2-symmetric *rac*-like metallocene conformation in the solid state and gave elastomeric polypropene [131].



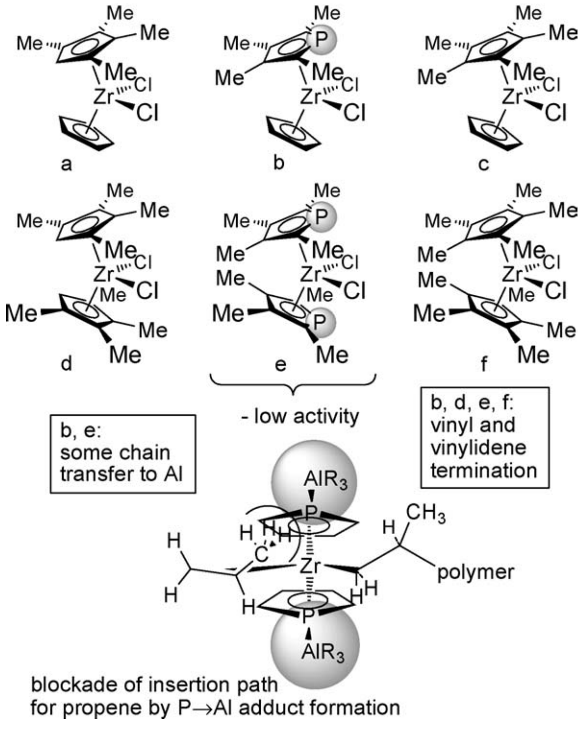
11

Horton et al. employed phospholyl, C_4PH_2-2,5-R_2 containing metallocene complexes of the type (C_4PH_2-2,5-R_2)$_2$ZrCl$_2$ and (C_5H_5)(C_4PH_2-2,5-R_2)ZrCl$_2$ (R = H, cyclo-propyl, ^{t}Bu, SiMe$_3$, Ph) (**12**) in propene polymerization using MAO as cocatalyst. Atactic polypropene with M_n varying from 450 to >20,000 g mol^{-1} and vinylidene end groups was obtained with activities up to 1.7 × 10^5 g g$_{zr}{}^{-1}$ h^{-1}. The degree of polymerization increased steadily in the series dialkyl < alkyl, phenyl < diphenyl suggesting a higher importance of electronic over steric factors for M_n [132].



12

Janiak et al. compared the activities for zirconocenes with the tetramethyl-substituted phospholyl ligand C_4PMe_4 to the activities of zirconocenes with the tetramethyl- and pentamethyl-cyclopentadienyl ligand C_5HMe_4 and C_5Me_5, respectively (Scheme 5). Activities for the phospholyl complexes (C_5H_5)(C_4PMe_4)ZrCl$_2$ and (C_4PMe_4)$_2$ZrCl$_2$ were much lower (0.1 × 10^5 g mol$_{zr}{}^{-1}$ h^{-1}), by a factor of ∼100 than those of the per-methyl zirconocenes

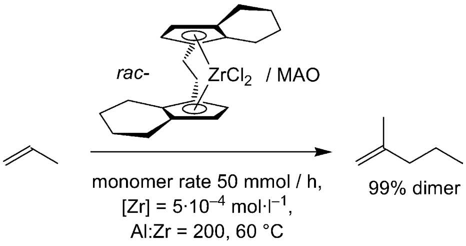


Scheme 5. Comparison of per-methyl zirconocenes with related phospholyl complexes for oligomerization activity and chain transfer reactions.

($6–13 \times 10^5$ g mol_{zr}^{-1} h^{-1}, 50 °C, $c_0(C_3H_6) = 1.75$ mol l^{-1}, [Zr] = 3×10^{-5} mol × l^{-1} with Al:Zr = 1000) [81,82,102]. This is explained by formation of a P–Al adduct [132,133] with the bulky "Al-substituent" becoming situated close to the maximum opening angle/gap aperture of the zirconium, that is, close to the meridional centroid–Zr–centroid angle (see Scheme 5). Such a bulky substituent in this position then blocks the pathway for the insertion of propene into the Zr–C bond (as is known for *ansa*-metallocenes with C_5-ring substituents in this position) [82,102,134]. Molecular weights for the oligopropenes obtained with the phospholyl systems were between $M_n = 300–380$ g mol^{-1} and at the low end of the permethyl zirconocene series ($M_n = 320–1500$ g mol^{-1}) with only decamethylzirconocene, $(C_5Me_5)_2ZrCl_2$ yielding a comparable low molar mass oligomer under the same conditions. With the phospholyl systems and with the symmetrical per-methyl zirconocenes $(C_5H_{5-n}Me_n)_2ZrCl_2$ (n = 4, 5) both vinylidene and vinyl/allyl-terminated oligopropenes are found. The vinyl:vinylidene ratio depends on the ligand or metal complex and increases from $(C_5H_5)(C_4PMe_4)ZrCl_2$ (21:79) and $(C_5HMe_4)_2ZrCl_2$ (35:65) over $(C_4PMe_4)_2ZrCl_2$ (39:61) to $(C_5Me_5)_2ZrCl_2$ (91:9). Furthermore, comparison of the molecular weight determinations by ^1H NMR and GPC together with MALDI–TOF MS shows that the phospholyl complexes exhibit some chain transfer to Al [81,82,102].

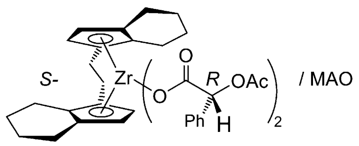
Ciardelli et al. tested $(C_5H_5)_2ZrMe_2$, $(Ind)_2ZrCl_2$ and $(C_5Me_5)_2ZrCl_2$ activated with MAO at Al:Zr ratios of 300–3000, at two different temperatures (20 and 70 °C) and 1 or 5 bar propene pressure. The highest activity was found for $(C_5H_5)_2ZrMe_2$ at Al:Zr = 3000 at 70 °C with 2.35×10^6 g mol_{zr}^{-1} h^{-1}, oligomer range $C_6–C_{30+}$. For $(Ind)_2ZrCl_2$ the oligomers were mostly $>C_{30}$ [56].

Kaminsky et al. obtained over 99% propene dimer in the oligomer mixture (by GC) with *rac*-$C_2H_4(Ind'H_4)_2ZrCl_2$/MAO, at a monomer rate of 50 mmol h^{-1}, [Zr] = 5×10^{-4} mol l^{-1}, Al:Zr = 200, 60 °C [Eq. (4)] [85].

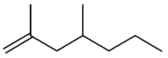
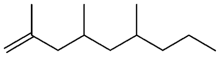


(4)

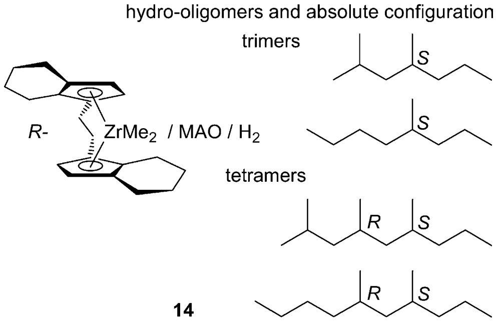
With asymmetric (S)-$C_2H_4(Ind'H_4)_2Zr$(O-acetyl-(R)-mandelate)$_2$/MAO (**13**) optically active propene oligomers could be obtained through enantiomorphic site control during the C–C bond formation. Optical activity is first observed in the trimers and in higher oligomers, the dimer does not contain a chiral carbon atom. Molar rotation angles for the trimer and tetramer mixture were as follows [45,135]:



13

oligo-propene:	main component	$[\alpha]^{25}_{589}$	$[\alpha]^{25}_{365}$
trimers		+1.1	+3.7
tetramers		+4.7	+14.6

Pino et al. polymerized propene in the presence of hydrogen with asymmetric (R)-$C_2H_4(Ind'H_4)_2ZrMe_2$/MAO to arrive at hydrooligomers (**14**) together with solid high polymer. The oligomers were separated and fractionated. The rotation of all the fractions was positive. Specific isomers of the trimers 2,4-dimethylheptane and 4-methyloctane and the tetramers 2,4,6-trimethylnonane and 4,6-dimethyldecane could be identified. The n-butyl groups indicate the chain termination by hydrogenolysis after a 2,1-insertion [96].

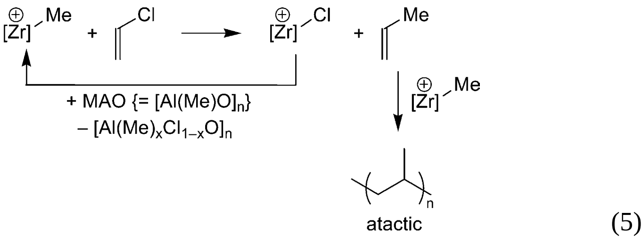


14

In a mechanistic study Siedle et al. used $(C_5H_5)_2ZrMe_2$/MAO and propene oligomerization in toluene to find β-H elimination as the predominant chain transfer which was different than for ethene oligomerization with the same system (see above) [80].

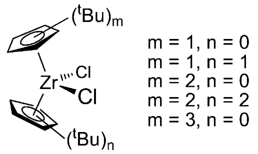
Jordan et al. noted that the complex $(C_5H_4Me)_2ZrMe(\eta^1-CB_{11}H_{12})$ oligomerizes propene under mild conditions. The carborane ligand $CB_{11}H_{12}^-$ coordinates to Zr via a single B–H–Zr bridge and is labile so that a free coordination site, necessary for catalytic activity, can be created [136].

