

# Homogeneous and heterogeneous oligomerization reactions of olefins with unbridged metallocene catalysts

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## ABSTRACT

1-Pentene and 1-hexene were respectively reacted with 13 homogeneous metallocene catalysts to give linear oligomerization products, predominantly dimers, with selectivities above 90%. The product distributions of the codimerization reactions of 1-pentene with 1-hexene reflected a binomial behavior. Therefore, the ratio for dimers is 1:2:1 ( $C_{10}$ : $C_{11}$ : $C_{12}$ ) while the trimers (pentadecenes up to octadecenes) show a proportion of 1:3:3:1. By changing the ratio of the 1-pentene/1-hexene mixture, the binomial distribution switched to the side of products of the higher concentrated monomer. Even when using methyl branched olefins, the binomial product distribution could be observed. Alkenes with an internal double bond could not be dimerized under these conditions. The reactions with olefins containing a methyl group in  $\beta$ -position, a tert-butyl group or a neopentyl group failed. Addition of appropriate additives like tributylphosphine or aluminum powder raised both the activities and the selectivities for dimers, which means that the fraction of undecenes obtained from the codimerization reactions of 1-pentene and 1-hexene increased. **Polyolefins J (2019) 6: 107-116**

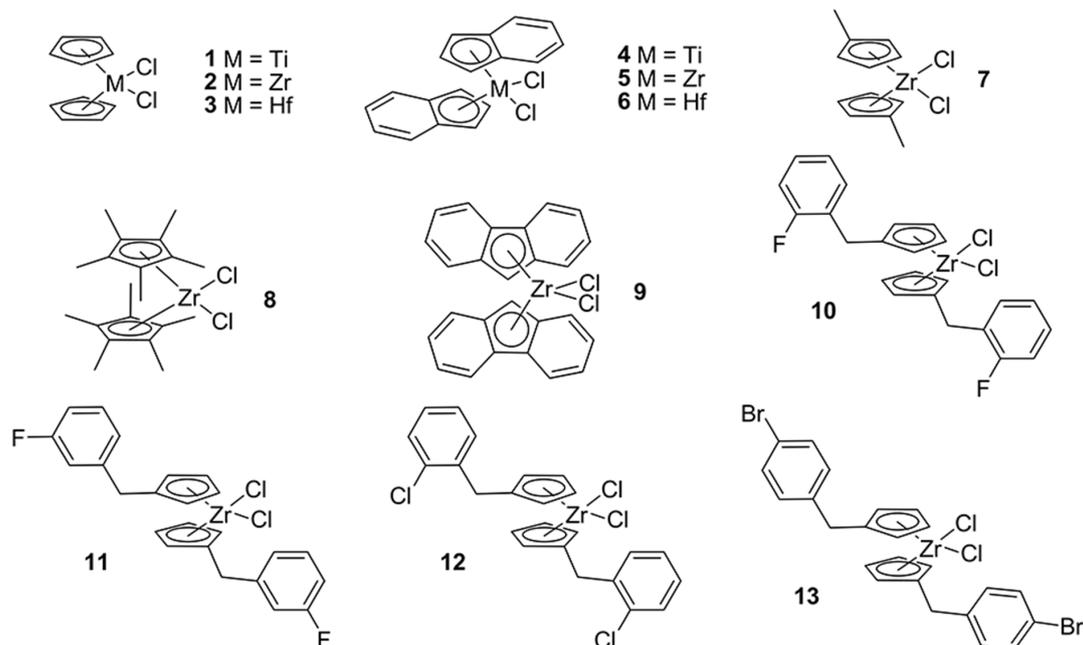
**Keywords:** Unbridged metallocene catalysts; homogeneous olefin oligomerization; homogeneous co-oligomerization of olefins; heterogeneous oligomerization of olefins; Influence of additives.

