

Supporting information

Comparative Study of new Chromium-based Catalysts for the Selective Tri- and Tetramerization of Ethylene

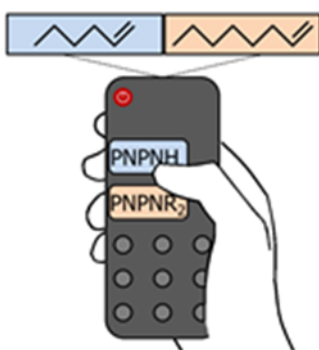
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Synthesis of the ligands

All manipulations were done under argon atmosphere using standard schlenk techniques. Solvents were purchased anhydrous and stored over molecular sieves or in a solvent purification system after degassing. Methylcyclohexylamine, N-Ethylmethylamine and $\text{LiCH}_2\text{SiMe}_3$ were purchased from Sigma Aldrich.

The synthesis of $\text{Ph}_2\text{PN}(i\text{Pr})\text{P}(\text{Ph})\text{N}(i\text{Pr})\text{H}$ (**1**) was described before.^[1]

Compounds $\text{Ph}_2\text{PN}(c\text{-Hex})\text{P}(\text{Ph})\text{Cl}$ ^[2] and $\text{Ph}_2\text{PN}(i\text{Pr})\text{P}(\text{Ph})\text{Cl}$ ^[3] were prepared according to published literature procedure.

$\text{Ph}_2\text{PN}(i\text{Pr})\text{P}(\text{Ph})\text{N}(c\text{-Hex})(\text{CH}_3)$ (**2**): 0.226g (2 mmol) of N-Methylcyclohexylamine, dissolved in 10 mL of THF, was lithiated at 0°C with 2 mL of $\text{LiCH}_2\text{SiMe}_3$ (1.0M in Pentane) and stirred for 6 hours at room temperature. Afterwards this solution was added dropwise at -40°C to a solution of 0.77g (2 mmol) of $\text{Ph}_2\text{PN}(i\text{Pr})\text{P}(\text{Ph})\text{Cl}$ in 10 mL of THF and stirred for additional 24 hours at room temperature. Evaporation to dryness under vacuum and extraction of the residue with n-Pentane gave a solution from which the product crystallized at 8°C. Isolated yield: 0.6 g (1.30 mmol, 65%), colourless crystals. Mp: 109°C. Anal. Calcd for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{P}_2$ (462.55 g/mol): C, 72.71; H, 7.84; N, 6.06; P, 13.39. Found: C, 72.86; H, 7.73; N, 6.23; P, 13.57. MS (high resolution): $(\text{M}+\text{H})^+$ calc.: 463.24265 measured: 463.24338 ¹H NMR (296 K, 400 MHz, C_6D_6): δ 0.62-1.60 (br, 16H $\text{CH}(\text{CH}_3)_2$ and $\text{CH}(\text{CH}_2)_5$), 2.35 (br, 3H NCH_3), 2.78 (br, 1H CH), 3.52 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 6.85-6.98 (m, 7H, C_6H_5), 7.06 (m, 2H, C_6H_5), 7.36-7.46 (m, 4H, C_6H_5), 7.56 (m, 2H, C_6H_5) ppm; ¹³C NMR (296 K, 75 MHz, C_6D_6) δ 25.1, 25.40 ($\text{CH}(\text{CH}_3)_2$); 25.9, 26.2, 26.5, 31.8, 32.4 (CH_2); 30.5 (NCH_3), 51.4 ($\text{CH}(\text{CH}_3)_5$); 62.3 ($\text{CH}(\text{CH}_2)_2$); 127.7-128.1 (4 signals), 128.4, 129.0, 131.4, 132.8, 133.9, 140.4, 142.3, 143.2 (C_6H_5) ppm; ³¹P NMR {¹H} (296 K, 162 MHz, C_6D_6) δ 48.6 (br), 92.5 (br) ppm.

