Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS

Accepted Article

Title: Chromium Catalyzed Highly Selective Oligomerization of Ethene to 1-Hexene with N,N-bis{chloro(aryl)-phosphino}-amine Ligands

Authors: Uwe Rosenthal, Martha Höhne, Normen Peulecke, Katharina Konieczny, and Bernd Harald Müller

To be cited as: *ChemCatChem* 10.1002/cctc.201700448

Link to VoR: http://dx.doi.org/10.1002/cctc.201700448

A Journal of
ChemPubSoc Europe

WILEY-VCH

www.chemcatchem.org

Chromium Catalyzed Highly Selective Oligomerization of Ethene to 1-Hexene with N,N-bis{chloro(aryl)-phosphino}-amine Ligands

Martha Höhne,[a] Normen Peulecke,[a] Katharina Konieczny,[a] Bernd H. Müller[a] and Uwe Rosenthal*[a]

In memory of Günther Wilke (passed away december 9, 2016).

Abstract: Different N,N-bis{chloro(aryl)-phosphino}-amines were synthesized and characterized. All synthesized compounds were tested as ligands in the chromium catalyzed oligomerization of ethene. The dependence of successively increasing the steric bulk either at one of the phosphorus´ substituents or at the nitrogen center on the product distribution of the oligomerization reaction was examined. We found a highly active and selective trimerization system with purities of the hexene fraction up to 99.9 % of 1-hexene. Furthermore we suppose an *in situ* methylation of the chlorinated ligands into the corresponding N,N-bis{methyl(aryl)-phosphino}-amines.

Introduction

Linear alpha olefins (LAOs) are useful and versatile intermediates for many industrially important substances like co-monomers for high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), surfactants for detergents, base stock and additives for synthetic lubricants or alcohols for plasticizers. Since the conventional technologies for producing LAOs result in a Schulz-Flory or Poisson product distribution whose purification is very cost-intensively the demand for the development of alternative selective catalyst systems is immense.[1] A selective trimerization of ethene was first described by Manyik *et al*. at Union Carbide Corporation in the late 1960s.[2] Thereupon a multitude of selective oligomerization systems were invented and investigated in order to produce LAOs which match the market demand. A lot of these systems lack of sufficient activity combined with highest selectivity to 1-hexene (1-C6). High purities of the hexene (C6) fraction is essential for the use of 1-hexene as comonomer. Herein we present a P-N-P based ligand class that leads to high C6 percentages with very high purities within the hexene fraction. Moreover a correlation between the ligands structure and the product distribution in the catalyzed oligomerization reaction could be observed.

[a] M. Höhne, Dr. N. Peulecke, K. Konieczny, Dr. B. H. Müller, Prof. U. Rosenthal*
Leibniz Institute for Catalysis at the University of Rostock
Albert-Einstein-Str. 29A, 18059 Rostock (Germany)
E-mail: uwe.rosenthal@catalysis.de

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

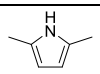
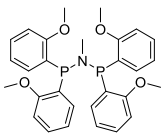
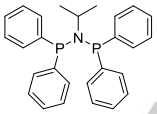
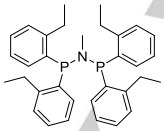
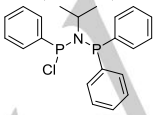
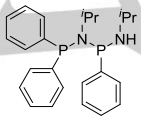
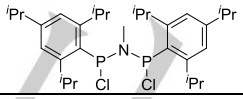
Results and Discussion