## INTRODUCTION

In refineries short chain olefins are byproducts that cannot be added to gasoline or diesel fuels because of their low boiling points. Therefore, it is attractive to oligomerize these components to obtain products with higher boiling points that can be added to these fuels [1-11]. An elegant approach to transform short chain olefins to species with a higher molecular weight by oligomerization is the Shell-Higher-Olefin-Process

(SHOP) [12]. In the literature there are many reports dealing with ethylene and propylene dimerization and oligomerization reactions. Indeed, the modification of typical ethylene and propylene polymerization catalysts or cocatalysts and the variation of reaction parameters can favor dimerization and oligomerization instead of polymerization reactions. Representative examples are a series of diimine nickel complexes [13-19], va-

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**Scheme 1.** Metallocene complexes applied for the catalytic oligomerization of 1-pentene and 1-hexene.

nadium complexes [20-21], iron complexes [22-24] and many more. Recently, chromium-promoted cobalt on carbon catalysts [25] were described and nickel atoms in metal-organic frameworks [26]. Chain- and regioselective ethylene and styrene dimerization reactions can be catalyzed with the cationic ruthenium hydride complex  $[(C_6H_6)(PCy_3)(CO)RuH]^+ BF_4^-$  (Cy = cyclohexyl) [27]. Metallocene complexes in combination with methylaluminoxane (MAO) are very versatile and efficient catalysts for the polymerization of ethylene and propylene [28-32]. In this context, we tested 13 different unbridged metallocene complexes with the metals Ti, Zr and Hf in combination with the cocatalyst methylaluminoxane (MAO) to see whether they are able to dimerize or oligomerize 1-pentene and 1-hexene to give the linear hydrocarbons 1-decene and 1-dodecene that can be added to diesel fuels. These components have advantageous cetane numbers of 56 and 71. The codimerization of 1-pentene and 1-hexene should give 1-undecene with a cetane number of 65.

## EXPERIMENTAL

### Materials and methods

All reactions were carried out under an inert gas atmosphere of pure oxygen-free argon using standard

Schlenk techniques. n-Pentane, n-hexane, diethyl ether, toluene, and tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride. Toluene was additionally distilled over phosphorus pentoxide. Methylene chloride and carbon tetrachloride were dried over phosphorus pentoxide. Deuterated organic solvents ( $CDCl_3$ ,  $CD_2Cl_2$ , and  $C_6D_6$ ) for NMR spectroscopy were purchased from Euriso-Top and stored over molecular sieves (3 Å). Argon (5.0) and ethylene (3.5) were purchased from Rießner Company. Methylaluminoxane (10% in toluene) was purchased from Chemtura Europe Limited (Bergkamen). All other starting materials were commercially available and used without further purification.

### GC/MS

GC/MS spectra were recorded with a Thermo FOCUS gas chromatograph combined with a DSQ mass detector. A 30 m HP-5 fused silica column (internal diameter 0.32 mm, film 0.25  $\mu$ m and flow 1 ml/min) was used and helium (4.6) was applied as carrier gas. The measurements were recorded using the following temperature program:

- Starting temperature: 50°C, duration: 2 minutes;
- Heating rate: 20°K/minute, duration: 12 minutes;
- Final temperature: 290°C, duration: 27 minutes.

**Table 1.** Results of catalytic oligomerization reactions of 1-pentene with the activated complexes 1-13.

complex	1	2	3	4	5	6	7	8	9	10	11	12	13
Activity [kg/mol·h]	-	16	1	-	1	-	32	1	-	23	14	15	1
conversion [%]	-	97	18	-	26	-	95	2	-	66	42	65	16

### Mass spectrometry

Mass spectra were recorded with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 EV) and a VARIAN MAT 8500 spectrometer at the Zentrale Analytik of the University of Bayreuth.

### Catalyst precursors

The applied metallocene complexes 1-3 and the olefins were commercially available. Complexes 4-13 were prepared according to published methods [51-53].

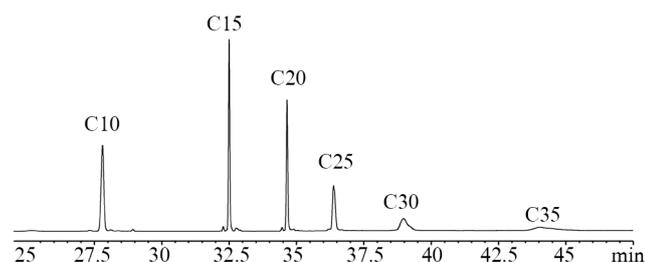
## RESULTS AND DISCUSSION

### Homogeneous oligomerization reactions of 1-pentene with the activated complexes 1-13

The monomer 1-pentene was applied as a pure liquid. The activated catalysts were added at room temperature and after one hour reaction time, the products were identified by GC/MS. Table 1 describes the results, and Figure 1 shows the GC of the products that are formed when complex 2/MAO was applied as catalyst.

