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Alkyl-substituted cyclopentadienyl- and phospholyl-zirconium/MAO catalysts for propene and 1-hexene oligomerization[☆]

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Abstract

The directed oligomerization of propene and 1-hexene was carried out with a series of $Cp'(C_5H_5)ZrCl_2$ and Cp'_2ZrCl_2 pre-catalysts ($Cp' = C_5HMe_4$, C_4Me_4P, C_5Me_5, $C_5H_4{}^tBu$, C_5H_3-1,3-${}^tBu_2$, C_5H_2-1,2,4-${}^tBu_3$) together with $(C_5H_5)_2ZrCl_2$. Oligomers in the molar mass range 300–1500 g/mol for propene and 200–3000 g/mol for 1-hexene were synthesized at 50 °C. The majority of oligomer molecules contain a double-bond end group. Oligomer characterization was carried out by gel permeation chromatography (GPC), ^1H and ^{13}C NMR. Vinylidene double bonds (from β-hydrogen elimination) are solely found for the *tert*-butyl-substituted zirconocenes and for most of the unsymmetrical methyl-substituted $Cp'(C_5H_5)ZrCl_2$ systems (except Cp′ = phospholyl). With $(C_4Me_4P)(C_5H_5)ZrCl_2$ and with the symmetrical methyl-containing Cp'_2ZrCl_2 pre-catalysts, also vinyl end groups (from β-methyl elimination) are observed in the case of oligopropenes. The vinylidene/vinyl ratio depends on the ligand and the vinyl content increases from C_5HMe_4 (65/35) over C_4Me_4P (61/39) to C_5Me_5 (9/91). The phospholyl zirconocenes and $(C_5HMe_4)_2ZrCl_2$ also exhibit chain-transfer to aluminum thereby giving saturated oligomers.

Keywords: Metallocene–methylalumoxane; Oligomerization; Polymerization; SHELL-higher-olefin process

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1. Introduction

Single-site metallocene–methylalumoxane (MAO) catalysts are currently introduced in industry as a new generation of Ziegler–Natta catalysts for the *polymerization* of olefins (for reviews, see [1–13]; for notes concerning the industrial application, see, e.g. [14–16]; for recent examples, see [17–37]). *Oligomerization* of α-olefins are expanded potential applications of metallocene catalysts. Here 11 different achiral, unbridged zirconocene/MAO catalysts (**2–12**) are studied for the oligomerization of propene and 1-hexene. The unsubstituted parent system zirconocene dichloride (**1**) was included as a reference point (see Scheme 1).

Olefin oligomers are used as intermediates for specialty chemicals. This drives the interest in the catalytic oligomerization [38]. The SHELL-higher-olefin process (SHOP) uses nickel chelate complexes in the manufacturing of ethene oligomers ([38], for

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[☆] Dedicated to Prof. Dr. Walter Kaminsky on the occasion of his 60th birthday

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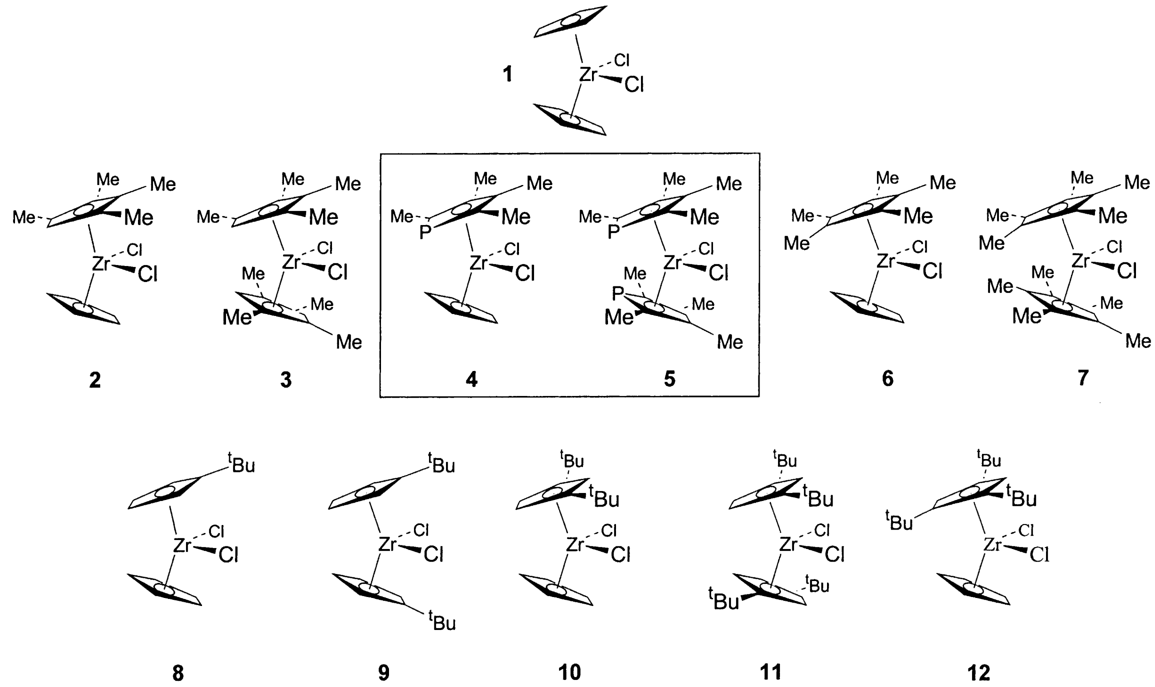
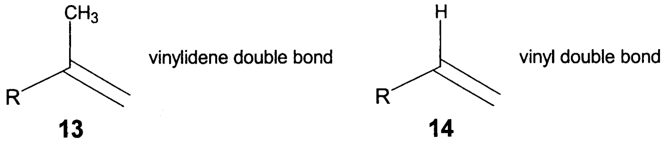


Scheme 1.

recent reports, see [39–49]). Processes for oligomerizations involving well-defined catalysts are rare, however [50]. Propene, 1-butene, 1-pentene and 1-hexene polymerizations are described on zeolites [51–57], mordenite [58,59], silica-supported (Lewis) acids [60–62] or (Lewis) acids alone [63,64].

Low molar mass products from propene polymerizations with zirconocene catalysts were found early on and generally regarded as unfortunate [65–69]. Now, it is more and more recognized that metallocene catalysts can be used effectively for the directed oligomerization of α-olefins [50,70–85]. The C–C bond forming insertion catalysis proceeds with high regioselectivity in the coordination sphere of the zirconium center and the chain-termination reaction gives oligomers with mostly double-bond end groups, predominantly of the vinylidene type (**13**). In special cases also a vinyl double bond (**14**) can be formed (see Scheme 2).