The most important systems for the homogeneously catalyzed selective oligomerization of ethene are illustrated in Table 1 and compared to the new system we present herein. For better comparability all systems discussed are based on a chromium source and activated with methylaluminoxane, commonly called MAO except the one of Chevron Phillips. The Phillips ethylene oligomerization catalyst is the pioneer in the field of selective trimerization and was developed during the 1980´s. It consists of a chromium source, a 2,5-dimethylpyrrole ligand, $AlEt_3$ as cocatalyst and a modifier. In comparison to a non-selective Schulz-Flory distribution the product mixture contains up to 90% C6, unfortunately nothing is said concerning the purity of the hexene fraction.[1a, 3] In 2002 Wass *et al*. at BP chemicals discovered P-*ortho*-methoxyaryl diphosphinoamines to be excellent ligands for trimerization catalysts in combination with $CrCl_3(THF)_3$ and a large excess of MAO as cocatalyst in toluene. The Wass system achieved high activities and an 1-hexene purity within the C6 fraction above 99.9 Wass assumed the *o*Me group at the aryl substituent to act as a pendant donor to the chromium center.[4] Later on Bollmann *et al*. at Sasol found the possibility to switch the Wass system towards octene (C8) when omitting the *ortho* methoxy group. The combination of the $N^iPr(PPh_2)_2$ ligand, $CrCl_3(THF)_3$ and MAO as cocatalyst leads to 32.7 % C6 (86.5 % 1-C6) and 60.6 % octene (99.2 % 1-C8).[5] As reported by Blann and Overett *et al.* at Sasol *ortho* alkyl substituted derivatives (without donor functionality) proved to be highly active and selective towards ethene trimerization (93 % C6; 99.8 % 1-C6) when combined with $CrCl_3(THF)_3$ and MAO. They claimed that the sterical demand of the aryl substituents in $Ar_2PN(R)PAr_2$ has an effect on the product distribution.[6] McGuinness and coworkers took up the ideas of pendant donor functionalities as well as encumbered ligands and performed theoretical and experimental investigations. They could find a relation between additional donors at the ligands or different coordinating anions as well as steric bulk and the selectivities in the oligomerization reaction.[7] Even NOVA Chemicals developed a oligomerization system based on a PNP type ligand similar to the $(Ph)_2PN(^iPr)P(Ph)_2$ of Sasol differing in that at least one halide substituent is directly bound to at least one phosphorus atom of the ligand. Their catalyst system results in a mixture of C6 (20-40 %) and C8 (35-75 %) and reaches purities above 95 % within in the 1-olefin fractions.[8] The group of Rosenthal *et al*. in an association with SABIC and Linde succeeded in developing another highly selective trimerization system using a PNPNH ligand, which is used in combination

with $Cr(acac)_3$. In dependence on the cocatalyst it is possible to change the product distribution and the purity of its fractions. It is possible to reach 92.2 % C6 containing 99.0 % 1-C6 when using $AlEt_3$.[9]

Now we could shows that a diphosphinoamine ligand neither requires two sterical demanding substituents nor a chlorine atom at the phosphorus centers of for a highly active

Table 1. Different catalyst systems for the selective oligomerization of ethylene.

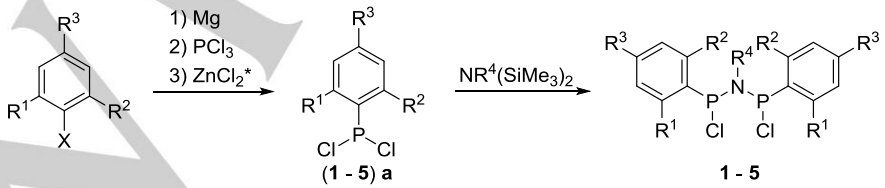
company	year	catalyst, cocatalyst	ligand	product distribution	purity of fraction
Chevron Phillips[1a, 10]	1990´s	Cr-source; $AlEt_3$		> 90 % C6	n.d.
BP[4]	2002	$CrCl_3(THF)_3$; MAO		91.5 % C6	99.7 % 1-C6
Sasol[5-6]	2004	$CrCl_3(THF)_3$; MAO		C6/C8 (32.7 % /60.6 %)	86.5 % 1-C6/ 99.2 % 1-C8
	2004	$CrCl_3(THF)_3$; MAO		93.0 % C6	99.8 % 1-C6
NOVA Chemicals[8]	2012	Cr-source, MAO		C6/C8 (20-40 % C6/ 35-75 % C8)	> 95 %
SABIC, Linde[9, 11]	2015	$Cr(acac)_3$; MAO		C6/C8 (28.7 % /61.8 %)	78.3 % 1-C6/ 97.4 % 1-C8
		$Cr(acac)_3$; $AlEt_3$*		C6/C8 (92.2 % /0.4 %)	99.0 % 1-C6/ 65.8 % 1-C8
herein	2016	$Cr(acac)_3$; MMAO		94.7 % C6	99.9 % 1-C6