In Figure 2 the product distribution of the 9 active catalysts is presented

The titanium complexes 1 and 4 did not show any activities. The reason could be insufficient stability of these complexes under the reaction conditions. The inertness of the bis(indenyl) hafnium complex 6 and

**Figure 1.** Products from the catalytic oligomerization reaction of 1-pentene with 2/MAO (Zr : Al = 1 : 500).

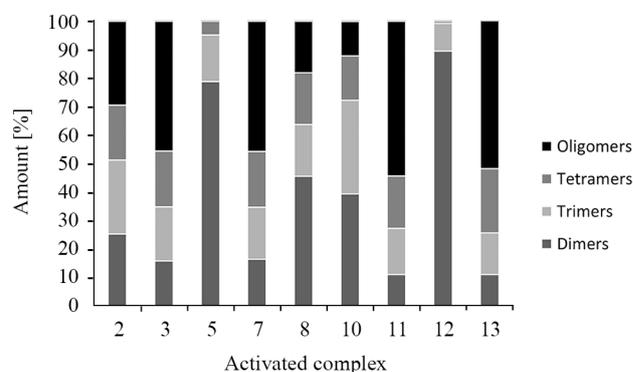
the bis(fluorenyl) zirconium complex 9 could have steric reasons in addition to a ring slippage behavior [33] of the fluorenyl ligands in 9 from  $\eta_5 \rightarrow \eta_3 \rightarrow \eta_1$ . The bis(methylcyclopentadienyl) zirconium complex 7/MAO showed the highest oligomerization activity (32 kg/mol·h) but produced comparatively low dimerization product (16%). The best dimer selectivity with 90% was obtained with 12/MAO (activity 15 kg/mol·h).

According to the reaction products, we assume the same reaction mechanism as in the case of olefin polymerization reactions but with an early chain termination reaction like  $\beta$ -hydrogen elimination. A Schulz-Flory distribution of the products is a good support for this suggestion.

### Homogeneous oligomerization reactions of 1-hexene with the activated complexes 2-8 and 10-13

In an analogous manner as in the case of the 1-pentene oligomerization reactions, the MAO activated complexes 2-8 and 10-13 were applied for the catalytic oligomerization of 1-hexene. Table 2 describes the results, and Figure 2 shows the product distributions that were obtained from the various catalysts.

Complexes 4 and 6 proved as inactive under the reaction conditions applied. The highest activity was observed for 2/MAO (97%) as in the case of the 1-pentene oligomerization reactions (see [34-38]). Janiak reported higher activities with the same catalyst

**Figure 2.** Products from the oligomerization reactions of 9 activated metallocene complexes.

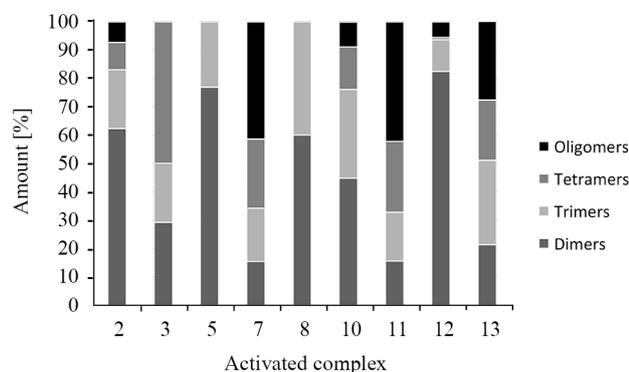
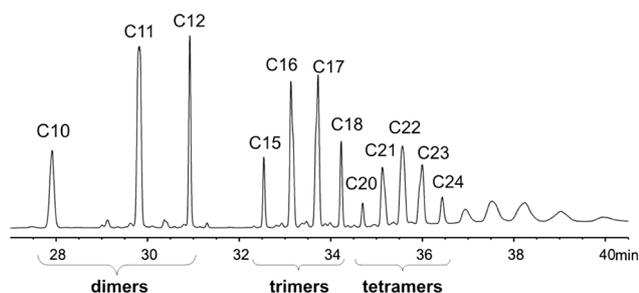
**Table 2.** Activities and productivities of catalytic 1-hexene oligomerization reactions.