A variety of functionalization reactions with such double bonds are possible leading to organic specialities with possible applications as adhesives, blend compatilizers [86], fragrances, lubricants, additives for fuels or in the paper and leather industry [50]. Also, α-olefin oligomers or derivatives thereof may be used as (macro)monomeric building blocks for novel graft copolymers containing oligo-olefin side chains [73–76]. The functionality of a double bond at the end of each chain together with the product homogeneity are the advantages of oligomers from metallocene



Scheme 2.

catalysis. Furthermore, as in the well-established polymerization reactions, metallocene catalysts should also allow for the possibility to tailor *oligomer properties* such as molar mass and molar mass distribution through a rational ligand design at the transition metal center. In addition, olefin oligomerization is used to study mechanistic aspects of metallocene catalysis for reasons of homogeneity of the reaction mixture and because the oligomeric products are easier to investigate than high molar mass polymers [87–99].

2. Results and discussion

Compounds **1–12** were activated with MAO and reacted with propene or 1-hexene. The oligomerization results for propene and 1-hexene are compiled in Tables 1 and 2, respectively. Figs. 1 and 2 give a graphical representation of the oligomerization activity of **1–7** towards propene and 1-hexene, respectively. To ensure reproducibility in terms of both activity and oligomer parameters, each oligomerization was carried out at least twice.

The trends in the activities along the catalyst series for propene or 1-hexene can be explained by a combination of the steric hindrance of the ligand substituents and by the tendency of prochiral α-olefin monomers to show higher activities in more directing or stereospecific environments. An increase in steric bulk at the ligand affects the reaction path of the incoming monomer or the outgrowing chain and will normally decrease the insertion rate [100,101]. Such is evident when comparing the activities of the unsubstituted zirconocene dichloride, **1**, with the decamethyl or tetra-*tert*-butyl zirconocenes, **7** or **11**, for propene or 1-hexene oligomerization. At the same time, a more stereospecific environment can help in the pre-orientation of chain end and

Table 1
Results for propene oligomerization with **1**–**12**/MAO

Pre-catalyst[a]	Activity (kg oligomer/(mol Zr h))	Conversion (%)	M_n (g/mol)		Dispersity, $Q = M_w/M_n$[b]	Vinylidene/vinyl end-group ratio (%)
			^{1}H NMR[c]	GPC[d]		
Methyl-substituted zirconocenes						
1	960	51	330	350	1.5	100/0
2	1300	66	620	530	2.5	100/0
3	1300	63	1600	1500	2.9	65/35
4[e]	10	4	640	380	1.5	79/21
5[e]	10	4	1200	300	2.0	61/39
6	870	46	1300	1300	2.4	100/0
7	600	28	190	320	1.3	9/91
tert-Butyl-substituted zirconocenes						
1	410[f]	43	350	470	1.3	100/0
8	400	42	290	400	1.2	100/0
9	400	42	410	510	1.3	100/0
10	670	70	680	960	1.7	100/0
11	1	4	580	560	1.9	100/0
12	84	9	1100	1300	2.3	100/0

[a] Al:Zr = 1000:1, $T = 50\,^\circ$C, reaction time = 1 h, pre-activation time = 10 min—methyl-substituted zirconocenes: **1**–**3**, **6**, **7**: a pre-catalyst amount of 1.5×10^{-5} mol yielding a concentration of 7.1×10^{-5} mol/l together with a reaction time of 1 h was employed so that the conversion did not exceed 70% of the monomer. Only in the case of the very low-active phospholyl systems **4** and **5** twice the amount of catalyst and a reaction time of 4 h was employed; cf. footnote e. *tert*-Butyl-substituted zirconocenes: **1**, **8**–**12**: a pre-catalyst amount of 3×10^{-5} mol yielding a concentration of 1.4×10^{-4} mol/l and a reaction time of 1 h were employed; the conversion did not exceed 70%.

[b] From GPC.

[c] Molar mass based on the integral ratio of the vinylidene and vinyl protons relative to the alkyl protons.

[d] Gel permeation chromatography, see Section 4 for details.

[e] Because of the low activity of this catalyst system, a zirconocene concentration of 1.4×10^{-4} mol/l and a reaction time of 4 h was used here.

[f] The change in polymerization activity for **1** is due to the change in catalyst concentration; see footnote a.

Table 2
Results for 1-hexene oligomerization with **1–12**/MAO

Pre-catalyst[a]	Activity (kg oligomer/(mol Zr h))	Conversion (%)	M_n (g/mol)		Dispersity, $Q = M_w/M_n$[b]
			^{1}H NMR[c]	GPC[d]	
Methyl-substituted zirconocenes					
1	5000	44	410	300	1.8
2	6300	55	1200	1100	1.9
3	5500	49	7000	1500	2.3
4	120	1	2700	500	1.2
5	70	1	5600	500	1.3
6	3300	29	3800	3300	2.6
7	2900	24	1600	1400	2.0
tert-Butyl-substituted zirconocenes					
1[e]	5900	52	510	530	1.7
8	7900	70	480	540	1.5
9	1700	13	330	390	1.4
10	2700	24	1200	970	2.0
11	260	2	200	240	1.1
12	310	3	240	270	1.2

[a] A pre-catalyst amount of 3×10^{-6} mol yielding a concentration of 5.2×10^{-5} mol/l together with a reaction time of 1 h was employed so that the conversion did not exceed 70% of the monomer—Al:Zr = 4000:1, $T = 50\,^\circ$C, reaction time = 1 h, no pre-activation time.

[b] From GPC.

[c] Molar mass based on the integral ratio of the vinylidene and vinyl protons relative to the alkyl protons.

[d] Gel permeation chromatography, see Section 4 for details.

[e] The slight change in polymerization activity for **1** is due to aging of MAO in the course of time.

prochiral monomer [100], thereby avoiding a decelerating steric repulsion between the growing chain and the alkyl group of the monomer. This leads to higher oligomer yields with the tetramethylcyclopentadienyl zirconocenes **2** and **3** for both propene and 1-hexene compared to the unsubstituted zirconocene **1**.

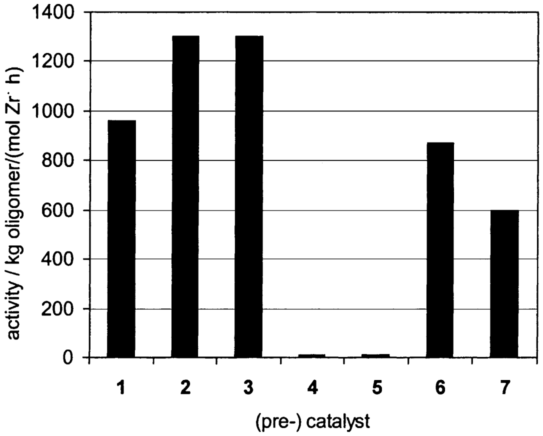


Fig. 1. Oligomerization activity of **1–7**/MAO with propene.

Among the *tert*-butyl-substituted series, the mixed 1,3-di-*tert*-butyl-cyclopentadienyl zirconocene **10** or the mono-*tert*-butyl-cyclopentadienyl zirconocene **8** give higher yields than the parent compound **1**.