Stockland and Jordan found that the reaction of vinyl chloride with *rac*-$C_2H_4(Ind')_2ZrMe_2$/MAO (Al:Zr = 17,000) proceeds by generation of *rac*-$C_2H_4(Ind')_2ZrMe^+$, vinyl chloride insertion, and β-Cl elimination to yield propene and a *rac*-$C_2H_4(Ind')_2ZrCl^+$-species [(Eq. (5)]. The latter is realkylated by MAO (or its $AlMe_3$ content). This process is stoichiometric in Al–Me groups. The propene is oligomerized by *rac*-$C_2H_4(Ind')_2ZrMe^+$ to atactic oligopropene (M_n = 500 g mol^{-1}) as a colorless oil with the predominant chain transfer mechanism being vinyl chloride insertion/β-Cl elimination. Similar results were said to have been obtained with *rac*-$C_2H_4(Ind')_2ZrCl_2$/MAO and $(C_5Me_5)_2ZrCl_2$/MAO. In the presence of trace levels of O_2, *rac*-$C_2H_4(Ind')_2ZrMe_2$/MAO polymerizes vinyl chloride to poly(vinyl chloride) by a radical mechanism [137,138].



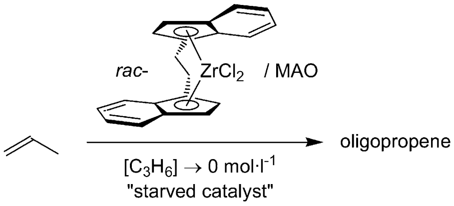
(5)

Janiak et al. used a series of *tert*-butyl substituted zirconocene (**15**)/MAO complexes to illustrate the potential for tailoring propene oligomers with extremely narrow molar mass distribution down to $M_w/M_n \approx 1.2$. This small dispersion is explained on the basis of a chain-length dependent propagation rate. At 50 °C, $c_0(C_3H_6) = 1.75\,mol\,l^{-1}$ and $[Zr] = 3 \times 10^{-5}\,mol\,l^{-1}$ with Al:Zr = 1000 activities were $4.0 \times 10^5\,g\,mol_{zr}{}^{-1}\,h^{-1}$ for the zirconocenes with the mono-substituted ligands $(C_5H_5)(C_5H_4{}^tBu)ZrCl_2$ and $(C_5H_4{}^tBu)_2ZrCl_2$. A maximum was observed for the mixed zirconocene with one di-substituted ligand, $(C_5H_5)(C_5H_3\text{-}1,3\text{-}{}^tBu_2)ZrCl_2$ with $6.7 \times 10^5\,g\,mol_{zr}{}^{-1}\,h^{-1}$. Upon further increase in steric demand the activities decreased to $0.8 \times 10^5\,g\,mol_{zr}{}^{-1}\,h^{-1}$ for $(C_5H_5)\,(C_5H_2\text{-}1,2,4\text{-}{}^tBu_3)ZrCl_2$ and $0.01 \times 10^5\,g\,mol_{zr}{}^{-1}\,h^{-1}$ for $(C_5H_3\text{-}1,3\text{-}{}^tBu_2)_2ZrCl_2$. Molecular weights were between $M_n = 400\text{–}1300\,g\,mol^{-1}$. Solely vinylidene terminated oligomers were found [43,81,82,102].



15

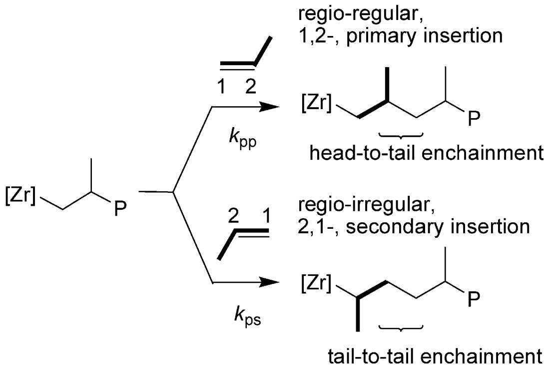
Resconi et al. observed that under “starved catalyst” conditions, that is, with monomer concentration approaching zero ($[C_3H_6] \rightarrow 0\,mol\,l^{-1}$) *rac*-$C_2H_4(Ind')_2ZrCl_2$/MAO produces atactic propene oligomers ($M_n = 1080\,g\,mol^{-1}$) [Eq. (6)]. The loss of stereospecificity with the decrease in monomer concentration is explained by postulating an equilibrium between an isospecific site having a coordinated monomer and an aspecific one without coordinated monomer. As a consequence the aspecific site is assumed to be able to racemize the chiral carbon of the last inserted unit [139].



(6)

Mechanistic studies

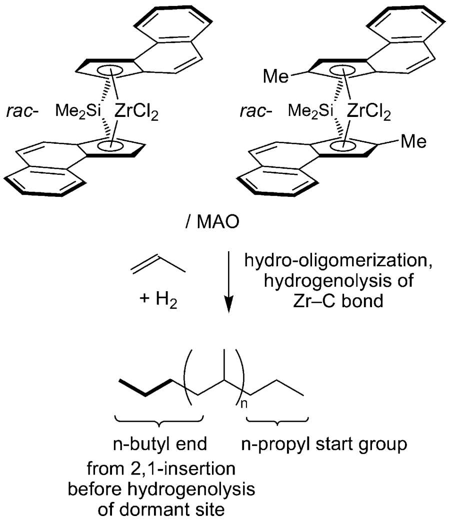
Busico et al. carried out kinetic studies of Ziegler–Natta polyinsertions with metallocene/MAO catalysts combining ^{13}C NMR characterizations of polymers with GC/MS analyses of oligomers which resulted from fast H_2-induced chain transfer (hydrooligomerization). This approach allowed for the evaluation of the ratios between kinetic constants governing the formation of the various possible constitutional and configurational sequences. Specifically, the ratio for the rate of chain propagation via regular 1,2-, primary insertion (k_{pp}) and the rate of regioirregular 2,1-, secondary insertion (k_{ps}) (Scheme 6), i.e. k_{ps}/k_{pp} for the two catalyst systems *rac*-$C_2H_4(Ind')_2ZrCl_2$ ($k_{ps}/k_{pp} = 1.0 \times 10^{-2}$) and *rac*-$Me_2Si(Ind')_2ZrCl_2$/MAO ($k_{ps}/k_{pp} = 0.8 \times 10^{-2}$) were based on the ratio between 1,2-, primary-terminated and 2,1-, secondary-terminated chains in the hydrooligomer, measured by GC [140–143].



Scheme 6. Differences in monomer enchainments and possible end group structures after 1,2- or 2,1-insertion.

Mülhaupt et al. used propene oligomerization studies with $(C_5H_5)_2ZrCl_2$/MAO to demonstrate that reversible deactivations which are second order relative to the zirconium active site concentration account for the decay of the polymerization rate. With MAO injection during the reaction the polymerization rate can be enhanced again. A sequence of dynamic equilibria involving the formation of active cationic metallocene intermediates as well as inactive zirconocene species is proposed [119,120].

Mülhaupt et al. also found that propene polymerization with *rac*-Me_2Si(benz[e]indenyl)$_2ZrCl_2$ and with *rac*-Me_2Si(2-Me-benz[e]indenyl)$_2ZrCl_2$ in the presence of H_2 reduced the polymer molecular weight and the amount of 2,1-units in the polymer [Eq. (7)]. The NMR signals of *n*-propyl (start) and *n*-butyl (end) groups had almost the same intensity. The *n*-butyl groups result from the hydrogenolysis of Zr-2,1-units. Hydrogenolysis of a Zr-1,2-unit would produce isopropyl end groups which could hardly be detected. This shows that most metallocenes with dormant sites have a 2,1-inserted propene as the last unit (under the assumption of a similar rate for the chain transfer to H_2 from a Zr-2,1- and a Zr-1,2-unit). The subsequent monomer insertion at a sterically hindered “dormant” site with a 2,1-last-inserted unit is slower than the hydrogenolysis reaction. In the absence of H_2 such dormant sites, resulting from 2,1-propene insertion, can be reactivated either by β-H transfer to zirconium or to propene, both yielding 2-butenyl end groups, or by 1,2-insertion of propene, yielding head-to-head regio-irregularities [144].

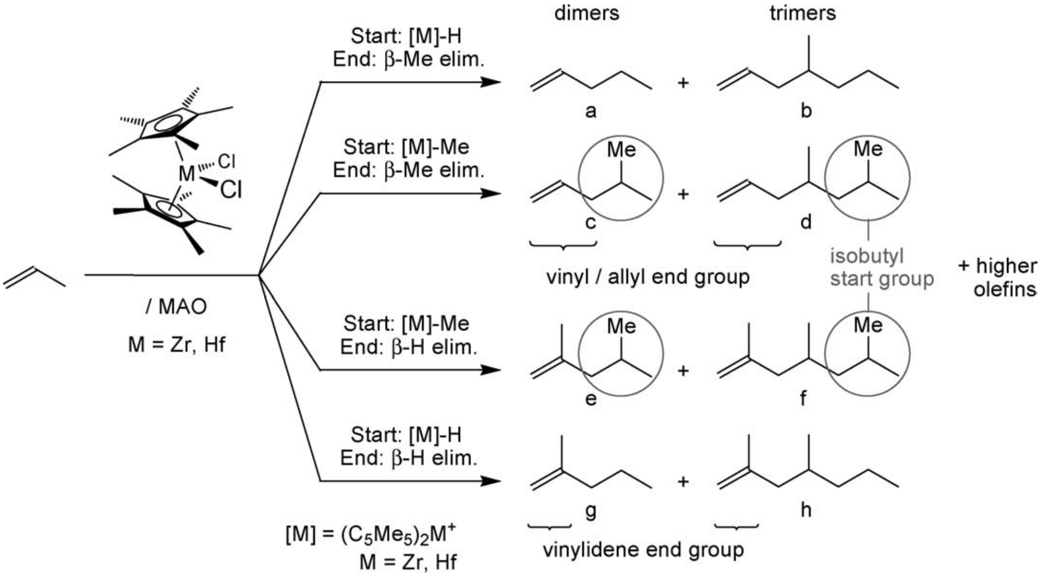


(7)

Mise et al. observed the formation of "abnormal" oligomers in the oligomerization of propene by $(C_5Me_5)_2MCl_2$/MAO catalysts (M = Zr, Hf) with the product mixture analyzed by quantitative GC/MS and ^{1}H NMR and separated in part by vacuum distillation. Oligomers with a vinyl/allyl end group (see Scheme 7), such as the dimer 1-pentene (a) and the trimer 4-methyl-1-heptene (b) had to form from β-Me transfer termination (elimination) from a growing carbon chain which was initiated by insertion of propene into an M–H bond. The dimer 4-methyl-1-pentene (c) and the trimer 4,6-dimethyl-1-heptene (d) are indicative of insertion into an M–Me bond with termination from β-Me elimination. Oligomers with a vinylidene end group, such as the dimer 2,4-dimethyl-1-pentene (e) and the trimer 2,4,6-trimethyl-1-heptene (f) start with an M–Me bond and terminate with the usual β-H elimination. Finally, an M–H start group and β-H transfer termination was the case in the dimer 2-methyl-1-pentene (g) and the trimer 2,4-dimethyl-1-heptene (h) (Scheme 7) [79].