complex	1	2	3	4	5	6	7	8	9	10	11	12	13
activity [kg/mol·h]	-	27	1	-	1	-	15	1	-	12	4	24	3
conversion [%]	-	97	2	-	4	-	23	1	-	34	6	27	5

but with a much higher MAO content (Zr : Al = 1 : 4000 [35]). The dimer selectivity of 2/MAO was 62%. The best share of dimers (83%) was obtained with 12/MAO. It is interesting to note that complexes 5 and 8 showed low activities (1 kg/mol·h) but high selectivities. They produced only dimers (77 and 60%) and trimers (23 and 40%). The highest share of tetramers (50%) was obtained with 3/MAO. A 40% share of higher oligomers ( $n > 4$ ) produced from 7/MAO indicates a slow chain termination process, presumably by  $\beta$ -hydrogen elimination. A similar observation was made with 11/MAO (42% higher oligomers).

### Homogeneous co-oligomerization reactions of 1-pentene and 1-hexene with the activated complexes 2, 5, 7, 10 and 12

Based on the results of the catalytic mono oligomerization reactions of 1-pentene and 1-hexene, 1:1 mixtures of these olefins were applied and co-dimerized

**Figure 3.** Product distribution of catalytic 1-hexene oligomerization reactions.**Figure 4.** GC of the products obtained from catalytic co-dimerization reactions of 1-pentene and 1-hexene with 2/MAO.

[39, 40] with complexes 2, 5, 7, 10 and 12 after activation with MAO (Zr : Al = 1 : 500). Table 3 describes the activities of the different catalysts.

The GC of the reaction product (Figure 4) obtained with catalyst 2/MAO shows mainly peaks of coproducts.

The products were generated according to a binomial distribution (Figures 5 and 6).

The ratios are for dimers  $C_{10} : C_{11} : C_{12} = 1:2:1$ , for trimers  $C_{15} : C_{16} : C_{17} : C_{18} = 1:3:3:1$  and for tetramers  $C_{20} : C_{21} : C_{22} : C_{23} : C_{24} = 1:4:6:4:1$ . These results indicate that the combination of 1-pentene and 1-hexene is faster than the combination of two 1-pentenes or two 1-hexenes. The same situation was observed for 12/MAO. Obviously kinetic reasons are dominating steric reasons.

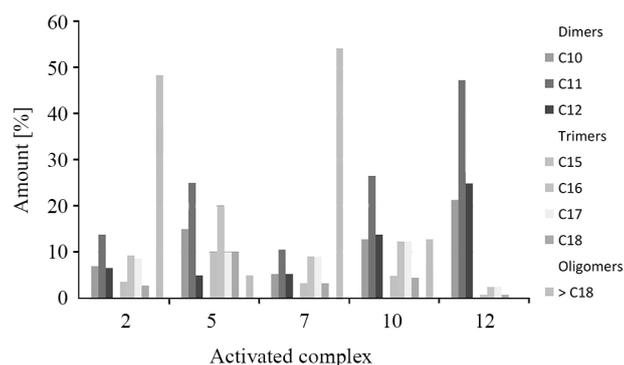
Catalyst 12/MAO showed the best selectivity (94%) for the generation of the dimers  $C_{10}H_{20}$ ,  $C_{11}H_{22}$ , and  $C_{12}H_{24}$  with an activity of 20 kg/mol·h. The missing 6% consisted of trimers. Complex 7 generated 89% olefin transformation with the same activity as 12 but with only 21% dimers. Catalyst 5/MAO favors 1-pentene in the dimerization reaction because  $C_{10}$  isomers are formed with 15% and  $C_{12}$  isomers with only 5%.  $C_{16}$  isomers consisting of two pentene molecules and one hexene molecule are 20%. The  $C_{17}$  fraction consisting of two hexene molecules and one pentene molecule is only 10%. The highest undecene ( $C_{11}H_{22}$ ) yield of 47% was achieved with 12/MAO.

In order to test different 1-pentene/1-hexene ratios in the co-dimerization reaction, 1:2 olefin mixtures were applied (Figure 7) with 2/MAO as catalyst.