$\text{Ph}_2\text{PN}(c\text{-Hex})\text{P}(\text{Ph})\text{NEt}(\text{CH}_3)$ (**3**): The preparation of **3** was conducted the same manner as described for **2** by using $\text{Ph}_2\text{PN}(c\text{-Hex})\text{P}(\text{Ph})\text{Cl}$ and N-Ethylmethylamine (2 mmol each). Recrystallization from ethanol yielded 0.673g (1.50 mmol, 75%) microcrystalline white **3**. Mp. 126°C. Anal. Calcd for $\text{C}_{27}\text{H}_{34}\text{N}_2\text{P}_2$ (448.53 g/mol): C, 72.30; H, 7.64; N, 6.25; P, 13.81. Found: C, 72.31; H, 7.77; N, 6.22; P, 13.78; MS (high resolution): $(\text{M}+\text{H})^+$ calc.:449.227 measured: 449.22694

¹H NMR (296 K, 300 MHz, C_6D_6): δ 0.89-2.33 (m, 13H, $\text{CH}(\text{CH}_2)_5$ and CH_2CH_3); 2.60 (br, 3H, NCH_3); 3.03 (br, 2H, CH_2CH_3); 3.31 (m, 1H, $\text{CH}(\text{CH}_2)_5$); 7.05-7.19 (m, 7H, C_6H_5), 7.25 (m, 2H, C_6H_5), 7.55-7.68 (m, 4H, C_6H_5), 7.79 (m, 2H, C_6H_5) ppm;

¹³C NMR (296 K, 75 MHz, C_6D_6) δ 14.4 (CH_2CH_3); 25.9, 26.4, 26.9, 36.2, 36.5 ($\text{CH}(\text{CH}_2)_5$); 35.8 (NCH_3), 49.7 (CH_2CH_3), 59.5 ($\text{CH}(\text{CH}_2)_5$); 127.8, 128.0, 128.1, 128.2, 128.3, 129.2, 131.5, 132.2, 134.2, 140.7, 142.4, 143.4 (C_6H_5) ppm; ³¹P NMR {¹H} (296 K, 121 MHz, C_6D_6) δ 48.1 (br), 93.0 (br) ppm.

Experimental test rig for ethylene oligomerization experiments

All catalytic ethylene oligomerization experiments were performed in a 0.3 L Parr autoclave (D01) equipped with a hollow shaft gas-entrainment stirrer. The ethylene supply was afforded by a 2 L aluminium gas cylinder (D03) on a balance (W1) to monitor and record the ethylene consumption over time with the aid of a software.^[4] The ethylene pressure exposed to the reactor was controlled by a pressure reducer (PC01) and was monitored at the reactor by a common manometer (PI3). The reaction temperature was measured by a thermocouple (TIC1) situated in the reactor's liquid phase and controlled electronically by an electrical heating jacket and a water cooling-coil, submerged in the liquid phase. Using a hose, the reactor could be connected to a rotary vane vacuum pump (ca. 10^{-1} mbar) and a low pressure argon supply (ca. 0.5 bar (g)), both used for inertization. A complete overview of the test rig is given in figure 1.

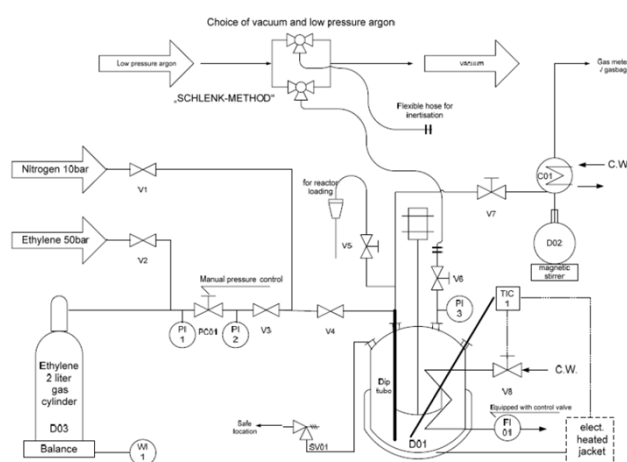


Figure 1. Piping and Instrumentation diagram of the test rig.

General procedure of the ethylene oligomerization experiments

Before each experiment the reactor was baked out at 105 °C and reduced pressure for at least two hours to eliminate traces of water and oxygen. After cooling down to the desired reaction temperature, the autoclave was purged with argon – including the tube for reactor loading – and subsequently evacuated in order to suck in a previously prepared catalyst solution from a 100 mL Schlenk-flask. After that, the gas entrainment stirrer was set to 1000 rpm to exclude gas-to-liquid mass transfer limitation and the reaction was ultimately started by pressurizing the reactor with ethylene (30 bar(g)). This pressure was maintained over the whole reaction time (semi-batch reaction). The same was realized for the temperature which was kept as constant (isothermic) as possible over the reaction time.

After the reaction time, the ethylene supply was closed and the stirrer was stopped. In the next step, the liquid and gaseous components of the reaction mixture were discharged through the dip tube, using the headspace pressure of the reactor as driving force. While the liquid compounds were collected in a flask, the gases were passed through the attached reflux condenser and subsequently the gas meter, thus determining the gas volume, and were eventually collected in a gas bag.