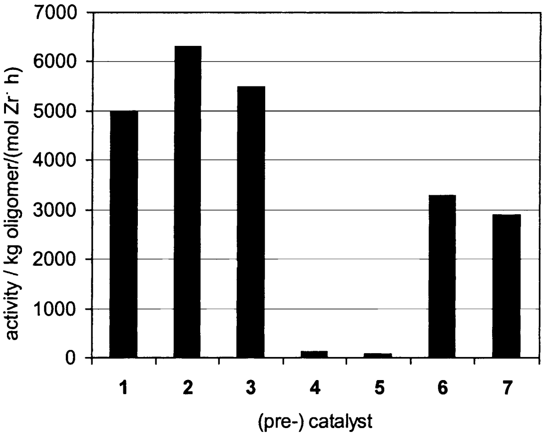


Fig. 2. Oligomerization activity of **1–7**/MAO towards 1-hexene. The apparent higher activity compared to Fig. 1 is mainly due to the higher monomer concentration of 1-hexene and the lower molar amount of catalyst (see text).

Despite the difficulty to compare data from different sources, it is evident that the oligomerization rate with non-*ansa*-metallocenes **1**–**12** is in general much slower than the polymerization rate with *ansa*-metallocenes (see, e.g. Refs. [102,103] for propene and Ref. [104] for 1-hexene). Generally, the reason for obtaining oligomeric or low molar mass polymeric products from insertion reactions with the non-*ansa*-metallocenes **1**–**12** must be due to an increased rate of chain-transfer/termination (k_T) and/or a decreased rate of chain propagation (k_P). The mean degree of polymerization, P_n, which is proportional to the number of average molar mass M_n is given by the ratio of the growth rate to the rate of transfer, $M_n \sim P_n \approx k_P/k_T$.

The low oligomerization rate may be due to olefin coordination equilibria with reorientation before the actual insertion. It could further be associated with the more frequent chain-transfer reactions such that the $Cp_2Zr–H^+$ species obtained from β-hydride elimination (see below) is less active because of the higher bond strength of Zr–H versus Zr–C [105]. Based on the end-group analysis (see below), we can, however, rule out that an increase in regioirregular 2–1 additions are the source of the rate decrease. A 2–1 insertion represents a steric hindrance to further chain growth, leaves the active site in a deactivated state for further olefin insertion and often leads to β-hydride elimination to give vinyl and 2-butenyl end groups [106–110]. When the vinyl end group is found in our products, their ^{13}C NMR intensity correlates with isopropyl or $Zr–CH_3$ start groups due to β-methyl elimination.

A rough comparison of the activities of the catalysts **1**–**12** for the different monomers requires at least a normalization of the polymer yield with respect to monomer and metallocene concentration. The result of such a normalization is given in Table 3, thereby also including data from an earlier ethene polymeri-

Table 3
Normalized activities for ethene polymerization and propene, hexene oligomerization with **1**–**12**/MAO

Pre-catalyst[a]	Activities normalized to zirconocene and monomer concentration (kg product/[(mol/l Zr) h (mol/l monomer)])		
	Ethene[b]	Propene[c]	1-Hexene[d]
Methyl-substituted zirconocenes			
1	270.0×10^3	160	55
2	160.0×10^3	250	72
3	58.0×10^3	220	61
4	92.0×10^3	1.2	1.0
5	5.0×10^3	1.2	0.6
6	130.0×10^3	140	32
7	12.0×10^3	88	28
tert-Butyl-substituted zirconocenes			
8	97.0×10^3	62	100
9	5.4×10^3	66	13
10	9.5×10^3	130	25
11	–	0.1	2.2
12	2.5×10^3	11	2.6

[a] For the catalyst concentration and reaction conditions, see footnote a in Table 1 for propene and Table 2 for 1-hexene.

[b] Data taken from column B of Table 3 in Ref. [112]. The ethene polymerization activity was given there in kg PE/(g Zr h bar). For the normalization to zirconocene concentration, the activity data were multiplied by $M(\mathrm{Zr})\cdot \mathrm{mol(Zr)}/c(\mathrm{Zr}) = (91.22\ \mathrm{g/mol})\cdot$ solution volume $= (91.22\ \mathrm{g/mol})(0.3\ \mathrm{l})$; for normalizing to monomer concentration, the data had to be multiplied by the ethene pressure of 5 bar and then divided by the ethene concentration of 0.39 mol/l at the polymerization conditions of a constant ethene pressure of 5 bar and 70 °C.

[c] Factors for normalizing the activity values from Table 1 to zirconocene concentration: multiplication by $\mathrm{mol(Zr)}/c(\mathrm{Zr}) =$ solution volume $= 0.21\ \mathrm{l}$; for normalizing to propene concentration: division by average monomer concentration, $c_{av} = c_0(C_3H_6)(1 - 0.5\ \mathrm{conversion}/100\%)$; $c_0(C_3H_6) = 1.75\ \mathrm{mol/l}$ (5 bar at 50 °C).

[d] Factors for normalizing the activity values from Table 2 to zirconocene concentration: multiplication by $\mathrm{mol(Zr)}/c(\mathrm{Zr}) =$ solution volume $= 0.058\ \mathrm{l}$; for normalizing to 1-hexene concentration: division by average monomer concentration, $c_{av} = c_0(C_6H_{12})(1 - 0.5\ \mathrm{conversion}/100\%)$; $c_0(C_6H_{12}) = 6.9\ \mathrm{mol/l}$.

zation study with **1**–**12** [111,112]. Normalization for propene and 1-hexene was carried out by taking into account the decrease of monomer concentration for propene and hexene during the oligomerization process as there was no constant feed of monomer in these two cases. A linear decrease in monomer concentration was assumed during the reaction time and an average monomer concentration was calculated based on the conversion. Subtraction of *half* of the fraction of reacted monomer from the starting concentration (c_0) was taken as the average monomer concentration (c_{av}). The fraction of reacted monomer corresponds to the conversion number. Thus, $c_{av} = c_0(1 - 0.5\text{conversion}/100\%)$. The starting monomer concentrations were $c_0 = 1.75\,\text{mol/l}$ for propene (50 °C, 5 bar) and $c_0 = 6.9\,\text{mol/l}$ for 1-hexene (50 °C, ambient pressure). For ethene, the monomer concentration remained constant at 0.39 mol/l (70 °C, 5 bar). For propene and ethene, the initial monomer concentrations were based on the solubility coefficients, Λ, of these gases in toluene at the given temperature $\{\Lambda_{\text{ethene}} \approx 9 \times 10^{-2}\,\text{mol/(kg bar)}$; $\Lambda_{\text{propene}} \approx 4.1 \times 10^{-1}\,\text{mol/(kg bar)}$ and a toluene solvent density of $0.865\,\text{kg/l}\}$ [113].