Figure 7 shows only tiny differences in the formation of C11 dimers (24 - 26%) independent from the

**Table 3.** Turnover rates and activities of the catalysts in the dimerization reactions of 1-pentene /1-hexene mixtures (1 : 1).

Complex	Conversion [%]	Activity [g/mol·h]
2	89	12
5	1	5
7	89	20
10	20	7
12	36	20



**Figure 5.** Distribution of the products from codimerization reactions of 1-pentene and 1-hexene with the complexes 2, 5, 7, 10 and 12 after activation with MAO (Zr : Al = 1 : 500).

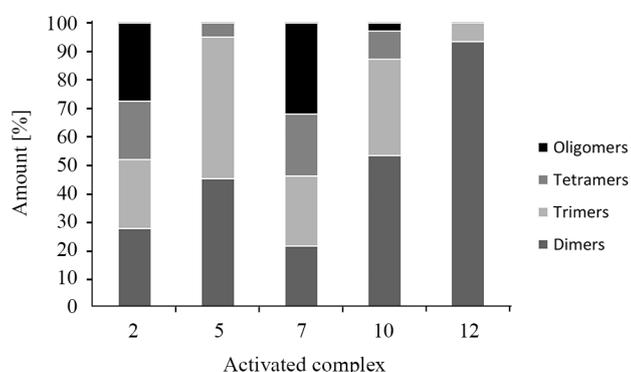
mixing ratio of the olefins. However, when an excess of an olefin was applied, homo dimerization was favored (Figure 8).

In the case of a 1-pentene/1-hexene mixing (2:1), a ratio of  $C_{10}:C_{11}:C_{12} = 4.3 : 3.9 : 1$  was obtained. When the monomer ratio was changed to 1:2, the  $C_{10}:C_{11}:C_{12}$  ratio became 1 : 3.9 : 3.5.

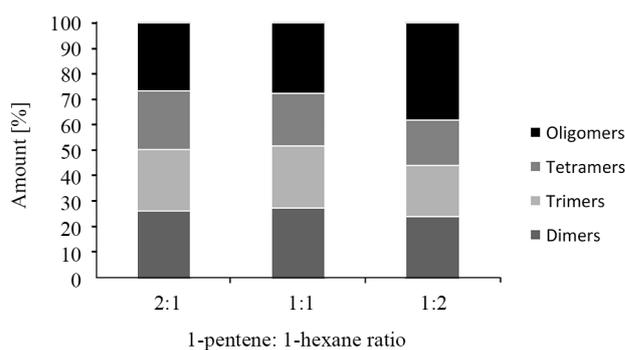
#### Effect of additives on the oligomerization of 1-pentene and 1-hexene with 2/MAO as catalyst

Since an activated metallocene catalyst is supposed to be a cationic species with Lewis acid character, it can be expected that Lewis basic components have an influence on the course of the catalysis. Seven different donor molecules, phosphanes and amines and aluminium powder were applied as additives (one equivalent) in the oligomerization reactions of 1-pentene/1-hexene mixtures with 2/MAO as catalyst. The results are summarized in Table 4.

All additives had remarkable positive influences on the activities and selectivities of the catalyst 2/MAO.



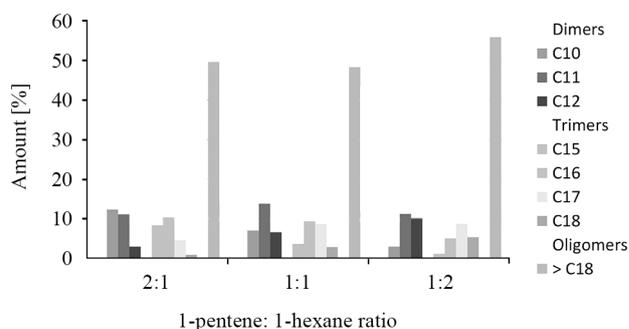
**Figure 6.** Products from co-dimerization reactions of 1-pentene and 1-hexene with the complexes 2, 5, 7, 10 and 12 after activation with MAO (Zr : Al = 1 : 500).



**Figure 7.** Products from co-dimerization reactions of 1-pentene and 1-hexene with different mixing ratios and 2/MAO as catalyst.