When aluminoxanes were used as co-catalysts, the liquid product was treated with 20 mL of a 10 wt % HCl solution and a magnetic stirrer to ensure rapid catalyst quenching. Due to the use of significantly lower amounts of aluminium alkyl activator when TEAL was used instead of MMAO, this wasn't considered necessary in this case.

Subsequently the liquid fraction was weighed and filtered using a suction strainer. The filter paper was dried and weighed to determine the solid content in the liquid phase. After opening the autoclave the residues – normally mainly consisting of solvent-swollen polymer – were weighed and dried. In order to yield the overall solid content, the mass of the dried solid was added to the mass determined by the filter weighing, whereas the mass difference of the wet and dried reactor solid was added to the mass of the liquid fraction.

Qualitative analysis of the organic liquid- and gaseous fraction were conducted by GC-FID measurements. In connection with the quantitative product data (weighing of the liquid phase/volume determination of the gas phase) and the recorded ethylene consumption, it was possible to set up an ethylene mass balance. In addition, the mass balances for the applied solvents were also calculated, as the input-mass was known by weighing.

General catalyst preparation procedure and materials

All manipulations – except the treatment of the solid compounds Cr(acac)₃ (97%, Aldrich), **1** and DoTriMAC (99 %, Aldrich) – were conducted excluding water and oxygen by using standard Schlenk techniques or in the nitrogen atmosphere of a glovebox. As a precautionary measure **2** and **3** were also handled under exclusion of air and moisture. If solids were used for the catalyst preparation instead of the corresponding stock solutions in dry solvents, they were loaded into the flask first.

A 100 mL Schlenk-flask with a magnetic stir bar was charged with a weighed amount of about 100 mL dried solvent, whereupon a certain amount of a stock solution containing Cr(acac)₃ – in the range of several μmol/mL – and 1.2 equivalents of ligand was added. The final step before transferring the reaction mixture to the reactor was the addition of the aluminium activator.

All chemicals were used as purchased if not stated differently. The used solvents were all purchased from Aldrich (except for toluene). Prior to use, the solvents (except for toluene) were poured into a Schlenk-flask with activated molecular sieve (4Å) where they were further stored under argon. Toluene was dried over sodium using benzophenone as a moisture indicator and was freshly distilled in an inert nitrogen atmosphere for each experiment. The activators triethylaluminium (93 %, Albemarle, ultra low hydride) and modified methylaluminoxane-3A (7 wt % Al in heptane, Akzonobel) were used as received. The gases argon (4.8), ethylene (3.0), helium (4.6), hydrogen (5.0) and synthetic air (80 % N₂, 20 % O₂) were purchased from Linde Gas.

Product analysis and data evaluation

The gaseous and liquid products of the reactions were analysed via gas chromatography on an Agilent 6890N Chemstation, equipped with an Agilent 19091 J-413 Column (HP-5, 5 % methyl phenyl siloxane, 30 m x 320 μm x 0.25 μm) and a FID detector. Gaseous samples were injected manually using a

conventional GC syringe, while liquid samples were injected by the aid of an Agilent 7683 B series autosampler.

The qualitative determination of the gaseous products was based on experiences from former oligomerization experiments. Peaks that couldn't be assigned to ethylene, 1-butene, 1-hexene, toluene or 1-octene were added up in fractions. A peak found when MMAO was used as co-catalyst (probably isobutene) was not considered a reaction by-product since it could be directly assigned to a quench-product of MMAO.

It was further assumed that all gases have the same response factor for the analysis with the FID detector. Consequently, the quantification of a particular peak depicted in area % by the GC software, represents the weight percentage of the compound in the gas phase. Thus, the mass of each component could be calculated using its molar mass, the measured gas volume and the ideal gas law.

The qualitative and semi-quantitative (weight % in the analysed sample) determination of the liquid samples was realized by external calibration.

