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

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Two new ligands, Ph<sub>2</sub>PN(*i*Pr)P(Ph)N(*c*-Hex)(CH<sub>3</sub>) (**2**) (Ph = phenyl, *i*Pr = isopropyl, *c*-Hex = cyclohexyl) and Ph<sub>2</sub>PN(*c*-Hex)P(Ph)NEt(CH<sub>3</sub>) (Et = ethyl) (**3**) were synthesized. **2** was characterized by X-ray analysis. To compare their applicability with the previously known Ph<sub>2</sub>PN(*i*Pr)P(Ph)N(*i*Pr)H (**1**) these ligands were investigated together with chromium(III)acetylacetonate, different co-catalysts and solvents for the catalytic oligomerization of ethylene. The in situ prepared catalysts proved to be highly active, yielding highly pure 1-octene as the main product and 1-hexene as the main byproduct. It was possible to reach productivities of several hundred kg product per gram chromium and hour, up to almost 65 wt % 1-octene with about 99 % purity and overall 1-hexene plus 1-octene yields of more than 85 wt %.

### Introduction

Due to their high reactivity, Linear Alpha Olefins (LAOs) are important intermediates for a variety of industrially relevant chemical reactions. Their utilization is strongly dependent on the chain length, which also entails different physical properties. The quantitatively most important usage of LAOs is as co-monomers in the production of high density (HDPE) and linear low density polyethylene (LLDPE) (C<sub>4</sub>-C<sub>8</sub>). Other significant applications are in the synthesis of plasticizer alcohols, lubricants and poly-alpha-olefins (C<sub>6</sub>-C<sub>12</sub>), detergent alcohols (C<sub>10</sub>-C<sub>16</sub>) or oil field chemicals and wax replacements (C<sub>16</sub>-C<sub>30+</sub>).<sup>1a-d</sup>

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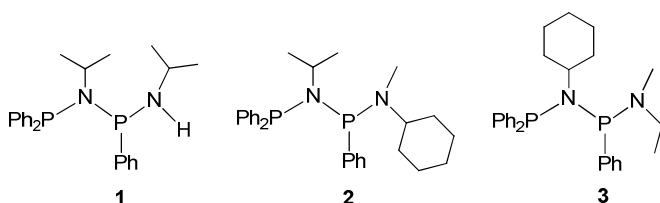
† Electronic Supplementary Information (ESI) available: A detailed description of the experimental setup, the catalyst preparation, additional experimental results and crystallographic details for **2** are given in the supporting information. See DOI: 10.1039/b000000x/

LAOs can be produced by cracking of Fischer-Tropsch products.<sup>1e-f</sup> Currently the main suppliers of LAOs rely on full-range ethylene oligomerization technologies. These technologies are based on homogeneous catalysts, which are all producing even numbered olefins ranging from four to more than 30 carbon atoms (C<sub>30+</sub>). The composition of the product mixtures follows mathematical distributions (e.g. Schulz-Flory or Poisson), reflected by the statistically determined chain growth/ $\beta$ -hydride-elimination mechanism. Though the product distribution of these processes can be tuned to a minor degree by changing process parameters, the range of flexibility remains strongly limited. Thus, demand dependent chain-length adaptation is a great challenge.<sup>1b-d</sup> The co-monomer grade short-chain LAOs (C<sub>4</sub>-C<sub>8</sub>) for HDPE and LLDPE production represent the quantitatively biggest part of the overall LAO demand along with the highest predicted growth rates. Taking this into consideration, it is not surprising that the selective oligomerization of ethylene aroused much academic and commercial interest in the last decades.<sup>2a-f</sup> So far, only a few selective oligomerization processes are commercialized: Axens Alphabutol™ titanium based process for 1-butene is successfully applied since the first unit went on-stream in 1986 in Thailand. In comparison, the first commercial 1-hexene process developed by Chevron Phillips based on chromium in conjunction with 2,5-dimethylpyrrole is relatively young, as the first plant in Qatar went operational in 2003. In the case of 1-octene, the commercialization of SASOL's selective ethylene tri- and tetramerization system based on chromium and a diphosphinoamine ligand was realized in Lake Charles in 2013.<sup>1a-c, 2c,e</sup> Most of the catalytic systems for selective ethylene oligomerization, including Phillip's trimerization and Sasol's tetramerization systems, use chromium compounds in

connection with an organic ligand and an organoaluminium co-catalyst. There are also very efficient vanadium and iron containing catalysts for the oligomerization of ethylene.<sup>2g</sup> Their selectivity is based on a metallacycle-based mechanisms which were originally reported by Manyik et al.<sup>3</sup> and described in more detail by Briggs.<sup>4</sup> By now the involvement of metallacycles in the mechanism has been supported by experiments with deuterium labelled ethylene<sup>5a-c</sup> as well as quantum mechanical calculations<sup>6a-f</sup> and is widely accepted.