In all cases the yield of dimers was higher than in the reactions without additives. Tri-*n*-butylphosphane had the best performance and nearly tripled the dimer selectivity from 27% (without additive) to 75%. In Figure 9 the dimer selectivities are given depending on the additives.

A big surprise is the enormous increase of catalyst activity by a factor 4, when aluminium powder is applied as additive (47 kg/mol·h). Since aluminium is not a Lewis base that can interact with the active centre of the catalyst, a different mechanism must be considered for this effect like the interaction of aluminium powder with the MAO counter anion of the catalyst. Every additive has a different influence on the course of the catalytic oligomerization reaction indicating the sensitivity of the kinetics in these reactions. The addition of  $NEt_3$  favors the generation of trimers (31%),  $NHPh_2$  the formation of tetramers (22%).  $PPh_3$  and  $NPh_3$  addition gave a very similar product distribution but the activity of the catalyst decreased by 50% in the case of  $NPh_3$ . A comparison with the amine derivatives showed that the phosphane additives delivered



**Figure 8.** Product distribution in 1-pentene/1-hexene oligomerization reactions dependent on the mixing ratio of the two olefins and 2/MAO as catalyst.

**Table 4.** Influence of additives on the activity of the 2/MAO catalyst in oligomerization reactions of 1-pentene/1-hexene mixtures (1:1).

Additive	Activity [kg/mol·h]	Dimers [%]	Co-Dimers [%]
-	12	27	14
$\text{PPh}_3$	32	47	24
$\text{NPh}_3$	16	44	22
$\text{NHPPh}_2$	20	36	18
$\text{P}(\text{n-Bu})_3$	15	<b>75</b>	<b>38</b>
$\text{N}(\text{n-Bu})_3$	13	40	20
$\text{NEt}_3$	22	47	24
$\text{NBz}_3$	18	36	18
$\text{Al}$	<b>47</b>	36	19

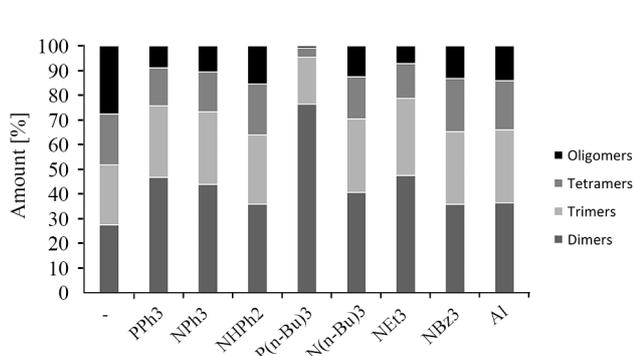
better yields of dimers and better catalyst activities. Figures 10 and 11 summarize the product distributions depending on the corresponding additives.

### Catalytic oligomerization reactions of various linear and methyl branched 1-olefins with 2/MAO

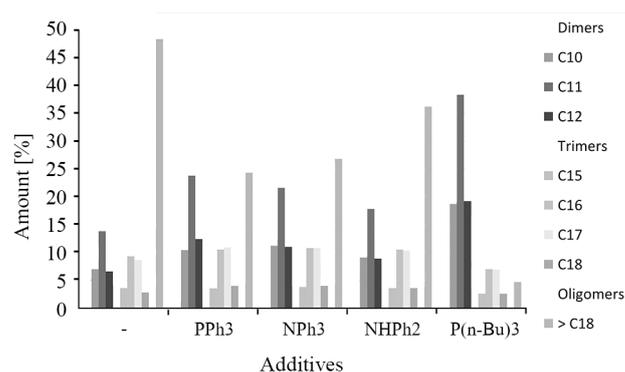
In order to test the scope of oligomerization reactions, 17 different 1-olefins were applied. Table 5 summarizes the results.

Sterically demanding olefins like K, L, M and O did not give any products, 4-methyl-1-pentene (N) could be oligomerized (34% dimer) with low catalyst activity (7 kg/mol·h). The methyl group in 4-position of the olefin has a disadvantageous effect compared to the isomer 1-hexene (27 kg/mol·h). The best catalyst activity for co-oligomerization reactions was observed for the combination 1-pentene/1-hexene (64 kg/mol·h); nearly as good as the catalyst activity for neat 1-pentene (94 kg/mol·h).