A comparison of the normalized activity data in Table 3 reveals a general decrease in activity when going from ethene over propene to 1-hexene as the monomer. The non-*ansa*-metallocene catalysts **1**–**12** show a strong preference for ethene which is polymerized about 1000 times faster than other α-olefins [114]. Stereospecific *ansa*-systems polymerize propene at rates of only four to five times slower than ethene [115]. With **1**–**12**, the higher α-olefin 1-hexene is oligomerized only at moderately lower rates than those for propene. This behavior has also been observed for *ansa*-metallocenes [66,116]. For complexes **1**–**7**, this comparison is valid because of the very similar catalyst concentrations employed with both monomers (7.1×10^{-5} mol/l versus 5.2×10^{-5} mol/l). For catalysts **8**–**12**, the direct comparison between propene and hexene, especially the higher activity of **8** towards 1-hexene has to be viewed with caution, since here the catalyst concentration for propene was more than twice that for hexene (1.4×10^{-4} mol/l versus 5.2×10^{-5} mol/l).

Furthermore, there is a pronounced drop in activity for the phospholyl systems **4** and **5** towards propene or 1-hexene as monomers. The activity towards α-olefins is one to two magnitudes smaller than those of the comparative methylcyclopentadienyl zirconocenes. Yet, the activity of **4** and **5** towards ethene polymerization is only somewhat lowered relative to what is expected for the steric environment of the ligands [112]. This behavior is explained in comparison to *ansa*-zirconocene complexes with C_5-ring substituents close to the meridional centroid–Zr–centroid plane. Such zirconocene complexes are propene-inactive due to a steric interaction of the substituent with the alkyl group of the olefin, but are still rather active in the polymerization of the sterically less demanding ethene (Fig. 3) [1–13,117]. The sterically demanding ring substituents in the case of the phospholyl complexes probably arise from the aluminum coordination to the phosphorus atoms (Fig. 4). An indication of formation of these P–Al adducts in an equilibrium reaction was provided by ^{31}P NMR [112,118]. The same situation is encountered in the tetra-*tert*-butyl complex **11** which is so sterically demanding that it becomes the least active complex.

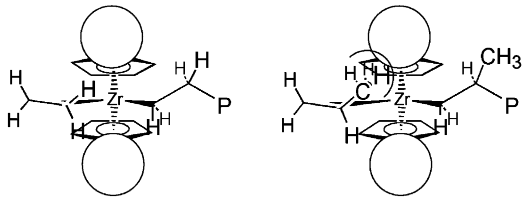


Fig. 3. Schematic drawing of a zirconocene complex with a large substituent on the C_5-ring close to the meridional centroid–Zr–centroid plane. This substituent blocks the insertion of propene but not of ethene. In the case of the phospholyl systems **4** and **5**, the bulky substituent can be an aluminum moiety coordinating to a ring phosphorus atom. In the case of the low-active complex **11**, it can be a *tert*-butyl group.

2.1. Effect of catalyst concentration

In Table 1, a different catalyst concentration was used for the methyl- and *tert*-butyl-substituted zirconocene series to compromise oligomer yield and conversion for the respective series. For the $(C_5H_5)_2ZrCl_2$ (**1**) reference point, an increase in the zirconocene concentration from 7.1×10^{-5} to 1.4×10^{-4} mol/l resulted in a drop in activity. Normalization to zirconocene concentration instead of moles zirconocene does not change this effect. The data in Table 4

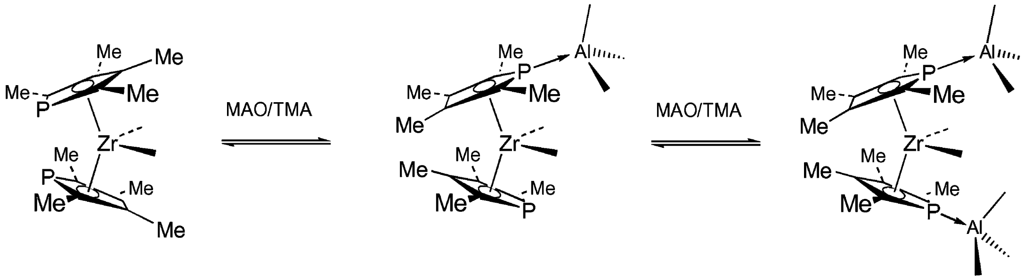


Fig. 4. Schematic representation of the adduct formation between the phosphorus donor atoms in **4** and **5** and an aluminum atom from an MAO oligomer or TMA. Such an adduct formation would change the steric situation around the zirconium reaction center drastically. In the solid-state structure of $(C_4Me_4P)_2ZrCl_2$, the phospholyl rings adopt a conformation which corresponds to the complex on the left. The phosphorus atoms are oriented towards each other, probably to minimize steric interactions [128].

illustrate the effects of catalyst concentration on the activity and the molar mass of the oligomers. Other variables, such as Al:Zr ratio, monomer concentration or temperature were left unchanged.

One observes both an increase in activity as well as an increase of molar mass of the oligomer upon a decrease in zirconocene concentration. Two possible explanations for these effects which were also observed elsewhere [67,111,112,114,119] are discussed. (a) A dilution effect favoring the active complex form over the inactive precursor or dormant species. Hence, the rate of chain propagation increases and the rate of chain-termination decreases. It is thereby assumed that chain terminations arise predominantly from “dormant”, i.e. temporarily inactive, zirconocene centers [1–13]. (b) A bimolecular chain-transfer mechanism involving the active complex and a second (active or inactive) zirconocene species [67,120]. A decrease in zirconocene concentration would then reduce the rate of the termination reaction.

2.2. Effect of activation time

Within the *tert*-butyl-substituted zirconocene series, the more sterically demanding complexes **11** and **12** showed rather low oligomerization activities.

Table 4
Influence of zirconocene concentration on the activity and oligomer data in propene oligomerization

Pre-catalyst[a]	Zirconocene concentration (mol/l)	Activity[b]	Conversion (%)	M_n (g/mol)	
				^{1}H NMR[c]	GPC[d]
1	1.4×10^{-4}	550	54	290	330
	7.1×10^{-5}	960	51	330	350
2	1.4×10^{-4}	840	88	530	470
	7.1×10^{-5}	1300	66	620	530
3	1.4×10^{-4}	820	91	920	600
	7.1×10^{-5}	1300	63	1600	1500
6	1.4×10^{-4}	860	86	1100	970
	7.1×10^{-5}	870	46	1310	1300
7	1.4×10^{-4}	350	37	190	190
	7.1×10^{-5}	600	28	190	320

[a] Al:Zr = 1000:1, $T = 50\,^{\circ}$C, reaction time = 1 h, pre-activation time = 10 min.

[b] In kg oligopropene/(mol/(l Zr h)).

[c] Based on the integral ratio of the vinylidene and vinyl protons relative to the alkyl protons.

[d] Gel permeation chromatography, see Section 4 for details.

Table 5
Influence of activation times on the propene oligomerization activity of zirconocene/MAO systems

Pre-catalyst[a]	Activity[b] after activation time[c] (molar mass in g/mol by ^{1}H NMR)	
	10 min	1 h
1	410 (350)	670 (400)
8	400 (290)	410 (330)
9	400 (410)	570 (350)
10	670 (680)	860 (850)

[a] Al:Zr = 1000:1, c(Zr) $= 1.4 \times 10^{-4}$ mol/l, $T = 50\,^\circ$C, reaction time = 1 h.