Ligand  $\text{Ph}_2\text{PN}(\text{iPr})\text{P}(\text{Ph})\text{N}(\text{iPr})\text{H}$  (**1**) was described as a part of selective ethylene oligomerization catalysts, which result either in selective trimerization of ethylene<sup>7a-k</sup> or in an oligomer distribution consisting of 1-hexene and 1-octene.<sup>7a,8</sup> It was pointed out that the N-H group of **1** is essential for trimerization activity since compounds of the structure  $[\text{PNPNR}_2]$  are totally inactive in catalysis when applied together with triethylaluminium as co-catalyst.<sup>7b</sup> Metalated products<sup>7b,g</sup> of **1** and an interesting rearrangement reaction<sup>7b</sup> in the presence of triethylaluminium were described. Furthermore, a heterobimetallic Cr/Al complex was presented containing the deprotonated ligand.<sup>7h</sup> Recently Wasserscheid, McGuinness and co-workers reported in conjunction with **1** a study on a series of PNP derivatives bearing either a protic nitrogen connected to the PNP nitrogen backbone, which could react with alkylaluminium activators, or bearing donor functionalities, capable of forming a Lewis pair with alkylaluminium compounds.<sup>8</sup> In this paper a comparison of the catalytic behavior of **1** with two more examples of ligands with PNP backbone without an N-H functionality is reported (Chart 1).

**Chart 1.** PNP ligands with (**1**) and without (**2**, **3**) N-H-group.

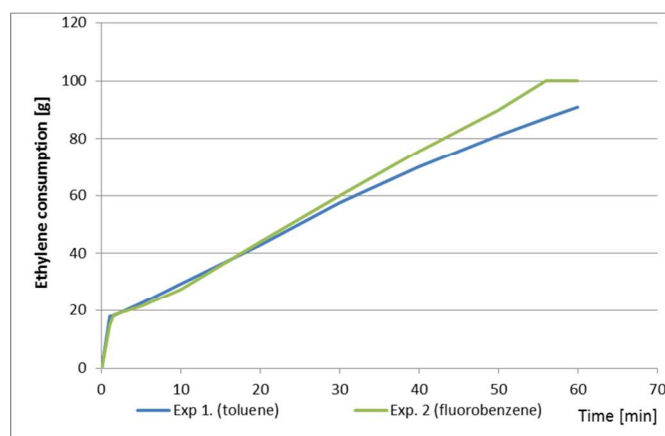


## Results and Discussion

### Solvent studies of the trimerization system

Only a catalyst system consisting of the ligand  $\text{Ph}_2\text{PN}(\text{iPr})\text{P}(\text{Ph})\text{N}(\text{iPr})\text{H}$  (**1**), chromium(III)acetylacetonate and dodecyltrimethylammonium chloride (DoTriMAC) with triethylaluminium (TEAL) as co-catalyst and toluene as solvent shows significant activities. Referring to experiments of other groups<sup>9,10a-c</sup> halogenated benzene derivatives were regarded as

promising alternative solvents. In addition, the chlorinated aliphatic solvents 1-chlorohexane and chlorocyclohexane were tested. The main results of these experiments are summarized in Table 1. As can be seen from this table, a suitable productivity is only reached for the experiments 1-2, using toluene and fluorobenzene. In these cases only a slight difference in productivity, selectivity and 1-olefin purity was observed, thus yielding mainly 1-hexene (>85 wt %). The main byproducts, not included in the table, are branched C10 olefins. An incomplete DoTriMAC solvation upon TEAL addition was observed for the nearly inactive experiments 5 and 6 using 1-chlorohexane and chlorocyclohexane, but the preceding solvation of  $\text{Cr}(\text{acac})_3$  already took about 1 h in these solvents. Consequently, the poor solubility of the active chromium species might also be a reason for the inactivity of these systems. In the case of bromobenzene (experiment 3),  $\text{Cr}(\text{acac})_3$  is entirely dissolved only after addition of TEAL, instantaneously yielding a yellow solution as observed in experiments 1 and 2. In these cases sudden changes of color to green after some seconds are observed. Regarding the ethylene uptake of the productive experiments 1 and 2 in Fig. 1, it is also evident that the experiments proceed in a very similar fashion. After a short period required for pressurization – caused by saturation of the solvent with ethylene and filling the remaining reactor headspace – a practically constant ethylene uptake was observed in both experiments over the entire reaction time, thus indicating a constant reaction rate with no significant catalyst deactivation.