Figure 12 shows the product distribution resulting from co-oligomerization reactions of 1-pentene with the co-monomers 1-hexene (E), 1-heptene (F), 1-octene (G) and 4-methylpentene (P). The co-oligomerization of 1-pentene with 1-octene gave the lowest yields (13 kg/mol·h). 4-Methyl-pentene as co-monomer delivered an activity of 55 kg/mol·h and a good dimer selectivity of 49%.



**Figure 9.** Dimer selectivities depending on various additives in co-oligomerization reactions of 1-pentene/1-hexene mixtures (1:1) with 2/MAO.



**Figure 10.** Product distribution of catalytic 1-pentene/1-hexene oligomerization reactions with 2/MAO depending on the addition of various additives.

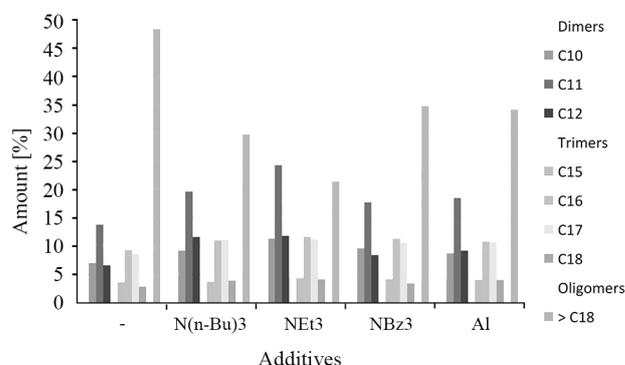
tene (G) and 4-methylpentene (P). The co-oligomerization of 1-pentene with 1-octene gave the lowest yields (13 kg/mol·h). 4-Methyl-pentene as co-monomer delivered an activity of 55 kg/mol·h and a good dimer selectivity of 49%.

In an analogous manner 1-hexene could be oligomerized with the same co-monomers to give products as shown in Figure 13.

The best catalyst performance was observed for the co-oligomerization of 1-hexene with 1-heptene (48 kg/mol·h). Different from all other co-oligomerization reactions, the products from the co-oligomerization of 1-hexene with 4-methyl-pentene (Q) did not show a binominal distribution of 1:2:1 for dimers or 1:3:3:1 for trimers but products with a higher hexene content as depicted in Figure 14. Obviously steric parameters of the olefins favor the incorporation of 1-hexene instead of 4-methyl-1-pentene.

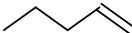
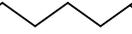
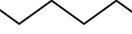
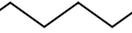
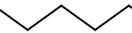
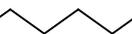
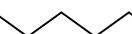
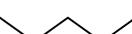
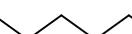
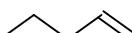
### Heterogeneous oligomerization of olefins

For industrial applications of olefin polymerization re-



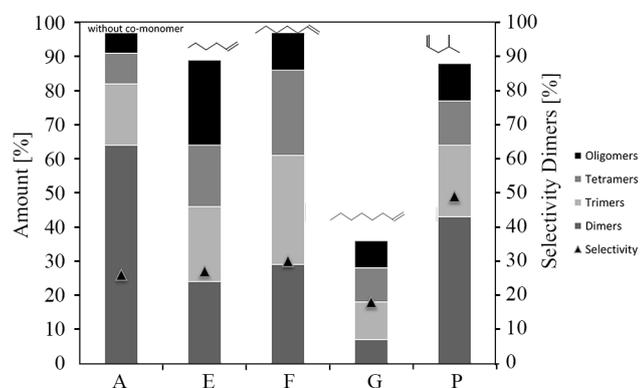
**Figure 11.** Product distribution of catalytic 1-pentene/1-hexene oligomerization reactions with 2/MAO depending on the addition of various additives.