The content of a specific carbon number in the oligomeric product (C_x) is displayed in wt % and comprises the 1-olefin as well as the accompanying fractions (1-C_x and C_{xf}). Connecting these two values also enables the calculation of the 1-olefin purity of a given carbon number. The just mentioned definitions are illustrated in the following equations:

$$C_x = \frac{m_{1-C_x} + m_{C_{xf}}}{m_{olefins}} [\text{wt } \%]; \quad p(1-C_x) = \frac{m_{1-C_x}}{m_{1-C_x} + m_{C_{xf}}} [\%]$$

For the calculation of the combined overall yield (in wt %) of the desired, valuable products 1-hexene and 1-octene (1-C₆ + 1-C₈), the polymer mass (m_{polymer}) was also taken into account. Accordingly, the overall polymer content (PE) in wt % was calculated, thus leading to the following expressions:

$$1-C_6 + 1-C_8 = \frac{m_{1-C_6} + m_{1-C_8}}{m_{olefins} + m_{polymer}} [\text{wt } \%]$$

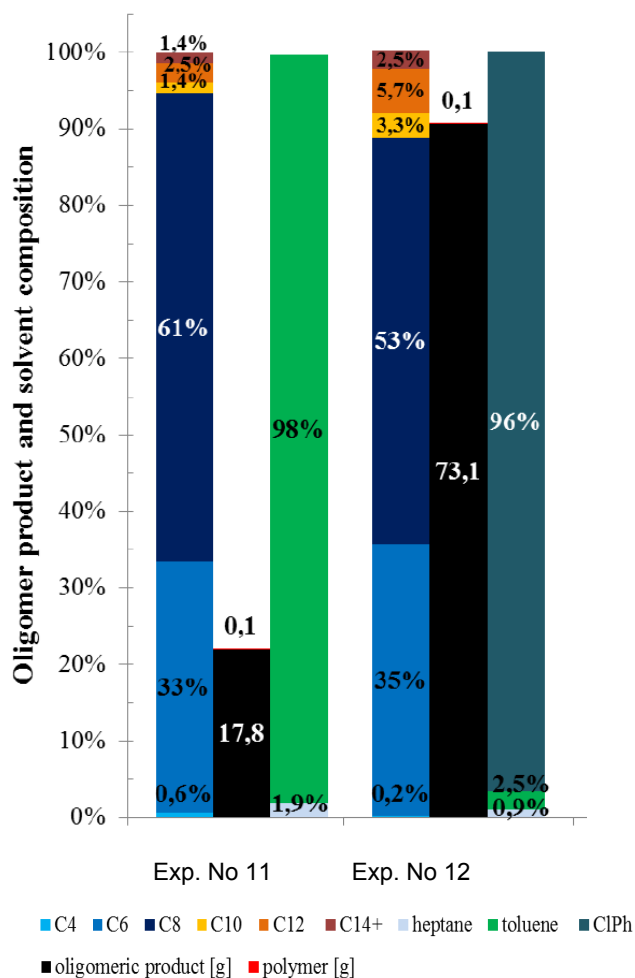
$$PE = \frac{m_{polymer}}{m_{olefins} + m_{polymer}} [\text{wt } \%]$$

The overall product mass of a reaction was therefore calculated by addition of m_{olefins} and m_{polymer}.

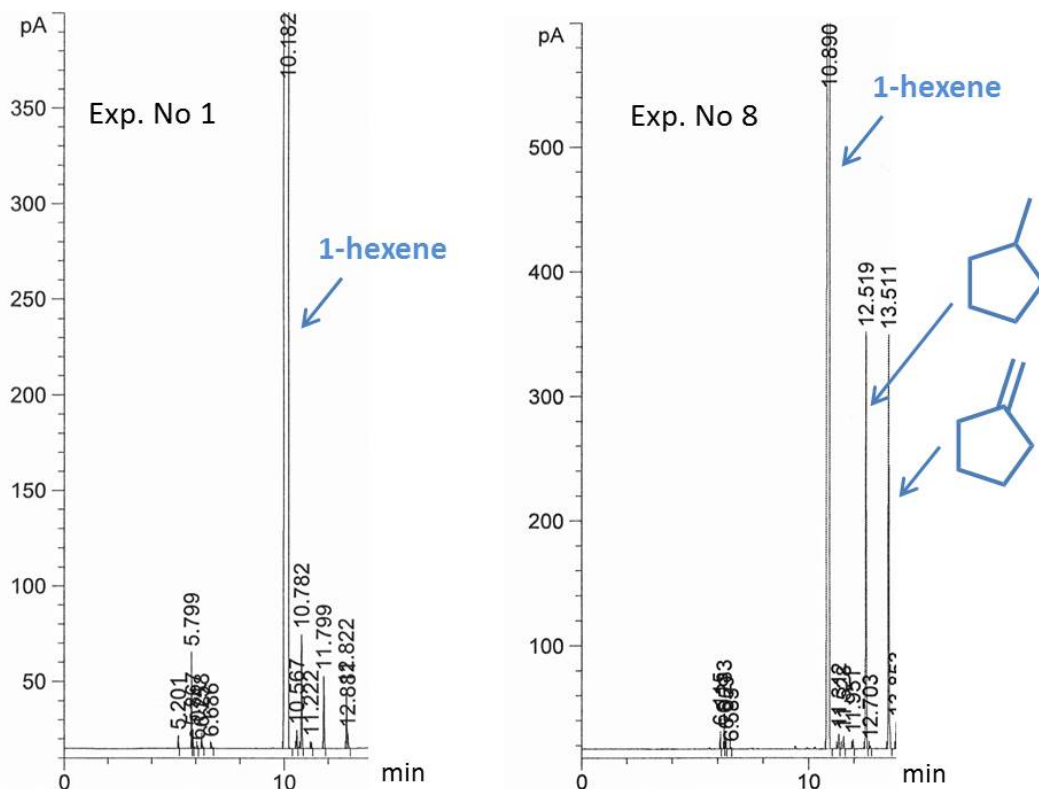
For example the oligomer product and solvent composition for Exp. No 11 and 12 are given below in a chart.