[b] Activity in kg oligopropene/(mol Zr h).

[c] Conditions of activation: the reactants were dissolved in 200 ml of toluene, previously thermostated to 50 °C, after the set pre-activation time the reactor was pressurized with 5 bar of propene.

Since it might have been possible that the more bulky complexes were activated more slowly, we carried out a brief investigation on the influence of activation or aging times, i.e. the time the zirconocene dichloride and MAO were allowed to react before pressurizing with propene. The results are summarized in Table 5. Normally, the activation time was 10 min. Extending this time to 1 h leads to slight increases in activity. Concomitant with the slight increase in activity, one observes again a slight increase in molar mass of the oligomer (see above). An increase of activity with aging (5–60 min) has been reported for $(C_5H_5)_2ZrCl_2$/MAO + TMA (trimethylaluminum) in ethene polymerization, yet a decrease was seen with $(C_5H_5)_2ZrCl_2$/MAO in the polymerization of propene [121,122]. For $(C_5Me_5)_2ZrCl_2$/MAO and ethene, it was found that the maximum of the polymerization rate shifted towards shorter activation times [67].

2.3. Effect of reaction time

Table 6 summarizes activity data for **1**–**12** in 1-hexene oligomerization with different reaction times. The activity can be expected to drop with increasing time due to deactivation processes and a decrease in monomer concentration. At the same time, the yield increases and almost quantitative conversion can be reached with the C_5Me_5–zirconium compounds **6** and **7** after 24 h. It is evident that the methyl-substituted zirconocenes form long-lived catalysts. The conversion increases from 1 h over 6–24 h. Some of the *tert*-butyl-substituted zirconocenes appear to be short-lived. For **8**, the conversion does not increase anymore after 1 h. With **10** and **11**, there is only a very minor increase when going from 3 to 24 h reaction time. With respect to a preliminary account on the oligomerization with the *tert*-butyl systems [70], the activity of these catalysts can be increased by lowering the reaction time.

Table 6
Influence of reaction time on the 1-hexene oligomerization activity with **1**–**12**/MAO

Pre-catalyst[a]	Reaction time for activity[b] (conversion, %)		
	1 h	6 h/3 h[c]	24 h
Methyl-substituted zirconocenes			
1	5000 (44)	1000 (53)	420 (89)
2	6300 (55)	1500 (77)	420 (88)
3	5500 (49)	1400 (73)	410 (88)
4	120 (1)	–	66 (14)
5	67 (1)	–	53 (11)
6	3300 (29)	1600 (86)	450 (96)
7	2900 (24)	1200 (66)	480 (98)
tert-Butyl-substituted zirconocenes			
1	5900 (52)	3100 (82)	–
8	7900 (70)	2700 (70)	330 (71)
9	1500 (13)	470 (13)	70 (29)
10	2700 (24)	1700 (45)	230 (49)
11	260 (2)	26 (1)	10 (2)
12	310 (3)	100 (3)	20 (7)

[a] Al:Zr = 4000:1, c(Zr) $= 5.2 \times 10^{-5}$ mol/l, $T = 50\,^\circ$C.

[b] Activity in kg oligohexene/(mol Zr h).

[c] Reaction time = 6 h for **1**–**7**, reaction time = 3 h for **8**–**12**.

An increase in reaction time leads to a slight decrease in the number-average molar mass (not listed). This change is understandable since the monomer concentration and with it the insertion rate drops so that chain-transfer occurs more frequently. From NMR studies of the oligohexene product, we found no evidence for a re-insertion of the vinylidene-terminated hexene oligomers.

2.4. Effect of temperature

Table 7 compiles the activity and oligomer data for the 1-hexene oligomerization at two different temperatures. A comparison of oligomerization activity is not very meaningful because of a chosen reaction

Table 7
Influence of temperature in the 1-hexene oligomerization with **1**, **8**–**12**/MAO

Pre-catalyst[a]	$T = 25\,^{\circ}C$			$T = 50\,^{\circ}C$		
	Activity[b] (conversion, %)	M_n[c] (g/mol)	Q[d]	Activity[b] (conversion, %)	M_n[c] (g/mol)	Q[d]
1	230 (49)	510/660	2.6	310 (67)	230/360	1.3
8	380 (81)	430/600	1.6	330 (71)	270/370	1.2
9	52 (11)	490/620	1.4	70 (29)	310/410	1.2
10	210 (46)	1700/1700	2.3	230 (49)	670/740	1.6
11	29 (6)	210/n.d.	n.d.	10 (2)	190/n.d.	n.d.
12	13 (3)	380/n.d.	n.d.	20 (7)	440/670	2.0

[a] Reaction conditions: Al:Zr = 4000:1, $c(\mathrm{Zr}) = 5.2 \times 10^{-5}$ mol/l, reaction time = 24 h.
[b] Activity in kg oligohexene/(mol Zr h).
[c] Number-average molar mass from ^{1}H NMR/GPC; n.d., not determined.
[d] Dispersion, $Q = M_w/M_n$.

time of 24 h (see above). It is more feasible to compare the conversion here. Only for catalysts **9** and **12**/MAO, the conversion increase with temperature. The conversion drops slightly for complexes **8** and **11** when going from a reaction temperature of 25 to 50 °C. For compound **10**, it stays invariant. Also, with compounds **8**, **10** and **11**, the maximum conversion was reached after a relatively short reaction time (see above). This supports the notion that **8**, **10** and **11** in combination with MAO may be thermally instable and more prone to decomposition/deactivation than the other *tert*-butyl zirconocenes. As expected, the number-average molar mass of the hexene oligomers and their dispersion decrease considerably with increasing temperature [67,114,123]. The zirconocene **12** with the $C_5H_2{}^tBu_3$-ring is a notable exception.