**Table 5:** Results of oligomerization reactions of 17 different olefins with 2/MAO as catalyst.

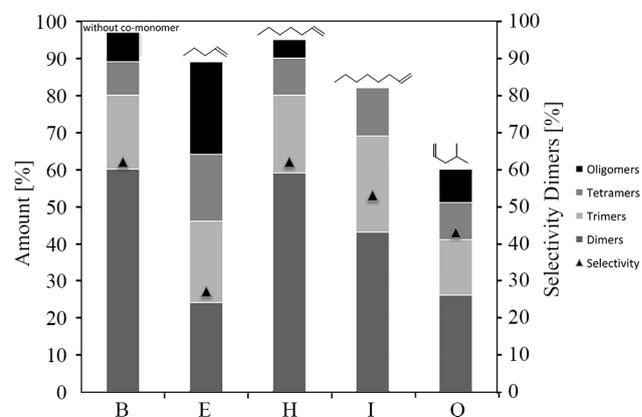
No.	Monomer 1	Monomer 2	Conversion	Dimers	Activity
			[%]	[%]	[kg/mol·h]
A		-	97	26	94
B		-	97	62	27
C		-	96	55	41
D		-	92	54	39
E			89	27	12
F			97	30	64
G			36	18	13
H			95	62	48
I			82	53	53
J			94	43	58
K		-	0	-	-
L		-	0	-	-
M		-	0	-	-
N		-	24	34	7
O		-	0	-	-
P			88	49	55
Q			60	43	49

actions, it is necessary to use heterogeneous catalysts in continuous processes [41-45]. Therefore a fixed bed reactor is the right choice for olefin oligomerization reactions [46-49]. Since the metallocene complex

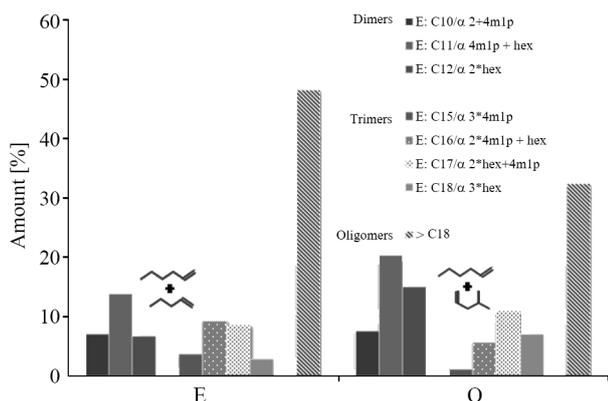
$\text{Cp}_2\text{ZrCl}_2$  has proved as suitable catalyst precursor, a good support material was necessary. From a selection of 17 different support materials (various silica, alumina, zeolites and mixtures thereof), the best per-



**Figure 12.** Product distribution resulting from co-oligomerization reactions of 1-pentene without comonomer (A) and with the co-monomers 1-hexene (E), 1-heptene (F), 1-octene (G) and 4-methylpentene (P).



**Figure 13.** Product distribution resulting from co-oligomerization reactions of 1-hexene without comonomer (B) and with the co-monomers 1-pentene (E), 1-heptene (H), 1-octene (I) and 4-methylpentene (Q).



**Figure 14.** Comparison of product distributions from the co-oligomerization reactions of 1-hexene with 1-pentene and 4-methyl-1-pentene.

formance was obtained with silica SI 1102 (Davicat, Grace Davison). The TON was 2934, 91% transformation rate of 1-hexene. Further parameters in this reaction are the flow speed of the monomer, the catalyst load on the support and the temperature. All these aspects were studied in detail [50].

## CONCLUSION

13 unbridged metallocene complexes in combination with methylaluminumoxane were applied as catalysts for the dimerization and oligomerization of higher 1-olefins ( $C > 5$ ). These reactions are highly dependent on the nature of the olefin, the metallocene complex and additives. Tiny changes of the parameters can have a strong impact on the product formation due to early or late termination reactions in the catalytic processes. The starting catalyst is supposed to be a cationic  $[Cp'_2MMe]^+$  species ( $Cp'$  = monosubstituted cyclopentadienyl,  $M = Ti, Zr, Hf$ ). Since all investigated metallocene catalysts show good performances in ethylene polymerization reactions and produce polyethylenes with comparatively high molecular weights, it is obvious that spacious olefinic monomers reduce the activities of the catalysts and the molecular weights of the products. Because of these steric reasons, the insertion of the olefin into the growing chain is slower than the termination step. Additives like aluminum powder increase the activities of metallocene catalysts. An explanation for its positive influence is still open.

## Acknowledgements

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