**Fig. 1** **1**/ $\text{Cr}(\text{acac})_3$ /DoTriMAC/TEAL/solvent system at 50°C, 30 bar.

**Table 1.** Solvent dependency of the **1**/ $\text{Cr}(\text{acac})_3$ /DoTriMAC/TEAL oligomerization system.

Exp. No	Solvent	Product [g]	Productivity [kg/(g <sub>Cr</sub> ·h)]	Polyethylene [wt %]	C6 (1-C6) [wt %, %]	C8 (1-C8) [wt %, %]	1-C6 + 1-C8 [wt %]
1 <sup>a</sup>	toluene	73.6	44	0.3	92.2 (99.0)	0.4 (65.8)	91.3
2	fluorobenzene	61.5	41	0.3	87.6 (98.4)	2.2 (21.2)	86.4
3	bromobenzene	2.3	1	3.0	80.8 (97.6)	10.4 (2.4)	76.7
4	1-chlorohexane	1.8	1	13.1	23.0 (91.8)	11.8 (1.0)	20.9
5	chlorocyclohexane	7.2	3	1.7	81.3 (98.2)	12.0 (1.9)	73.1

Conditions:

100 mL solvent, 30 μmol  $\text{Cr}(\text{acac})_3$ , 1.2 eq ligand, 8 eq. DoTriMAC, 24 eq TEAL, 50°C, 30 bar ethylene, 60 min. <sup>a</sup> 64 min.

## Studies using methylaluminoxanes as co-catalysts

From recent publications<sup>7a,9</sup> it is known that the application of aluminoxanes with  $\text{Cr}(\text{acac})_3$  and  $\text{Ph}_2\text{PN}(\text{iPr})\text{P}(\text{Ph})\text{N}(\text{iPr})\text{H}$  (**1**) yields 1-octene as the most abundant oligomeric product. Therefore, the previously discussed system was modified through replacing TEAL/DoTriMAC with the modified methylaluminoxane MMAO-3A. Since aluminoxane activators are usually applied in higher excess<sup>11a,b</sup> than TEAL, the number of equivalents was initially set to a rather high value of about 700. Lowering this value to 500 or 300 did not appear to have a significant effect on the reactions. Therefore, the number of aluminoxane equivalents was kept at 300. A solvent study is summarized in Table 2.

**Table 2.** Solvent dependency of the  $1/\text{Cr}(\text{acac})_3/\text{MMAO-3A}$  oligomerization system.

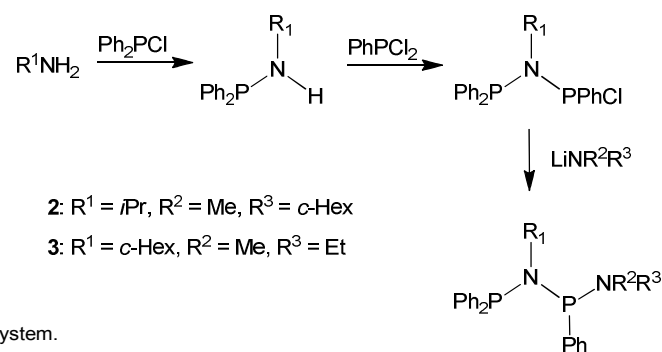
Exp. No	Solvent	Product [g]	Productivity [kg/(g <sub>Cr</sub> -h)]	Polyethylene [wt %]	C <sub>6</sub> (1-C <sub>6</sub> ) [wt %, %]	C <sub>8</sub> (1-C <sub>8</sub> ) [wt %, %]	1-C <sub>6</sub> + 1-C <sub>8</sub> [wt %]
6	toluene	7.5	5	4.6	28.7 (78.3)	61.8 (97.4)	78.8
7	chlorobenzene	48.4	31	3.7	46.2 (92.9)	46.0 (99.0)	85.1
8	o-dichlorobenzene	75.8	50	3.5	44.3 (83.9)	46.7 (99.1)	84.1
9	fluorobenzene	41.9	27	5.8	41.7 (88.0)	49.8 (98.5)	80.8
10	p-fluorotoluene	28.5	18	8.7	45.4 (88.3)	49.3 (97.5)	80.5

Conditions: 100 mL solvent, 30 μmol  $\text{Cr}(\text{acac})_3$ , 1.2 eq ligand, 300 eq. MMAO-3A, 50°C, 30 bar ethylene, 60 min.