2.5. Oligomer characteristics

2.5.1. Molar mass

Molar mass values were included in Tables 1 and 2. The average molar mass can be tailored through the steric ligand demand. There is, however, no immediately obvious correlation. Fig. 5 gives a graphical display of the number-average molar mass values of oligopropenes and oligohexenes obtained with catalysts **1**–**7**. The display includes both M_n values from ^{1}H NMR spectroscopy and GPC. It can be seen that usually the agreement between molar mass values from different methods is reasonable. Major exceptions are the propene and 1-hexene oligomers produced with the phospholyl zirconocenes **4** and **5** and in addition the oligohexene from octamethylzirconocene **3**. In these cases, M_n from ^{1}H NMR is much too high compared with the value from GPC. For the oligopropenes from **4** and **5**, a ^{13}C NMR investigation suggests that a certain fraction of the oligomers

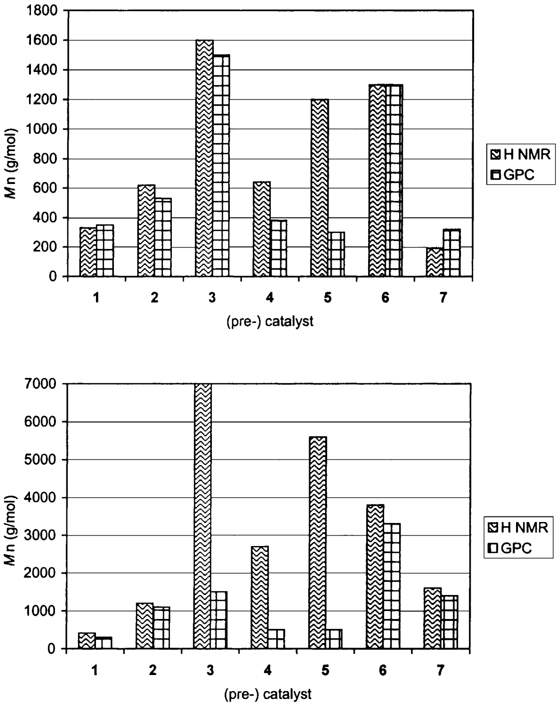
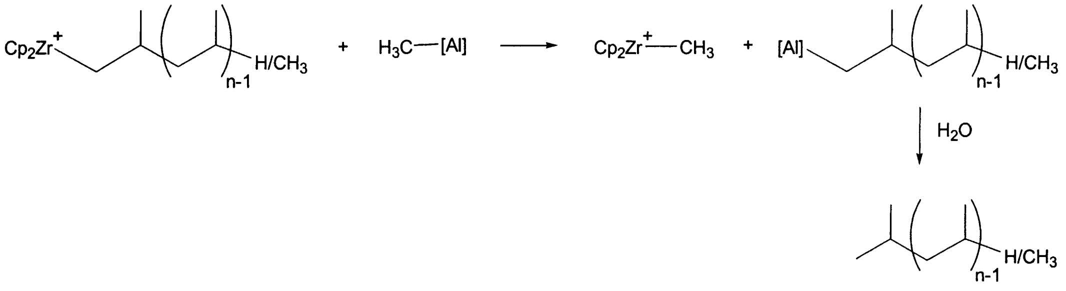


Fig. 5. Number-average molar mass values (M_n) by ^{1}H NMR and GPC for oligopropenes (top) and oligohexenes (bottom) with catalysts **1**–**7**/MAO. Entries from Tables 1 and 2.



Scheme 3.

carries no double bond. Instead, the signals for isopropyl start/end groups are very dominant. Estimation of M_n by ^{1}H NMR is based on the relative ratio of the olefinic to the aliphatic protons. Thus, less than 100% double-bond end groups will give too large a value for M_n. The saturated isopropyl groups can arise both from Zr–CH_3 start species and from transfer of the oligomer chain to aluminum and hydrolyzation upon quenching of the mixture (see Scheme 3, cf. Fig. 8). Chain-transfer to aluminum creates a new Zr–CH_3 start species due to the exchange of the alkyl chain with a methyl group on aluminum in MAO or TMA. A chain-transfer to aluminum is suggested for **4** and **5** because adduct formation to phosphorus (cf. Fig. 4) brings aluminum moieties close to the zirconium reaction center and the oligomer chain end.

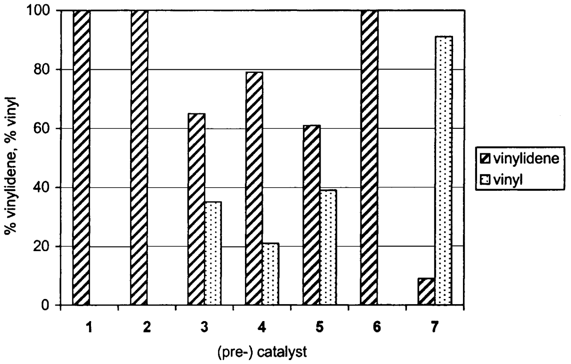
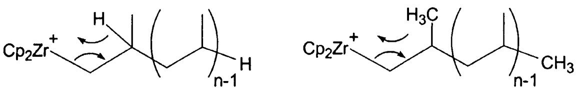


Fig. 6. The vinylidene/vinyl ratio for the double-bonded end groups of oligopropenes with catalysts **1**–**7**/MAO (entries from Table 1).

2.5.2. End groups

The majority of end groups contain a double bond. Only with the phospholyl zirconocenes **4** and **5** for both oligo-olefins and with **3** for oligohexene were saturated end groups observed to a significant extent (see above). The usual double bond is of the vinylidene type (**13**) and originates from a β-hydrogen elimination as the typical chain-termination reaction (**15**) (cf. Fig. 8). For *oligopropenes* and per-methylated zirconocenes also double bonds of the vinyl type (**14**) are observed. These are derived from a β-methyl elimination as chain-termination reaction (**16**). Vinyl double bonds are observed for the octamethylzirconocene (**3**), the mono-phospholyl and the bis-phospholyl zirconocene (**4** and **5**) and for decamethylzirconocene (**7**). The vinylidine/vinyl ratio was included in Table 1 and is graphically depicted in Fig. 6 (see Scheme 4).

The cause of the methyl instead of the hydrogen elimination is seen in enhanced steric interactions for the transition state of the latter [96]. The transition state for a β-methyl elimination is more easily accessible. With the sterically demanding *tert*-butyl-substituted zirconocenes, it was hoped for that β-methyl eliminations could also be initiated. This was not the case, however. The NMR spectra of the oligomer products from **8–12** did not show any evidence for the formation of vinyl double bonds (cf. Table 1). Apparently, the steric bulk of up to four *tert*-butyl groups in a zirconocene is not high enough. Also, in the case of oligohexenes, only vinylidene double bonds are found, based on ^{1}H and ^{13}C NMR studies. For oligohexenes, double bonds of the vinyl



15 **16**

Scheme 4.

type would have required an *n*-butyl elimination and are not observed.

2.5.3. Dispersity, molar mass distribution

The dispersity of many oligomers is rather narrow. Values of Q ($=M_w/M_n$) below 2 can be found in Tables 1 and 2. We showed earlier that narrow dispersities can be reproduced with a model which takes into account chain propagation and chain-transfer by β-hydrogen elimination and which is based on the decrease in the propagation rate over the first five insertions [70]. Values of Q around 1.3 were calculated for about 10-fold rate of the first versus the sixth insertion and an exponential drop-off in between. At the same time, the chain-transfer rate was about equal to the propagation rate. The same model also illustrated the effect of the chain-transfer rate on the molar mass.

At first, dispersities smaller than 2 seem to contradict a Schulz–Flory (or most probable) distribution. The key to an understanding for the narrow dispersity lies in a prerequisite to the Schulz–Flory distribution, namely a propagation rate independent of the chain length. Such a prerequisite is not fulfilled during the approximately first five insertion steps. This was demonstrated by Fink and Schnell [124–126] in ethylene oligomerizations with the soluble catalyst system $(C_5H_5)_2TiRCl/AlEt_2Cl$. Thus, one will have a decrease in the rate during the first insertions. For low molar mass oligomers, such a rate decrease during the first five insertions has a pronounced effect.