Resconi et al. used propene oligomerization (at 50 °C) in a mechanistic study on chain transfer via β-CH_3 elimination by $(C_5Me_5)_2MCl_2$/MAO catalysts (M = Zr, Hf). GC–MS, ^{1}H and ^{13}C NMR analyses of the oligomers showed the oligomeric products to be mainly allyl- and isobutyl-terminated (1/1 ratio), the former being the end, the latter the start group, respectively. The terminal group structures are produced by first monomer insertion into the M–CH_3 bond and then chain transfer by β-CH_3 elimination (c, d in Scheme 7). Only small amounts of vinylidene end groups from β-H elimination were found. The allyl:vinylidene ratio was 92:8 for Zr and 98:2 for Hf [77].

Teuben et al. based a mechanistic study on the oligomerization of propene by $[C_5Me_5)_2MMe(THT)]^+[BPh_4]^-$ (M = Zr, Hf, THT = tetrahydrothiophene) in *N*,*N*-dimethylaniline. At room temperature for M = Zr a rather broad molecular weight distribution is obtained (C_6–C_{24}), whereas for M = Hf only one dimer (4-methyl-1-pentene) and one trimer (4,6-dimethyl-1-heptene) are formed. With an increase in reaction temperature the product composition shifts to lower molecular weights. The oligomers are formed by β-CH_3 elimination from the growing oligopropene chain to the metal center. The molecular weight distributions of the oligomers produced at temperatures between 5 and 45 °C are satisfactorily described by the Schulz–Flory theory. From this the ratios of rate coefficients for propagation, k_p and termination, k_t could be calculated.

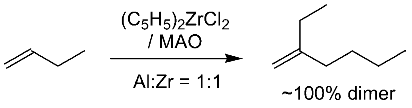


Scheme 7. Differences in the structure of isolated dimers and trimers and their mechanistic interpretation due to β-hydrogen or β-methyl elimination in propene polymerization with $(C_5Me_5)_2ZrCl_2$/MAO [77,79].

Values for $(\Delta G_p^{\ddagger}-\Delta G_t^{\ddagger})_{298\,K}$ were calculated as −1.9(3) and −1.4(4) kcal mol^{-1} for M = Zr and Hf, respectively [75,76].

3.4. 1-Butene oligomerization

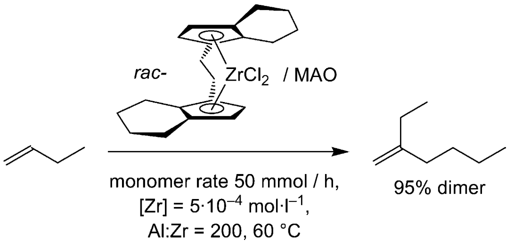
Christoffers and Bergman found that $(C_5H_5)_2ZrCl_2$ when activated by only 1 equiv. of MAO selectively and catalytically dimerizes 1-butene (and other α-olefins) to 2-ethyl-1-hexene without formation of any higher oligomeric species [Eq. (8)] [51].



(8)

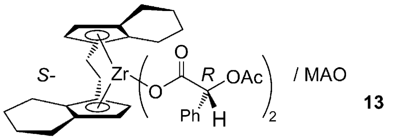
Plattner, Chen et al. prepared a $(C_5H_5)_2ZrMe^+$-cation from a stable solution of the $[B(C_6F_5)_4]^-$ salt by electrospray ionization tandem mass spectrometry (ESI–MS/MS). The cation was collided with 1-butene to observe multiple olefin additions to a gas phase metallocenium cation and to obtain a second-order rate constant of $k \approx 10^8$–19^9 l mol^{-1} s^{-1} at 70 °C [145].

Kaminsky et al. described the product distribution from dimer to heptamers in the oligomerization of 1-butene as a function of monomer flow, zirconocene concentration and reaction temperature. The zirconocenes employed were *rac*-$C_2H_4(Ind'H_4)_2ZrCl_2$, asymmetric (*S*)-$C_2H_4(Ind'H_4)_2Zr$(*S*-binaphtholate), and (*S*)-$C_2H_4(Ind'H_4)_2Zr$(*O*-acetyl-(*R*)-mandelate)$_2$ (**13**) activated with MAO. With the decrease of flow rate (from 217 to 0.8 ml min^{-1}), the shorter oligomers are preferred. Concomitantly, an increase in zirconocene concentration (from 7.3 to 116 × 10^{-5} mol l^{-1}) with simultaneous variation of the molar Al:Zr ratio (from 900 to 57) at constant monomer flow (leading to an effective decrease in monomer concentration) also increases the percentage of the shorter oligomers. Furthermore, the average molecular weight of the oligomeric products decreases with the increasing temperature (from 30 to 70 °C). With *rac*-$C_2H_4(Ind'H_4)_2ZrCl_2$/MAO, a monomer rate of 50 mmol h^{-1}, [Zr] = 5 × 10^{-4} mol l^{-1}, Al:Zr = 200 at 60 °C an amount of 95% 1-butene dimer was obtained (by GC) [Eq. (9)] [85].

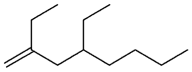
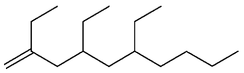


(9)

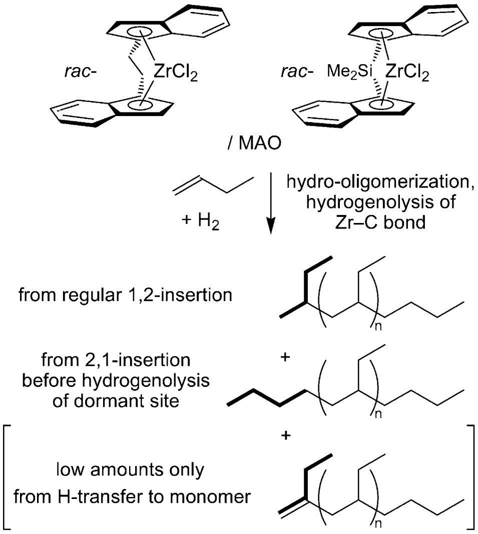
Optically active oligomers could be obtained using the enantiomeric zirconocenes, e.g. **13**, through enantiomorphic site control during the C–C bond formation. Optical activity is first observed in the trimers and in higher oligomers, the dimer does not contain a chiral carbon atom. Molar rotation angles for the trimer and tetramer mixture were as follows [45,85]:



13

oligo-1-butene: main component		$[\alpha]^{25}_{589}$	$[\alpha]^{25}_{365}$
trimers		−0.7	−2.5
tetramers		−2.6	−9.4

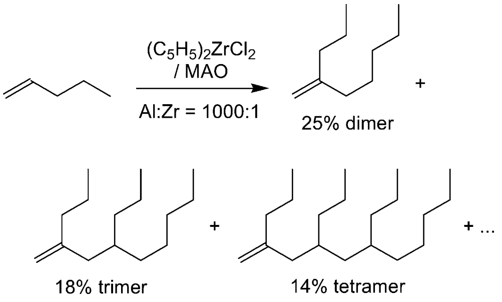
Busico et al. also extended the GC/MS characterization of saturated propene oligomers (see above [140]) to the case of 1-butene for the two catalyst systems *rac*-$C_2H_4(Ind')_2ZrCl_2$ and *rac*-$Me_2Si(Ind')_2ZrCl_2$/MAO. Each 1-butene *n*-hydrooligomer contained all diastereomers generated by chain transfer to H_2 after a sequence of *n* 1,2-monomer insertions, or of (*n* − 1) 1,2-insertions followed by a final 2,1-insertion, respectively [Eq. (10)]. The undetectability of internal 2,1-units confirms the above observations by Mülhaupt and co-workers [144] that the subsequent monomer insertion at a sterically hindered “dormant” site with a 2,1-last-inserted unit is slower than the hydrogenolysis reaction. Detected at low amounts were terminally unsaturated oligomers formed by a sequence of *n* 1,2-insertions followed by H-transfer to the monomer [Eq. (10)]. At low monomer concentration (<1 mol l^{-1}) and H_2 pressure (<10 bar) very low amounts of fully regioregular saturated oligomers were also found, initiated by a Zr–CH_3 bond. They can be traced to chain transfer to Al–CH_3. From a set of hydrooligomerization experiments at different monomer concentration and/or H_2 pressure, it was possible to extrapolate the ratio k_{pp}/k_{ps} (see Scheme 6) and the fraction of the dormant sites [91].