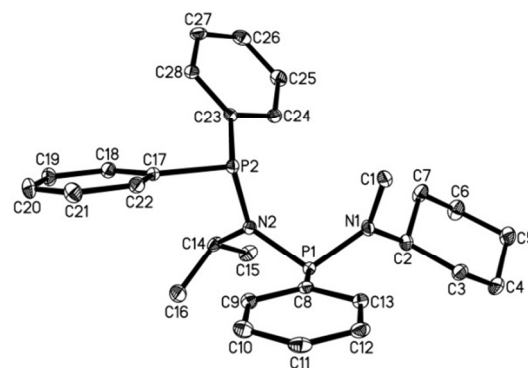
It is evident that all systems produced a considerable amount of 1-octene. In general, the 1-octene content of the C<sub>8</sub> fraction was very high (97-99%). It always significantly exceeded the corresponding 1-hexene purity, which nevertheless remained at a high level (78-93%). The two main byproducts within the C<sub>6</sub> fraction, appearing in a 1:1 ratio were identified as methylenecyclopentane and methylenecyclopentane (see SI for the GCs of two typical runs of the product distribution of all runs). The mechanism of the formation of these cyclic byproducts is interesting, especially as methylenecyclopentane is not a stoichiometric oligomer of ethylene. For the SASOL PNP selective oligomerization system it was assumed that starting from the metallacycloheptane a rearrangement competing with 1-hexene liberation leads to a chromium cyclopentylmethyl hydride species.<sup>12</sup>

The applied solvents apparently influence the activity tremendously. The results using toluene were unexpected and differ clearly. A quite low activity is connected with the highest percentage of C<sub>8</sub> fraction. Concerning the SASOL oligomerization system the formation of a cationic  $[\text{Cr}(\text{I}(\text{toluene})_2)]^+$  sandwich complex under reaction conditions was discussed as deactivation route.<sup>13a-c</sup> However, the biggest part of the ethylene consumption for most reactions took place during the first 10-15 minutes. After this time the ethylene uptake is considerably reduced, indicating a rapid catalyst deactivation. Only in o-dichlorobenzene the ethylene uptake is almost constant for one hour resulting in the highest productivity. Since the deactivation is supposed to be related to the degradation of the active species – in which the ligand is likely to be the most delicate element – new ligands with a PNP motif without a NH-group were investigated. The synthesis of these compounds is carried out stepwise allowing a wide range of substitution patterns (Scheme 1).

**Scheme 1.** Synthesis of compounds with a PNP motif.



Synthesis details are given in the supporting information. The structure of the ligand **2** was determined by X-ray crystallography. The asymmetric unit contains two molecules with only one of them depicted (Fig. 2).



**Fig. 2.** Molecular structure of  $\text{Ph}_2\text{PN}(\text{iPr})\text{P}(\text{Ph})\text{N}(\text{c-Hex})(\text{CH}_3)$  (**2**) with thermal ellipsoids set at 30% probability. All hydrogen atoms have been omitted for clarity. Important bond lengths [Å] and angles [deg]: P1-N1 1.679(2), P1-N2 1.719(2), P2-N2 1.716(2), N1-P1-N2 109.43(8), P1-N2-P2 123.16(9).