3. Summary

Olefin oligomers based on propene and 1-hexene were synthesized from metallocene/MAO catalysts. The catalyst behavior was analyzed in terms of activity, concentration, activation and reaction time, and temperature. With α-olefins such as propene or 1-hexene, a certain steric demand at the metal center leads to a higher catalytic activity before the activity decreases with increasing steric congestion. The activity increases with smaller catalyst concentration and with higher activation time. An increase in reaction time enhances the conversion. The effect of temperature depends on the catalyst. The oligomers were investigated with respect to molar mass, end group and molar mass distribution (dispersity). The main chain-transfer reaction is β-hydrogen elimination which gives olefin oligomers terminated by a vinylidene double bond. With per-methylated zirconocenes also β-methyl elimination is possible to give oligomers with a vinyl double bond. With phospholyl zirconocenes and with octamethylzirconocene, chain-transfer to aluminum is observed. The mechanism of chain-termination was elucidated by a combination of methods such as ^1H and ^{13}C NMR and GPC. The oligomers obtained at 50 °C had a molar mass range 300–1500 g/mol for propene and 200–3000 g/mol for 1-hexene. Towards the low mass range, the molar mass distribution Q can be quite narrow.

4. Experimental

4.1. General procedures

All experiments which involved air- and moisture-sensitive reagents were carried out under argon with standard Schlenk techniques. Solvents were dried over sodium metal (toluene and benzene), sodium benzophenone ketyl (pentane and diethyl ether) or potassium metal (hexane and THF) followed by distillation and storage under argon.

4.2. Materials

The known zirconocene dichlorides were prepared according to literature procedures, or slight modifications thereof: $(C_5HMe_4)(C_5H_5)ZrCl_2$ (**2**) [111], $(C_5HMe_4)_2ZrCl_2$ (**3**) [111,127], $(C_4Me_4P)(C_5H_5)ZrCl_2$ (**4**) [111], $(C_4Me_4P)_2ZrCl_2$ (**5**) [111,128], $(C_5Me_5)(C_5H_5)ZrCl_2$ (**6**) [111,129], $(C_5Me_5)_2ZrCl_2$ (**7**) [111,130], $(C_5H_4{}^tBu)(C_5H_5)ZrCl_2$ (**8**) [131], $(C_5H_4{}^tBu)_2ZrCl_2$ (**9**) [132], $(C_5H_3\text{-}1,3\text{-}{}^tBu_2)(C_5H_5)ZrCl_2$ (**10**) [112], $(C_5H_2\text{-}1,2,4\text{-}{}^tBu_3)(C_5H_5)ZrCl_2$ (**11**) [133] and $(C_5H_3\text{-}1,3\text{-}{}^tBu_2)_2ZrCl_2$ (**12**) [134]. All complexes were purified by sublimation and the purity was checked by elemental analysis, NMR and mass spectrometry [111,112]. The analytical data matched the literature values. $(C_5H_5)_2ZrCl_2$ was purchased from Merck and used as such. MAO was obtained from Witco (Bergkamen, Germany) as a 10 wt.% toluene solution (4.92 wt.% aluminum, density ≈ 0.9 g/ml, average molecular weight of the MAO oligomers 900–1100 g/mol). Propene (BASF

AG) was polymerization grade and 1-hexene (97%) was obtained from Aldrich and both monomers were used without further purification.

4.3. Oligomerizations

For the comparative oligomerization runs, we tried not to have the conversion exceed 50% so as to avoid drastic insertion rate changes when the monomer concentration becomes too low. The choice of catalyst concentration and reaction time which determines the conversion was a compromise between the low- and high-active catalysts of a series and the necessity to have the same reaction conditions for the catalyst series. A direct comparison of activity is only possible when the same reaction conditions were employed. In addition, an oligomer yield of at least 1 g was aimed at for the low-active catalysts in order to minimize losses from the work-up procedure and to have enough material for the oligomer analyses. Usually, oligomer yields ranged from 8 to 20 g of material. Propene oligomerizations were carried out in a 1 l Büchi-glass autoclave, thermostated to 50 °C and charged with 200 ml of toluene, 8.1 l gaseous propene, and the catalyst solution consisting of 19 ml of MAO and 1.5×10^{-5} or 3×10^{-5} mol of the zirconocene dichloride (see footnotes in tables for details; molar ratio Al:Zr = 1000:1, activation time 10 min). After an reaction time of 1 h, the propene was vented off.

1-Hexene oligomerizations were carried out in a 100 ml Schlenk-flask, thermostated to 50 °C and charged with 50 ml of 1-hexene and the catalyst solution consisting of 8 ml of MAO and 3×10^{-6} mol of the zirconocene dichloride (molar ratio Al:Zr = 4000:1, activation time 1 h) for an reaction time of 1 h, unless mentioned otherwise.

In both cases, the reaction was stopped and the catalyst deactivated by addition of methanol and slightly acidified water. The organic phase was separated and the toluene removed in vacuum (~1 Torr) at 40 °C to leave the oligomer.

To ensure reproducibility, oligomerizations were carried out at least twice with each zirconium complex, thereby also including the full range of oligomer analyses. A series of polymerization runs was performed by using the same toluene and MAO batch. To avoid aging effects of MAO [135], a series a comparative polymerizations was run within a week.

4.4. Oligomer analyses

^{1}H and ^{13}C NMR were obtained on a Bruker ARX 200 or ARX 400 in $CDCl_3$ (^{1}H and ^{13}C chemical shifts are referenced to TMS via the solvent signal).

4.4.1. ^{1}H NMR spectroscopy

Assuming that each oligomer possesses a double-bond end group, the ratio of olefinic protons to total 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 [136]. Furthermore, the relative content of different types of double bonds (if present) can be determined. The protons of the vinylidene double bond (**13**) appear as broad singlets at 4.67 and 4.75 ppm. The vinyl group (**14**) protons feature two overlapping doublets at 4.95–5.05 ppm and a multiplet (ddt) at 5.70–5.92 ppm (Fig. 7) [99,137].

4.4.2. ^{13}C NMR spectroscopy

From this method, information about the oligomer start and end groups can be obtained. The major start

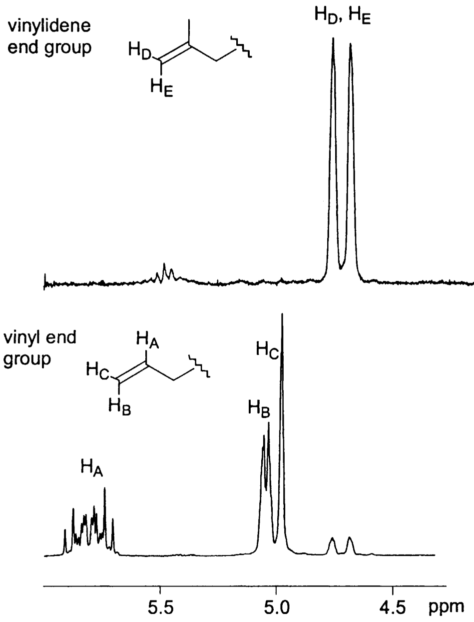


Fig. 7. Proton NMR spectra of the olefinic end group of a vinylidene-terminated (top) and vinyl-terminated (bottom) oligopropene (200 MHz, $CDCl_3$). The vinyl-terminated oligopropene was obtained with catalyst **7**/MAO (cf. Table 1).