(10)

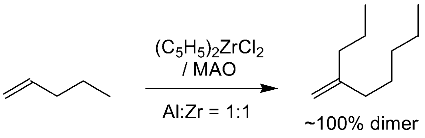
3.5. 1-Pentene oligomerization

Wahner et al. studied the oligomerization of 1-pentene using $(C_5H_5)_2ZrCl_2$, $(C_5H_5)_2HfCl_2$, $(C_5Me_5)_2ZrCl_2$, *rac*-$C_2H_4(Ind')_2ZrCl_2$, $Me_2Si(Ind')_2ZrCl_2$, Me_2Si(2-Me-benz[e]indenyl)$_2ZrCl_2$ [cf. Eq. (7)], $(C_5H_5)_2ZrCl\{O(Me)CW(CO)_5\}$, and $(C_5H_5)_2ZrCl(OMe)$, all activated with MAO. Highly depending on the metallocene catalyst, oligomers ranging from the dimer of 1-pentene to polymers with $M_w = 149{,}000\,g\,mol^{-1}$ were formed. The system $(C_5H_5)_2ZrCl\{O(Me)CW(CO)_5\}$/MAO is a highly active catalyst for the oligomerization of 1-pentene to low-molecular weight products [146]. $(C_5H_5)_2ZrCl_2$/MAO (Al:Zr = 1000) gave low molar mass oligomers from which the dimer (25%), the trimer (18%) and the tetramer (14%) could be isolated after distillation [Eq. (11)]. The analogous $(C_5H_5)_2HfCl_2$ complex yielded an atactic oligomer in the form of a viscous oil (at 60 °C, $M_n = 2500\,g\,mol^{-1}$). The sterically hindered catalyst $(C_5Me_5)_2ZrCl_2$/MAO also gave a viscous oil (at 60 °C with $M_n = 1000\,g\,mol^{-1}$). The catalysts $(C_5H_5)_2HfCl_2$ and $(C_5Me_5)_2ZrCl_2$ lead almost exclusively to the formation of vinylidene end groups, whereas the bridged catalysts *rac*-$C_2H_4(Ind')_2ZrCl_2$ and $Me_2Si(Ind')_2ZrCl_2$ give also internal double bonds of the type RCH=CHR′. These functional groups are formed if the chain termination is caused by β-H transfer after a 2,1-“mis”insertion (cf. Scheme 2). A MALDI–TOF mass spectrum of low-molar-mass oligo-1-pentene could be recorded using dithranol as matrix and adding silver trifluoroacetate to promote ion formation [53].



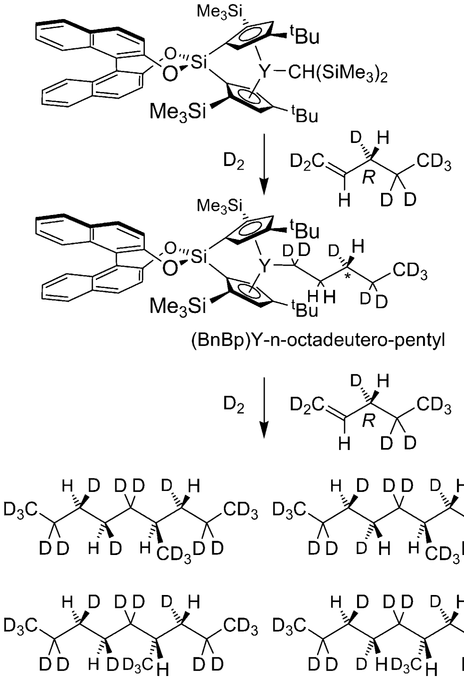
(11)

In work by Christoffers and Bergman, $(C_5H_5)_2ZrCl_2$ when activated by only 1 equiv. of MAO selectively and catalytically dimerizes 1-pentene (and other α-olefins) to 2-propyl-1-heptene without formation of any higher oligomeric species [Eq. (12)] [51].



(12)

Gilchrist and Bercaw used optically active (*R*)-octadeutero-1-pentene, $CD_3\text{-}CD_2\text{-}C^*HD\text{-}CH{=}CD_2$ (**16**) to evaluate the stereoselectivity for the optically pure C_2-symmetric catalysts (*R,S*)-(BnBp)Y-*n*-octadeutero-pentyl and (*S,R*)-(BnBp)Y-*n*-octadeutero-pentyl (**17**) and racemic (±)-(BnBp)Y-*n*-octadeutero-pentyl. Stirring the neat olefin (*R*)-octadeutero-1-pentene containing (BnBp)Y-$CH(SiMe_3)_2$ (**18**) as catalyst precursor under D_2 produced a mixture of deutero-oligomers from which the four possible deuterodimers were isolable by preparative GC [Eq. (13)]. These deuterodimers indicate the sense and magnitude of olefin facial selectivity for insertions into the metal-*n*-pentyl bond with the chiral 1-pentene providing the probe of the absolute stereochemistry for additions to α-olefin double bonds [147].



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(13)

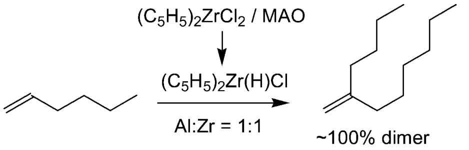
Kaminsky oligomerized 1-pentene with asymmetric (*S*)-$C_2H_4(Ind'H_4)_2ZrMe_2$/MAO to obtain optically active pentene trimers, tetramers and other oligomers through enantiomorphic site control during the C–C bond formation. Optical activity starts in the trimer, the dimer does not contain a chiral carbon atom [85].

3.6. 1-Hexene oligomerization

Suzuki et al. reported 1-hexene oligomers ($M_n \approx 1500\,g\,mol^{-1}$) with $(C_5H_4{}^tBu)_2ZrCl_2$ or $Me_2Si(C_5H_4)_2ZrCl_2$/MAO in activities of 4 or $8 \times 10^5\,g\,mol_{Zr}{}^{-1}\,h^{-1}$, respectively [148].

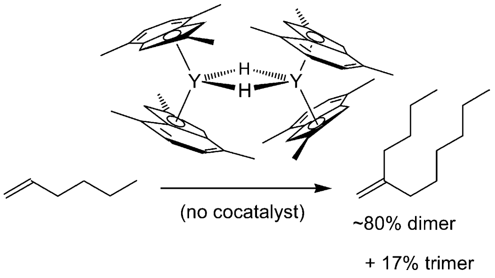
According to Christoffers and Bergman, $(C_5H_5)_2ZrCl_2$ when activated by only 1 equiv. of MAO selectively and catalytically dimerizes 1-hexene (and other α-olefins, see below) to 2-butyl-1-octene (=5-methyleneundecane) without formation of any higher oligomeric species [Eq. (14)]. Monitoring the reaction by ^1H NMR gave a turnover number of

~6 min^{-1} after an induction period of ~60 min. It is suggested that a Zr-hydrido complex is the actual active species [Eq. (14)]. $(C_5H_5)_2Zr(H)Cl$/MAO (1:1) also selectively dimerizes 1-hexene but with a significantly shorter induction period (~5 min) and a turnover number of ~30 min^{-1} [51].



(14)

Kretschmer et al. applied the dimeric yttrium complex $\{(2,4,7\text{-}Me_3\text{-}Ind'')_2Y(\mu\text{-}H)\}_2$ as a catalyst (without any co-activator) in the regioselective dimerization of 1-hexene to 5-methyleneundecane in 80% yield (plus 17% of the trimer) at 80 °C [Eq. (15)] [149].



(15)

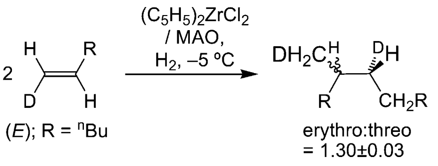
Janiak et al. used a series of *tert*-butyl substituted zirconocene/MAO complexes (see **15**) to illustrate the potential for tailoring 1-hexene oligomers with extremely narrow molar mass distribution down to $M_w/M_n \approx 1.2$. Molecular weights were between $M_n = 200–740\ g\,mol^{-1}$. The small dispersion is explained on the basis of a chain-length dependent propagation rate. At 50 °C, c_0(1-hexene) = 6.9 mol l^{-1}, [Zr] = 3×10^{-6} mol l^{-1} with Al:Zr = 4000 and a reaction time of 1 h [81,82,102] (reaction time was 24 h in [43]) the activity was highest for the mono-substituted zirconocene $(C_5H_5)(C_5H_4{}^tBu)ZrCl_2$ with $7.9 \times 10^6\ g\,mol_{zr}{}^{-1}\,h^{-1}$ followed by the mixed zirconocene with the one di-substituted ligand, $(C_5H_5)(C_5H_3\text{-}1,3\text{-}{}^tBu_2)ZrCl_2$ with $2.7 \times 10^6\ g\,mol_{zr}{}^{-1}\,h^{-1}$. Upon further increase in steric demand the activities decrease to $1.7 \times 10^6\ g\,mol_{zr}{}^{-1}\,h^{-1}$ for $(C_5H_4{}^tBu)_2ZrCl_2$, $0.26 \times 10^6\ g\,mol_{zr}{}^{-1}\,h^{-1}$ for $(C_5H_5)(C_5H_2\text{-}1,2,4\text{-}{}^tBu_3)ZrCl_2$ and $0.3 \times 10^6\ g\,mol_{zr}{}^{-1}\,h^{-1}$ for $(C_5H_3\text{-}1,3\text{-}{}^tBu_2)_2ZrCl_2$. The latter zirconocene rather selectively gave the dimer 5-methyleneundecane in 80–90% yield [43,81,82,102].