For all runs a detailed description of the product mixture is given in the table.

The side products methylcyclopentane and methylenecyclopentane of the C6 fraction were identified by the spiking method.



Exp. No	C4		C6		C8		C10		C12		C14+	
	fraction wt%	1-olefin of the fraction wt%	fraction wt%	1-olefin of the fraction wt%	fraction wt%	1-olefin of the fraction wt%	fraction wt%	1-olefin of the fraction wt%	fraction wt%	1-olefin of the fraction wt%	fraction wt%	1-olefin of the fraction wt%
1	1.8	99.8	92.2	99.0	0.4	65.8	5.4	1.4	0.1	22.0	0.1	14.2
2	2.1	95.6	87.6	98.4	2.2	21.2	7.8	2.0	0.2	19.0	0.1	7.9
3	1.9	23.0	80.8	97.6	10.4	2.4	3.5	1.6	3.3	1.9	2.7	0.0
4	3.9	79.2	23.0	91.8	11.8	1.0	42.7	0.2	18.6	1.3	n.d.	n.d.
5	2.0	77.3	81.3	98.6	12.0	1.9	4.2	0.6	0.5	1.6	n.d.	n.d.
6	2.2	99.2	28.7	78.3	61.8	97.4	3.0	21.1	2.9	11.7	1.5	15.5
7	0.5	99.7	46.2	92.9	46.0	99.0	3.0	6.4	3.2	4.0	1.2	0.3
8	0.4	99.6	44.3	83.9	46.7	99.1	2.9	7.2	3.2	4.6	2.5	0.5
9	1.2	99.4	41.7	88.0	49.8	98.5	2.8	8.1	3.2	4.4	1.2	0.2
10	0.8	98.4	45.4	88.3	49.3	97.5	1.9	9.0	1.9	4.4	0.7	0.6
11	0.6	61.4	32.9	94.0	61.2	99.3	1.4	0.6	2.5	0.5	1.4	6.7
12	0.2	99.5	35.4	94.6	52.9	99.2	3.3	7.2	5.7	3.7	2.5	0.2
13	0.4	99.6	31.3	87.5	64.5	98.6	1.1	33.4	1.6	10.2	1.0	0.3
14	0.2	100.0	35.0	92.6	56.9	99.3	2.3	14.9	3.8	5.4	1.9	0.4



Typical side products of the C6 fraction using TEAL (Exp. No 1) or MMAO-3A (Exp. No 8) as cocatalyst.

X-ray crystal structure analysis of 2

Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package (Sheldrick, G. M. *Acta Crystallogr.* **2008**, A64, 112.). XP (Bruker AXS) was used for graphical representation.

Crystal data for **2**: $C_{28}H_{36}N_2P_2$, $M = 462.53$, triclinic, space group $P\bar{1}$, $a = 11.4796(4)$, $b = 15.5902(6)$, $c = 15.8639(6)$ Å, $\alpha = 98.551(2)$, $\beta = 106.145(2)$, $\gamma = 104.953(2)^\circ$, $V = 2559.42(16)$ Å³, $T = 150(2)$ K, $Z = 4$, 50731 reflections measured, 11727 independent reflections ($R_{int} = 0.0612$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0427$, $wR_2 = 0.0910$, final R values (all data): $R_1 = 0.0755$, $wR_2 = 0.1039$, GOF on F^2 : 1.013, 583 parameters.

CCDC 1032505 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [4] Mettler Toledo Balance Link, Version 4.0.1., Mettler Toledo GmbH (Greifensee, Switzerland), **2006**.