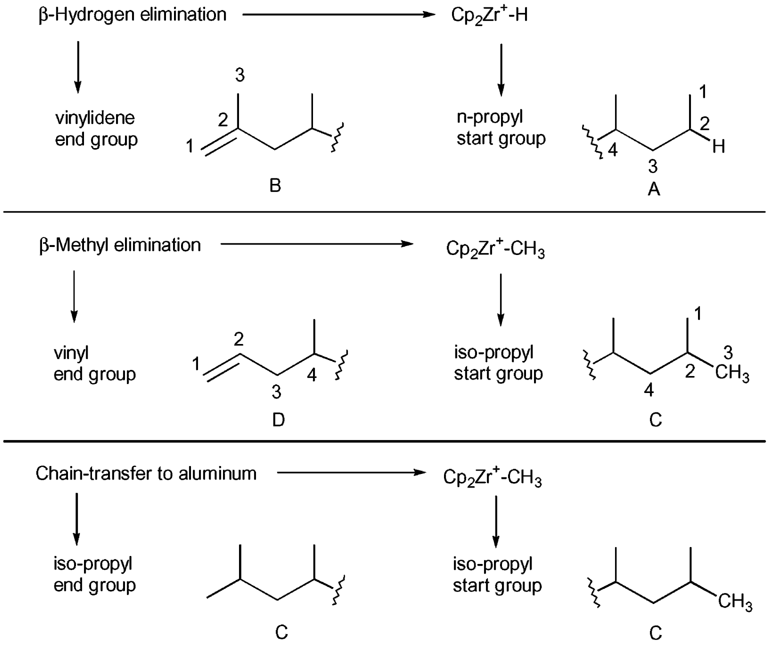


Fig. 8. Start/end groups of oligopropenes with their originating chain-termination reaction or start species. The ^{13}C NMR chemical shifts are tabulated in Table 8.

and end groups are sketched in Fig. 8 together with their originating reaction. The carbon chemical shifts of these groups are tabulated in Table 8 [96]. The start group and in part also the end group exhibit a characteristic pattern in the aliphatic region of the carbon NMR spectrum as shown in Fig. 9.

There is usually a correlated intensity between spectra of different oligomers in the signals of the vinylidene end group (B) and the corresponding *n*-propyl start group (A). The same can be observed for the peaks of the vinyl end group (D) and the corresponding isopropyl start group (C). The olefinic region of the ^{13}C NMR spectrum is also shown in Fig. 9.

Table 8
^{13}C NMR chemical shifts (in ppm) of start and end groups of propene oligomers/polymers[a]

	Group			
	A	B	C	D
C-atom 1	14.5	111.4	22.2–23.7	115.5
C-atom 2	20.6	144.8	25.2	137.7
C-atom 3	39.4–41.4	22.5	22.2–23.7	42.2–43.6
C-atom 4	29.7		47.1–47.9	30.0–31.1

[a] See Fig. 8 for the assignment. Compare also to the data given in Ref. [96].

4.4.3. Gel permeation chromatography

GPC was carried out either on a Waters 150-C equipped with μ-styragel columns (5×10^2–1×10^6 Å), eluent toluene, $T = 60\,°\mathrm{C}$, flow rate $2\,\mathrm{ml\,min^{-1}}$, sample volume 100 μl, concentration 0.5–1%, polyethene standards with a universal calibration according to Benoit et al. [138] (Mark-Houwing coefficients: polyethene: $k_\eta = 1.27 \times 10^{-2}$ ml/g, $A = 1.04$ [polyalkene, C_{10}–C_{18}]; polypropene: $k_\eta = 2.7\times10^{-2}$ ml/g, $A = 0.71$ [polypropene, atactic, solvent benzene, $T = 25\,°\mathrm{C}$]) [139–141] or on a Waters 410 equipped with 5 MIXED B-polystyrene gel columns ($7.5 \times 300\,\mathrm{mm}^2$, PL-gel 10 μm), eluent THF, $T = 35\,°\mathrm{C}$, flow rate $1.2\,\mathrm{ml\,min^{-1}}$, calibration with ethylbenzene, 1,3-diphenylbutane, 1,3,5-triphenylhexane, 1,3,5,7-tetraphenyloctane, and 1,3,5,7,9-pentaphenyldecane, lower limit $180\,\mathrm{g\,mol^{-1}}$. GPC analyses were done on the quenched reaction mixture after the removal of toluene in vacuum.

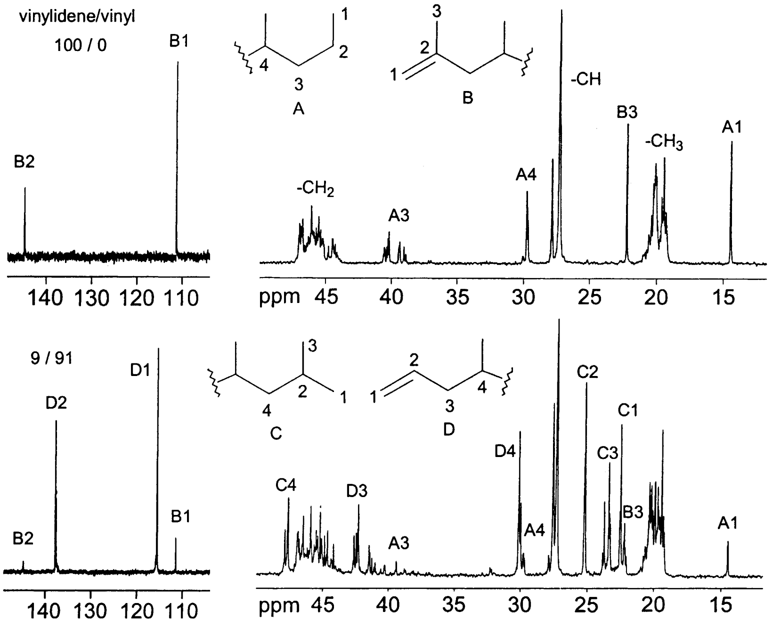


Fig. 9. Olefinic and aliphatic region of the ^{13}C NMR spectra (50.3 MHz, $CDCl_3$) of a vinylidene-terminated oligopropene (top) and of a mostly vinyl-terminated oligomer (bottom). The upper spectrum was obtained with catalyst **9**/MAO, the bottom spectrum with **7**/MAO (cf. Table 1). For the spectral assignment, see also Table 8.

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