The activities for zirconocenes with the tetramethyl-substituted phospholyl ligand C_4PMe_4 were also compared for 1-hexene to the activities of zirconocenes with the tetramethyl- and pentamethyl-cyclopentadienyl ligand C_5HMe_4 and C_5Me_5, respectively (propene comparison see above, Scheme 5). Activities for the phospholyl complexes $(C_5H_5)(C_4PMe_4)ZrCl_2$ and $(C_4PMe_4)_2ZrCl_2$ were much lower (~$0.1 \times 10^6\ g\,mol_{zr}{}^{-1}\,h^{-1}$), by a factor of ~50 than those of the permethyl zirconocenes ($3–6.3 \times 10^6\ g\,mol_{zr}{}^{-1}\,h^{-1}$, 50 °C, c_0(1-hexene) = 6.9 mol l^{-1}, [Zr] = 3×10^{-6} mol l^{-1} with Al:Zr = 4000) [81,82,102]. This is explained by formation of a P–Al adduct [132,133] with the bulky "Al-substituent" becoming situated close to the maximum opening angle/gap aperture of the zirconium, that is, close to the meridional centroid–Zr–centroid angle (see Scheme 5). Such a bulky substituent in this position then blocks the pathway for the insertion of hexene into the Zr–C bond (as is known for *ansa*-metallocenes with C_5-ring substituents in this position) [82,102,134]. Molecular weights for the oligohexenes obtained with the phospholyl systems were $M_n = 500\ g\,mol^{-1}$ and significantly lower than those of the permethyl zirconocene series ($M_n = 1100–3300\ g\,mol^{-1}$). As unsaturated end groups only vinylidene double bonds are found. Comparison of the molecular weight determinations by ^1H NMR and GPC together with MALDI–TOF MS shows that most of the permethylated complexes exhibit considerable chain transfer to Al. In 1-hexene oligomerization the bis-phospholyl $(C_4PMe_4)_2ZrCl_2$ exhibits about 80% chain transfer to Al. Catalysts based on $(C_5HMe_4)_2ZrCl_2$ and $(C_4PMe_4)_2ZrCl_2$ give over 60% saturated oligomers. The decamethylzirconocene $(C_5Me_5)_2ZrCl_2$ has over 35% saturated end groups and only for the less congested tetra- and pentamethylzirconocenes $(C_5H_5)(C_5H_{5-n}Me_n)ZrCl_2$ (n = 4, 5) chain transfer is less important (below 10 and 20%, respectively). This is attributed to steric causes which make it more difficult for the β-hydrogen to get oriented towards the metal center, so that chain transfer can become a major competing termination pathway [81,82,102].

In a mechanistic study Siedle et al. used $(C_5H_5)_2ZrMe_2$/MAO and 1-hexene oligomerization in toluene to find β-H elimination as the predominant chain transfer which was different than for ethene oligomerization with the same system (see above) [80].

Hungenberg et al. investigated the oligomerization of 1-hexene with $(C_5H_5)_2ZrCl_2$/MAO in bulk to establish a rate law which sufficiently allowed to describe time conversion curves and the resulting oligomer distribution. However, there was no dependence of the degree of polymerization or the oligomer distribution on conversion, i.e. on monomer concentration [7].

The hydrodimerization of (*E*)- or (*Z*)-1-deuterio-1-hexene by achiral zirconocene dichloride/MAO [Eq. (16)] presented by Krauledat and Brintzinger [150] as well as the hydrocyclization of *trans,trans*-1,6-d_2-1,5-hexadiene by a scandocene hydride, $Me_2Si(C_5Me_4)_2Sc(PMe_3)H$ [Eq. (17)] carried out by Piers and Bercaw [151] gave results, which were judged to provide experimental evidence for an α-agostic transition state (modified Green-Rooney mechanism) in metal catalyzed olefin polymerizations. The *erythro*:*threo* or *cis*:*trans* ratio differing from unity in Eqs. (16) or (17), respectively, is seen to stem from an H/D-isotope effect, whose basis is the expected preference of H over D in an α-agostic interaction for the transition states.



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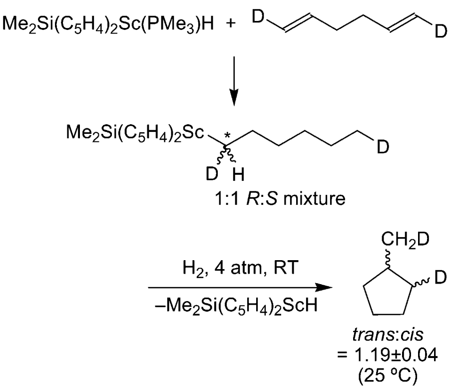


(17)

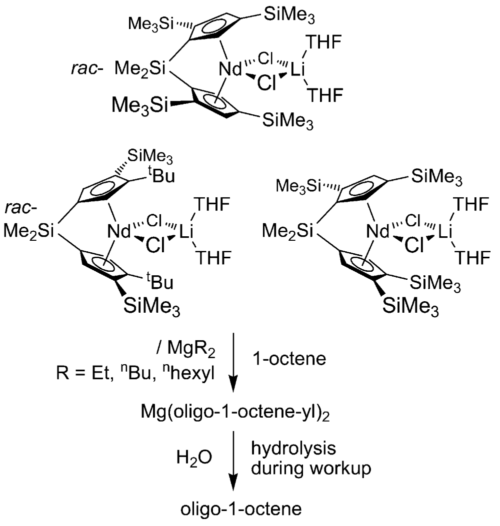
Ciardelli et al. carried out ethene/1-hexene co-oligomerizations to investigate the comonomer action as chain transfer agent. The co-oligomerizations used $(C_5H_5)_2ZrMe_2$/MAO at two different temperatures (20 and 70 °C), Al:Zr ratio = 1000 [56].

3.7. 1-Heptene oligomerization

Christoffers and Bergman activated $(C_5H_5)_2ZrCl_2$ by only 1 equiv. of MAO to selectively and catalytically dimerize 1-heptene (and other α-olefins) to 2-pentyl-1-nonene without formation of any higher oligomeric species [cf. Eq. (12) or (14)] [51].

3.8. 1-Octene oligomerization

Carpentier et al. showed that the trivalent neodymium complexes *rac*-$Me_2Si(C_5H_2\text{-}2,4\text{-}\{SiMe_3\}_2)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$, *rac*-$Me_2Si(C_5H_2\text{-}3\text{-}SiMe_3\text{-}4\text{-}{}^tBu)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$ and $Me_2Si(C_5H_2\text{-}2,4\text{-}\{SiMe_3\}_2)(C_5H_2\text{-}3,4\text{-}\{SiMe_3\}_2)Nd(\mu\text{-}Cl)_2Li(THF)_2$ when combined in situ with a dialkylmagnesium cocatalyst, initiated the oligomerization of 1-octene (and ethene) to yield di(oligoalkyl)magnesium species which were finally hydrolyzed to oligomers [Eq. (18)] (M_n = 400–1300 g mol^{-1}, M_w/M_n = 1.11–1.65). These bulky bridged complexes were found to be more active in 1-octene oligomerization than the related nonbridged systems $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(OEt_2)_2$ and $(C_5H_3\text{-}1,3\text{-}\{SiMe_3\}_2)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$ [111].

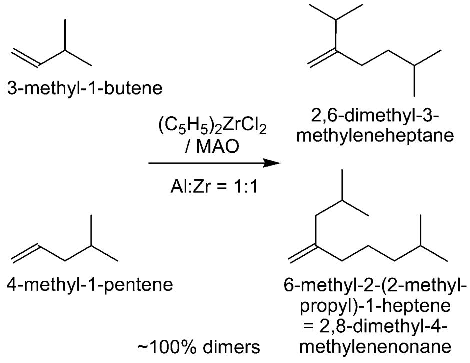


(18)

Ciardelli et al. carried out ethene/1-octene co-oligomerizations with $(C_5H_5)_2ZrMe_2$/MAO to investigate the comonomer action as chain transfer agent (temperatures 20 and 70 °C, Al:Zr ratio = 1000) [56].

3.9. Branched α-olefin oligomerization

Christoffers and Bergman reported that $(C_5H_5)_2ZrCl_2$ when activated by only 1 equivalent of MAO selectively and catalytically dimerizes the α-olefins 1-butene (→ 2-ethyl-1-hexene) [Eq. (8)], 1-pentene (→ 2-propyl-1-heptene) [Eq. (12)], 1-hexene (→ 2-butyl-1-octene = 5-methyleneundecane) [Eq. (14)], 1-heptene (→ 2-pentyl-1-nonene), **3-methyl-1-butene** (→ 5-methyl-2-(methylethyl)-1-hexene = 2,6-dimethyl-3-methyleneheptane) [Eq. (19)], **4-methyl-1-pentene** ([apparently wrongly named as 3-methyl-1-pentene] → 6-methyl-2-(2-methylpropyl)-1-heptene) [Eq. (20)] without formation of any higher oligomeric species [51].



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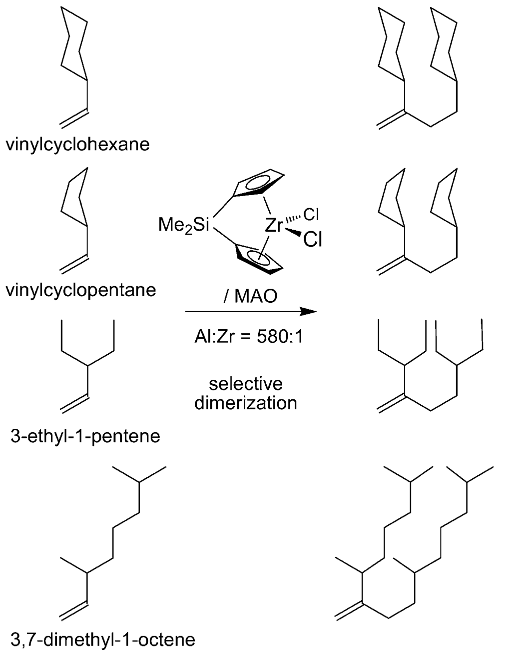
Longo et al. managed the selective dimerization of the γ-branched α-olefin **vinylcyclohexene** in the presence of $(C_5H_5)_2MCl_2$ (M = Ti, Zr, Hf) or $Me_2Si(C_5H_4)_2ZrCl_2$/MAO [Eq. (21)], with the latter one being by far the most active (8.9 g $(\text{mol l})_{Zr}^{-1}\cdot(\text{mol l})_{\text{monomer}}^{-1}\,h^{-1}$). The latter catalyst was also used for the selective dimerization of the γ-branched α-olefins **vinylcyclopentene** [Eq. (22)], **3-ethyl-1-pentene** [Eq. (23)] and **3,7-dimethyl-1-octene** [Eq. (24)]. Activities were even lower, however, with 3.5 g $(\text{mol l})_{Zr}^{-1}$ $(\text{mol l})_{\text{monomer}}^{-1}\,h^{-1}$ for vinylcyclopentene being still the highest. With **3-methyl-1-pentene** the product distribution was 19% dimer, 50% trimer, 24% tetramer, 4% pentamer and 3% of hexamer, with **3-methyl-1-butene** it was 11% dimer, 36% trimer, 35% tetramer, 14% pentamer and 4% hexamer [152].