The ligands **2** and **3** were investigated using  $\text{Cr}(\text{acac})_3$  together with MMAO-3A in two different solvents (Table 3). The product distribution is similar to the experiments with ligand **1**, but polymer formation is comparatively low. Generally, a high C<sub>6</sub>/C<sub>8</sub>-ratio entails a high C<sub>10</sub>/C<sub>12</sub>-ratio and vice versa, since C<sub>10</sub> and C<sub>12</sub> olefins are known to be formed by co-

**Table 3.** Solvent dependency of the **2** and **3**/Cr(acac)<sub>3</sub>/MMAO-3A oligomerization systems.

Exp. No	Ligand	Solvent	Product [g]	Productivity [kg/(g <sub>Cr</sub> ·h)]	Polyethylene [wt %]	C <sub>6</sub> (1-C <sub>6</sub> ) [wt %, %]	C <sub>8</sub> (1-C <sub>8</sub> ) [wt %, %]	1-C <sub>6</sub> + 1-C <sub>8</sub> [wt %]
11	<b>2</b>	toluene	17.5	23	0.4	32.9 (94.0)	61.2 (99.3)	91.4
12 <sup>a</sup>	<b>2</b>	chlorobenzene	73.2	220	0.2	35.4 (94.6)	52.9 (99.2)	85.9
13 <sup>b</sup>	<b>3</b>	toluene	16.0	34	1.5	31.3 (87.5)	64.5 (98.6)	89.6
14 <sup>c</sup>	<b>3</b>	chlorobenzene	65.7	421	1.0	35.0 (92.6)	56.9 (99.3)	88.0

Conditions: 100 mL solvent, 15 μmol Cr(acac)<sub>3</sub>, 1.2 eq ligand, 300 eq. MMAO-3A, 50°C, 30 bar ethylene, 60 min.  
<sup>a</sup> 7.5 μmol Cr(acac)<sub>3</sub>, 51 min. <sup>b</sup> 9 μmol Cr(acac)<sub>3</sub> <sup>c</sup> 3 μmol Cr(acac)<sub>3</sub>

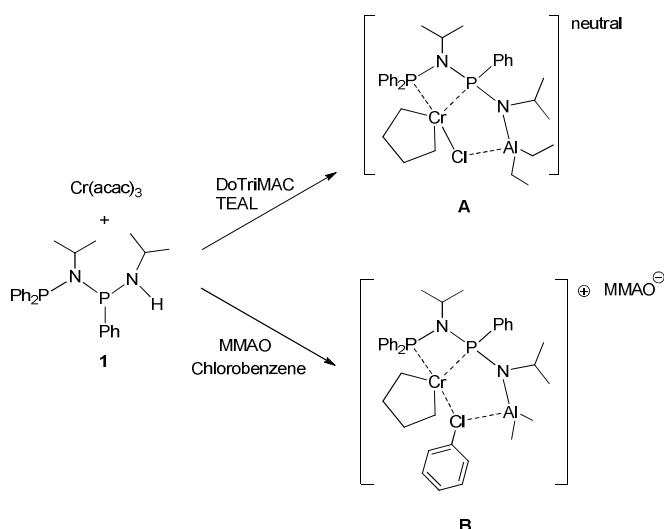
oligomerization (see SI for a more detailed description of the product distribution of all runs). In chlorobenzene the productivities are much higher than in toluene. The systems show almost stable reaction rates within one hour.

## Conclusions

This study comprises a screening of homogenous ethylene oligomerization systems using Cr(acac)<sub>3</sub> together with one of three aminophosphine ligands (**1-3**) and an aluminium alkyl activator (TEAL or MMAO) in different solvents. Only **1** shows high trimerization rates when TEAL is used as co-catalyst. This highly selective trimerization system can be switched to a selective tri- and tetramerization catalyst by using a modified methylaluminoxane. The aluminoxane activated systems containing **1** suffer from deactivation and high polymer formation, whereas the ligands **2** and **3** yield systems with almost stable reaction rates, high productivity values in the range of several hundred kg product per gram chromium and hour and considerably less polymer.

However, the strong influence of the solvent indicates that the solvent might be a part of the active species. Based on the observations described here and our previous work,<sup>7h</sup> the following considerations with respect to the active species, formed in the presence of **1** appear likely (Scheme 2).

**Scheme 2.** Assumed active species for the trimerization (A) and tri- and tetramerization (B) of ethylene formed from **1** under different conditions.



The N-H group of **1** is deprotonated and metallated by the aluminium alkyl activators. Cr(acac)<sub>3</sub> is reduced to lower oxidation states and coordinates to the phosphor atoms. Metallacyclopentanes are formed by oxidative coupling of two ethylene molecules. Whereas in the presence of a chloride source a neutral species with a chromium-chloride-aluminum motif is formed (A), the presence of the methylaluminoxane results in the formation of cationic species (B) maybe stabilized by the coordination of a chlorinated solvent.

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