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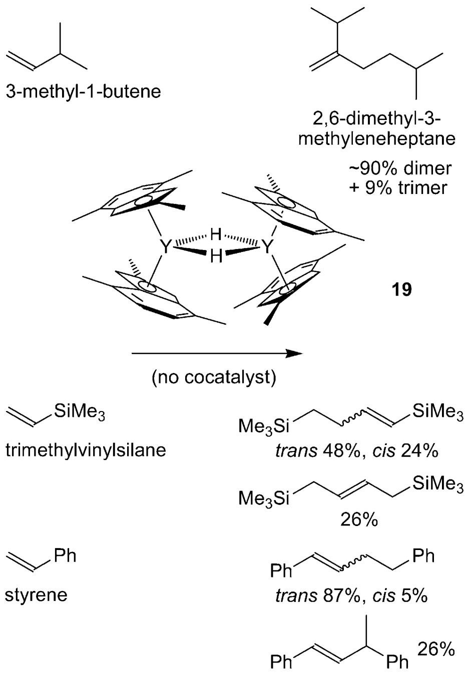
Kretschmer et al. applied the dimeric complex $\{(2,4,7\text{-}Me_3\text{-}Ind''')_2Y(\mu\text{-}H)\}_2$ (**19**) as a catalyst (without any co-activator) in the regioselective homo-dimerization of 1-hexene (→ 5-methyleneundecane, 80% yield plus 17% of the trimer) [cf. Eq. (15)], **3-methyl-1-butene** (→ 2,6-dimethyl-3-methyleneheptane, 90% yield plus 9% of the trimer) [Eq. (25)], **trimethylvinylsilane** (→ head-to-head coupling products (*E*)-1,4-bis(trimethylsilyl)but-1-ene, 48%, (*Z*)-∼ 24%, (*E*)-1,4-bis(trimethylsilyl)but-2-ene, 26%) [Eq. (26)], **styrene** (→ head-to-head coupling products (*E*)-1,4-diphenylbut-1-ene, 87%, (*Z*)-∼ 5%, (*E*)-1,3-diphenylbut-1-ene, 6%) [Eq. (27)]. The same catalyst was also used in the co-dimerization of **styrene with α-olefins** $H_2C{=}CHR$ (R = ^{n}Bu, ^{i}Pr, ^{t}Bu, $SiMe_3$, CH_2Ph, CH_2S^tBu and others) to give *trans*-1-phenyl-4-alkyl-buten-1-enes, Ph-CH=CH-CH_2CH_2-R in over 88% yield in benzene at 80–100 °C [Eq. (28)] [149].



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R = ^{n}Bu, ^{i}Pr, ^{t}Bu, $SiMe_3$, CH_2Ph, CH_2S^tBu and others

(28)

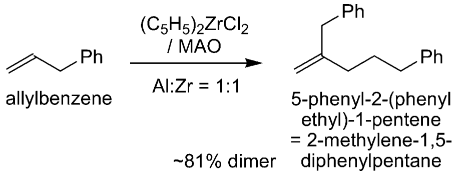
Ciardelli et al. co-oligomerized **ethene with 4-methyl-1-pentene** with $(C_5H_5)_2ZrMe_2$/MAO to investigate the comonomer action as chain transfer agent [56].

Shaffer and Ashbaugh oligomerized **isobutene (isobutylene)** to a low M_n material (6600 g mol^{-1}) with $Me_2Si(Ind'H_4)_2ZrMe_2/[Ph_3C][B(C_6F_5)_4]$ (1:1 ratio) in the presence of ∼2 equiv. of H_2O in chlorobenzene at −20 °C. With considerably less amounts of residual water in chlorobenzene high M_n poly(isobutylene) is obtained [72].

Hajela and Bercaw reacted $Me_2Si(C_5Me_4)_2ScH(PMe_3)$ with **isobutene** to observe the formation of 2-methylpentane, isobutane, 2-methyl-1-pentene, propane and *n*-pentane from a series of olefin insertion, β-Me and faster β-H elimination which proceed until only the 2-methyl-1-alkenes remain [153].

Kim et al. investigated the homopolymerization of **allylbenzene** with various metallocene/MAO catalysts. Among them, $(C_5H_5)_2ZrCl_2$/MAO gave amorphous polyallylbenzene with low molecular weight (M_w = 3400–1500 and M_w/M_n = 1.4–1.2 for a reaction temperature from −10 to 80 °C, respectively; highest activity at 60 °C with 6.8×10^3 g $mol_{Zr}^{-1}\,h^{-1}$ [154].

Christoffers and Bergman dimerized **allylbenzene** to 5-phenyl-2-(phenylmethyl)-1-pentene with $(C_5H_5)_2ZrCl_2$/MAO (molar ratio 1:1) [Eq. (29)] [51].



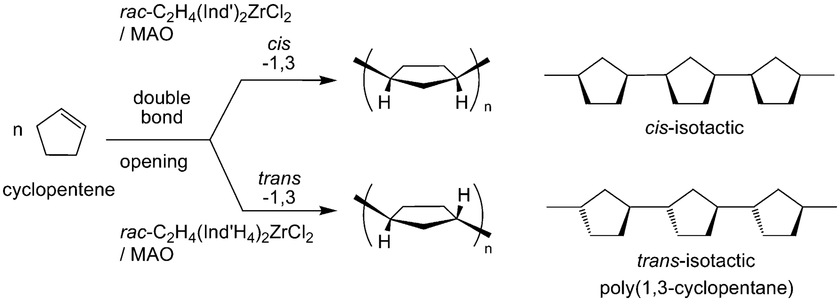
(29)

Okamato et al. derived at optically active oligomers from the bulky **allyltriphenylsilane** in the reactions using optically active $C_2H_4(Ind'H_4)_2M$(2,2′-biphenolate) or (binaphtholate)/MAO catalysts (M = Zr, Hf) [155].

3.10. Cyclic olefin oligomerization

3.10.1. Cyclopentene

Collins et al. demonstrated that the polymerization of cyclopentene with *rac*-$C_2H_4(Ind')_2ZrCl_2$/MAO leads to the formation of poly(*cis*-1,3-cyclopentane) [Eq. (30)] through the independent synthesis of the single, stereoisomeric tetramer under hydrooligomerization conditions [156]. In contrast, hydrooligomerization of cyclopentene with *rac*-$C_2H_4(Ind'H_4)_2ZrCl_2$/MAO led to the production of oligomers in which cyclopentene is incorporated in a *cis*- and *trans*-1,3-manner [Eq. (31)] as was also confirmed through independent organic synthesis of some of these saturated oligomers [92]. Steric reasons are seen responsible for having after the initial 1,2-insertion an isomerization (epimerization) through β-H elimination, followed by re-insertion of the olefin into the Zr–H bond to give the 1,3-insertion product [73].



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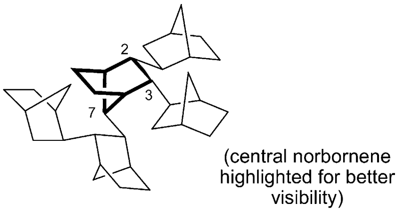
3.10.2. Norbornene

Fink et al. used the hydrooligomerization of norbornene, that is the norbornene polymerization in the presence of H_2, with *rac*-$Me_2C(Ind')_2ZrCl_2$/MAO to deliberately obtain oligomers in order to gain insight into the microstructure of polynorbornene. The oligomers were separated by preparative HPLC and their structures, e.g. that of a norbornene pentamer (**20**), determined by single-crystal X-ray diffraction. These studies show that in-between the regular *cis*-2,3-*exo* vinyl/addition insertions a metallocene-catalyzed σ-bond metathesis can take place. The *syn*-hydrogen on C7 (the bridgehead) of the previous to last inserted monomer interacts with the Zr atom which in the σ-bond metathesis becomes now bound to C7. Thus, the chain continues with the next insertion on the C7-bridgehead carbon atom of the previous to last monomer [157].

Arndt and Gosmann had earlier described the pentamer X-ray structure with the same bridgehead (C7) substitution in a central trisubstituted norbornene unit (**20**). The pentamer was isolated from a hydrooligomerization of norbornene catalyzed by *rac*-$C_2H_4(Ind'H_4)_2ZrCl_2$/MAO [158].



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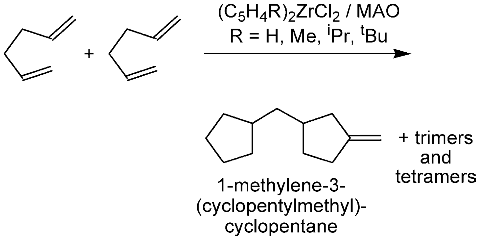
Tritto et al. studied the norbornene oligomerization by $(C_5H_5)_2Ti(^{13}Me)Cl$/MAO in order to test the validity of carbene mechanisms in α-olefin polymerizations. At 0 °C reaction temperature, the addition product 2-(^{13}C enriched)methylnorbornane has been identified. At higher temperatures, the identification of a ^{13}C enriched methylidene-norbornane dimer revealed the possibility of norbornene addition to Ti-carbenes through the formation of titanacyclobutane without the opening of the norbornene ring [159].

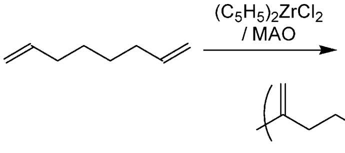
3.11. α,ω-Diene oligomerization

Thiele and Erker used optimized reaction conditions employing low substrate concentrations (1.0–1.3 mol l^{-1}, hexadiene:Zr = 1900–2400) and rather long reaction times (5 h) to cyclodimerize **1,5-hexadiene** to give 1-methylene-3-(cyclopentylmethyl)cyclopentane (36–58%) together with trimers (30–36%) and tetramers (12–29%) with $(C_5H_4R)_2ZrCl_2$/MAO (R = H, Me, ^{i}Pr, ^{t}Bu; Al:Zr = 360; temperature 50–70 °C) [Eq. (32)] [54].



(32)

Christoffers and Bergman accomplished the oligomerization of **1,7-octadiene** [Eq. (33)] with $(C_5H_5)_2ZrCl_2$/MAO to yield either lower oligomeric (1 d, RT, $M_w = 1600$, $M_w/M_n = 2.0$) or higher oligomeric materials (3 d, RT, $M_w = 5400$, $M_w/M_n = 2.6$) [160].

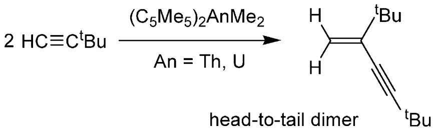


(33)

3.12. *Alkyne oligomerization*

The metallocene pre-catalyst $(C_5Me_5)_2AnMe_2$ (An = Th, U) promote the simultaneous production of a large number of differently sized oligomers in the presence of terminal alkynes, HC≡CR (R = alkyl, aryl, $SiMe_3$). The regioselectivity and the extent of oligomerization depend strongly on the alkyne substituent R.

According to Eisen et al. reaction with $HC{\equiv}C^tBu$ yields regioselectively the *E*-2,4-bis(trimethylsilyl)-1-buten-3-yne head-to-tail dimer [Eq. (34)] whereas $HC{\equiv}CSiMe_3$ is regioselectively trimerized to the head-to-tail-to-head trimer *E*,*E*-1,4,6-tris(trimethylsilyl)-1,3-hexadiene-5-yne [Eq. (35)]. Oligomerization with less bulky alkyl and aryl substituted alkynes produces a mixture of higher oligomers with no regioselectivity [161,162].



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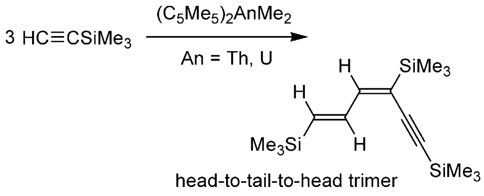
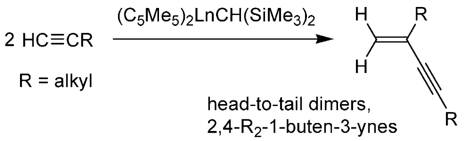


(35)

Wang and Eisen described the addition of the secondary silane Et_2SiH_2 to ensure the selective synthesis of short oligomers, that is the selective dimerization of terminal alkynes promoted by $(C_5Me_5)_2UMe_2$ [163].

Eisen et al. also developed a strategy for the controlled catalytic synthesis ("tailoring") of dimers or a mixture of dimers and trimers through the oligomerization of terminal alkynes by using nonbulky or bulky amines, respectively, with the actinioid catalysts $(C_5Me_5)_2AnMe_2$ (An = Th, U). The kinetics in the catalytic oligomerization of 1-hexyne, in the presence of $^iBuNH_2$, by $(C_5Me_5)_2ThMe_2$ are first order in alkyne and Th and inverse first order in amine concentration [161,164].

Heeres and Teuben investigated lanthanoid and group 3 carbyls $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Y, La, Ce) as catalysts for the oligomerization of terminal alkynes. The metal also influenced strongly the regioselectivity and the extent of oligomerization besides the alkyne substitutent. For Ln = Y, alkyl-substituted alkynes are dimerized selectively to head-to-tail 2,4-disubstituted 1-buten-3-ynes [Eq. (36)]. Mixtures of two enyne isomers, e.g. 2,4-disubstituted 1-buten-3-ynes and 1,4-disubstituted 1-buten-3-ynes are found for HC≡CPh and $HC{\equiv}CSiMe_3$ [Eq. (37)]. The reactions with Ln = La and Ce produce not only dimers but also various higher oligomers (trimers, tetramers) [165].



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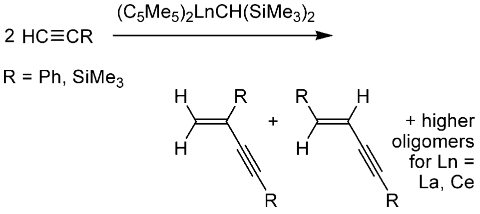
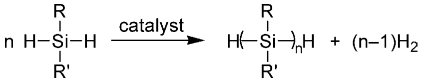


(37)

Brubaker et al. attached titanocene dichloride to a polymer support via a covalent linkage to the cyclopentadienyl ligand to form polymer-$(C_5H_4)(C_5H_5)TiCl_2$ which on reduction with excess ^nBuLi was found to oligomerize ethynyl propionate (=ethyl propiolate, HC≡C–OC(=O)Et) to a mixture of open and closed trimers. The closed trimers were identified as 1,2,4- and 1,3,5-tricarbethoxybenzene [166].

3.13. *Dehydrocoupling/dehydrooligomerization of hydrosilanes*

Polysilane polymers are of interest because of their unusual electronic, optical and chemical properties. One polymerization method for these materials is the dehydropolymerization of silanes with transition-metal catalysts [Eq. (38)] [167].



$$n\ H{-}\overset{R}{\underset{R'}{Si}}{-}H \xrightarrow{\text{catalyst}} H(\overset{R}{\underset{R'}{-Si-}})_nH + (n-1)H_2$$

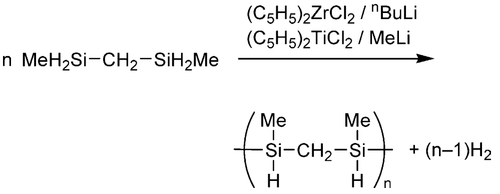
(38)

Hilty et al. suggested the step-growth nature of the dehydrocoupling based on the $(C_5H_5)_2ZrMe_2$-catalyzed dehydropolymerization of $^nBuSiH_3$, which produced low molecular weight oligosilanes [168]. Tilley et al. illustrated the step-growth character of the reaction by the slow dehydrocoupling of $PhSiH_3$ by $(C_5Me_5)_2HfH_2$, which allows observation of the early intermediates di-, tri- and tetrasilane, $PhH_2Si\text{-}(\text{–}SiHPh\text{–})_n\text{–}SiH_2Ph$ ($n = 0, 1, 2$) [167].

Shaltout and Corey described the conversion of $PhSiH_3$ to oligosilanes by *rac*- and *meso*-$Me_2C(C_5H_3SiMe_3)_2HfCl_2/^nBuLi$ at room temperature [169].

Woo et al. used $(C_5H_5)_2MCl_2/(^nBuLi$ or reduced Al) (M = Ti, Hf) for the dehydropolymerization of bis(silyl)alkylbenzenes such as bis(1-sila-*sec*-butyl)benzene and 2-phenyl-1,3-disilapropane, producing two phases of polymers. The molecular weights of the soluble polymers ranged from $M_n = 500–900$ and from $M_w = 700–5000\ g\ mol^{-1}$ (versus polystyrene) [170].

Dunoguès et al. synthesized poly(2,4-disilapentane) oligomers via dehydropolymerization of the monomer $MeH_2Si\text{-}CH_2\text{-}SiMeH_2$ [Eq. (39)] using $(C_5H_5)_2ZrCl_2/{}^nBuLi$ or $(C_5H_5)_2TiCl_2/MeLi$ [171].



$$n\ \mathrm{MeH_2Si{-}CH_2{-}SiH_2Me} \xrightarrow{\substack{(C_5H_5)_2ZrCl_2\ /\ {}^nBuLi \\ (C_5H_5)_2TiCl_2\ /\ MeLi}} \left[\mathrm{Si(Me)(H){-}CH_2{-}Si(Me)(H)}\right]_n + (n-1)H_2 \qquad (39)$$

Tilley et al. proposed a mechanism of the dehydropolymerization of hydrosilanes to polysilanes, as catalyzed by early-transition-metal metallocene derivatives. As part of their mechanistic studies they showed that the thermolytic decomposition of $(C_5H_5)(C_5Me_5)Hf(SiH_2Ph)Cl$ to $(C_5H_5)(C_5Me_5)Hf(H)Cl$ resulted in Si–Si bond formation with the production of polysilane oligomers [172].

Hengge and Weinberger obtained a mixture of the oligosilanes $Me_3Si(Me_2Si)_nSiMe_2H$ from a dehydropolymerization of pentamethyldisilane, $Me_3Si\text{-}SiHMe_2$ by means of $(C_5H_5)_2MMe_2$ (M = Ti, Zr) (no co-activator neces-

Table 1
Sandwich complexes with cyclic π-perimeters other than cyclopentadienyl for olefin oligomerization

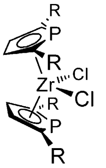
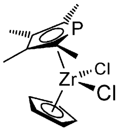
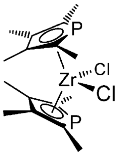
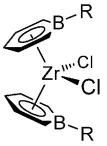
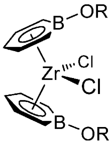
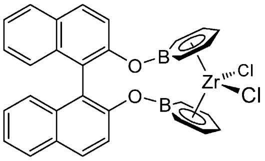
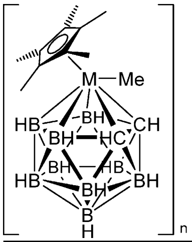
Sandwich complex	Monomer	Remarks	Ref.
 R = H, cyclo-Pr, ${}^tBu$, $SiMe_3$, Ph	Propene	MAO cocatalyst; see also text in Section 3.3	[132]
 	Propene, 1-hexene	MAO cocatalyst; see also text in Sections 3.3 and 3.6	[81,82,102]
 R = Me, Ph boratabenzene, $C_5H_5BR^-$ is a six π-electron aromatic anion, isoelectronic with benzene and resembling cyclopentadienide	Ethene 1-octene	MAO cocatalyst; at 25 °C, 1 atm of C_2H_4; mixture of 1-alkenes, 2-alkyl-1-alkenes and 2-alkenes; activities ~6.8–9.2 × 10^5 g mol_{zr}^{-1} h^{-1}. R = Ph, dimerization to 2-hexyl-1-decene	[178–181]
 R = Me, Et, ${}^tBu$, cyclohexyl, CH_2Ph, Ph 	Ethene 1-decene	MAO cocatalyst; mixture of 1-alkenes, 2-alkyl-1-alkenes and 2-alkenes; R = Et: 99% α-olefins; activities ~1.3–9.5 × 10^5 g mol_{zr}^{-1} × h^{-1}. R = Ph: decene dimerization to 2-octyl-1-dodecene	[179–183]
 M = Zr, Hf	Propene	Complex synthesis from $(C_5Me_5)MMe_3$ (M = Zr, Hf) with neutral carborane $C_2B_9H_{13}$	[184]

Table 2
Half-sandwich complexes for olefin oligomerization

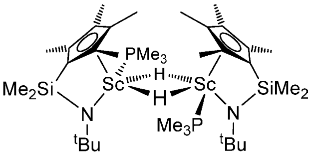
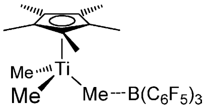
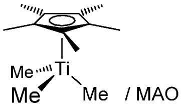
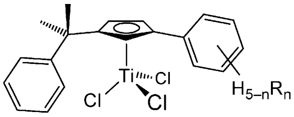
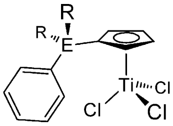
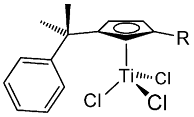
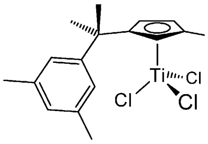
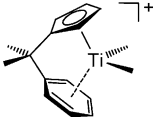
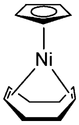
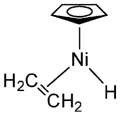
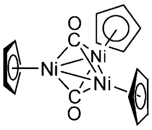
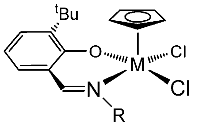
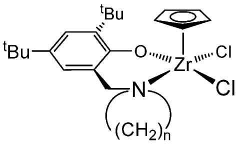
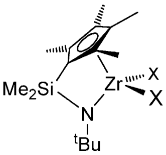
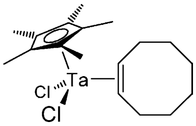
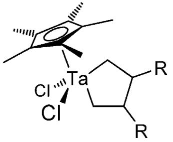
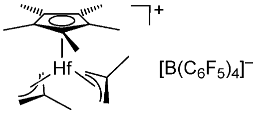
Half-sandwich complex	Monomer	Remarks	Ref.
	Propene, 1-butene, 1-pentene	max. $x_i \approx 70$ for oligo-1-butene; chain transfer by β-H elimination	[186,187]
	Ethene/styrene, ethene/*p*- or *m*-methylstyrene, ethene/*p*-^{t}Bu-styrene, ethene/*p*-chloro-styrene,	Co-oligomerization mainly to 6-phenyl-1-hexene; subsequent co-polymerization of this oligomer with ethene	[63,64]
	1-hexene		[188]
 R_n = 4-Me, 3,5-Me_2	Ethene	MAO cocatalyst; mostly trimerization to 1-hexene as main product; study of various substituent effects on trimerization product-% and productivity.	[189]
 $ER_2 = CH_2, CMe_2, CEt_2, SiMe_2$, >cyclohexyl, >$C{=}CH_2$, $-CH_2C(Me_2)-$	Ethene/1-hexene	co-trimerization to 5-methyl-non-1-ene	
 R = H, $SiMe_3$, ^{t}Bu, CMe_2Ph  R = H, $SiMe_3$, ^{t}Bu		Pendant, hemi-labile arene group coordination to active center suggested: 	
$(C_5H_5)TiCl_3$ immobilized on a cyclopentadienyl surface of silica with ^{n}BuLi	Ethene	MAO cocatalyst	[190]
 	Ethene, propene, ethene/propene	$AlEt_2(OEt)$ cocatalyst; propene conversion to branched dimers, mostly 2,3-dimethylbutenes	[191]
	Ethene	C_4–C_{20} olefins; turnover > 10^5 $mol(C_2H_4)\cdot mol_{complex}^{-1}\ h^{-1}$	[192]

Table 2 (*Continued*)

Half-sandwich complex	Monomer	Remarks	Ref.
 M = Ti, R = C_6F_5 M = Zr, R = C_6F_5, C_6H_2-2,4,6-Me_3  n = 4, 5	1-Hexene	MAO cocatalyst; activities between 2.6 and 5.6 × 10^3 g mol_M^{-1} h^{-1}	[193]
 X = Cl, Me	Ethene	Activation with Al^iBu_3/$[Ph_3C]$- or $[PhNHMe_2]$-$[B(C_6F_5)_4]$	[113,114]
	Ethene, propene 1-pentene, 1-octene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene	Intermediate:  R = H, Me, ^{n}Pr, ^{n}Hex, $CH_2{}^iPr$, $CH_2{}^tBu$; selective dimerization, mostly tail-to-tail dimers	[194]
	Propene	M_n = 2700 g mol^{-1}, activity 1.4 × 10^3 g g_{Hf}^{-1} h^{-1} at ambient temperature and 5 bar	[195]

sary). Analogously 1,1,2,2-tetramethyldisilane, Me_2HSi–$SiHMe_2$ reacts to a mixture of the oligosilanes Me_2HSi-$(Me_2Si)_nSiHMe_2$ [173].

Kesti and Waymouth noted that when group-IV metallocene catalysts, such as $(C_5H_5)_2ZrCl_2/^nBuLi$, are used for the hydrosilylation of olefins, silane coupling reactions compete with hydrosilylation in the case of less sterically hindered secondary or primary silanes and they produce oligomeric products from dehydropolymerization [174].

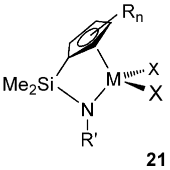
4. Complexes related to metallocenes for olefin oligomerization

4.1. Sandwich complexes with cyclic π-perimeters other than cyclopentadienyl

The term “metallocene” refers to compounds which have a metal atom bound to two cyclopentadienide anions in a π- or pentahapto/η^5-mode. The cyclopentadienyl rings can coordinate in a co-planar (parallel) or bent fashion to the metal center. Besides the two cyclopentadienyl rings, the metal can have additional ligands depending on its valence state [175]. The cyclopentadienyl ring can be modified in many ways by substituting the hydrogen atoms through alkyl or aryl groups or anellated rings (or a combination thereof – see the above metallocene examples and sketches) [175,116]. Furthermore, a C–H group can be replaced by an isoelectronic nitrogen [176] or phosphorus atom [102,177,133]. Although clearly not “metallocenes” we will briefly mention here related sandwich complexes which were also described for olefin oligomerization. Sandwich complexes have the metal placed in-between two cyclic π-perimeters, such as benzene rings or between a cyclopentadienyl and a benzene ring. Metallocenes also belong to the class of sandwich compounds. Table 1 compiles sandwich complexes with cyclic π-perimeters other than cyclopentadienyl which have been used for olefin oligomerization. The phospholyl complexes (first two entries) have been included for complete coverage but because of their isolobal nature to the metallocenes have already been mentioned in more detail in Sections 3.3 and 3.6 (propene and 1-hexene oligomerization, respectively).

4.2. Half-sandwich complexes

Half-sandwich complexes have only one cyclic π-perimeter, such as a cyclopentadienyl or a benzene ring bound to the metal center. In particular group-IV metal complexes with the cyclopentadienylsilylamido ligand, $Me_2Si(Cp)(NR)ML_2$ (**21**) are closely related to metallocene catalysts. These complexes are also known as "constrained geometry" or "Dow catalysts" [185]. In combination with MAO or borates the pre-catalysts **21** give rise to long-chain branching in ethene polymerization through the re-insertion of vinyl-terminated short-chain oligomers from β-hydrogen elimination.



M = Ti, Zr, Hf
X = Cl, Me
CpR$_n$ = C_5Me_4, substituted indenyl, fluorenyl
R' = Me, ^{t}Bu, Ph

21

Table 2 compiles half-sandwich complexes with cyclic π-perimeters which have been described for olefin oligomerization.

Tobisch and Ziegler [196] carried out theoretical studies (based on density functional theory, DFT) on the elementary steps of the selective linear ethene oligomerization to 1-hexene by the cationic $(C_5H_4CMe_2Ph)Ti^{IV}Me_2{}^+$ pre-catalyst or the $(C_5H_4CMe_2Ph)Ti^{II}(ethene)_2{}^+$ catalyst which were experimentally described by Hessen et al. [189]. Similarly, a theoretical analysis was presented of the catalytic abilities of the heavier group-IV metals for linear ethene oligomerization with the pre-catalytic complex $(C_5H_4CMe_2Ph)M^{IV}Me_2{}^+$ (M = Zr, Hf) [197]. In a separate study a computational analysis of the influence of modifications of the hemi-labile arene functionality in active species of the type $(C_5H_4CMe_2C_6H_{5-n}R_n)Ti^{II}(ethene)_2{}^+$ (M = Zr, Hf) has been presented [198].

Acknowledgments

Our work in the area of olefin oligomerization with metallocene catalysts was supported by the DFG through grant Ja466/3-1, the Fonds der Chemischen Industrie, the Gesellschaft der Freunde der TU Berlin and the Berlin Graduate college "Synthetic, mechanistic and reaction engineering aspects of metal catalysts". The Polyolefin Division of BASF AG, Ludwigshafen and Witco AG, Bergkamen are thanked for the donation of propene and MAO, respectively.

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