* With addition of 8 eq. DoTriMAC (dodecyltrimethylammonium chloride).

and selevtive trimerization catalyst system. To date there is no system with such an extraordinary C6 selectivity and high 1-hexene purity within it.

The ligands reported in this study are shown in Scheme 1 and were prepared as reported previously by Rosenthal *et al*. and references therein.[12] Dichloroarylphosphanes **2a** – **4a** were made by reacting the aryl halide with magnesium in THF. The resulting Grignard reagents were treated with a large excess of phosphorus trichloride to avoid multiple substitution of the PCl_3.

As starting with the aryl bromide compound **3a** requires an additional halogen exchange with $ZnCl_2$ to convert the $ArPX_2$ (X = Cl, Br) species into the bis-chloroarylphosphine. Due to the extended substituents at the aryl part, the reaction with heptamethyldisilazane proceeded very slowly. To avoid high reaction temperatures, which cause several byproducts, DMF was used as solvent.



ligand	R^1	R^2	R^3	R^4	bond angle [°] P-N-P
1	H	H	H	Me	111.72(8)
2	Me	Me	H	Me	
3	Me	Me	Me	Me	
4	^{i}Pr	^{i}Pr	^{i}Pr	Me	124.75(11)
5	H	H	H	Cy	120.52(6)

Scheme 1. Preparation of compounds **1**-**5** and structural data of **1**, **4**, **5** based on Rosenthal *et al*.[11] *When starting with the bromide (in case of **3a**) an additional halogen exchange with $ZnCl_2$ is necessary to avoid mixtures of the Cl/Br and Br/Br species.

Table 2. Ethene oligomerization using ligands **1**-**5** under different parameters.

Exp.no. (Ligand)	solvent	t [min]	Products [g]	activity [kg/(g_{Cr}*h)]	C4	C6 (1-C6)	C8	C10+	solid [g]
1 (**1**)	toluene	60	0	0.0	n.d.	n.d	n.d.	n.d.	-
2 (**1**)	chlorobenzene	60	20	19.2	4.4	26.4 (48.0)	50.6 (98.4)	18.6	1.20
3 (**2**)	toluene	60	25	24.0	1.6	86.9 (99.4)	2.5 (98)	9.0	0.45
4 (**2**)	chlorobenzene	40	80	115.4	0.8	89.4 (99.4)	3.1 (99+)	6.4	2.60
5 (**3**)	toluene	60	35	33.7	1.4	86.9 (99.4)	2.8 (99+)	8.9	0.40
6 (**3**)	chlorobenzene	30	80	153.9	0.9	89.6 (99.4)	3.1 (99+)	6.4	1.80
7 (**3**)[A]	chlorobenzene	60	70	67.3	1.0	86.5 (99.2)	7.1 (99)	5.4	2.0
8 (**3**)[B]	toluene	60	50	48.1	0.3	92.0 (99.1)	2.2 (99)	5.5	7.5
9 (**4**)	toluene	32	80	144.3	0.9	94.7 (99.9)	0.3 (99+)	4.1	0.45
10 (4)	**chlorobenzene**	**30**	**80**	**153.9**	**0.8**	**93.5 (99.9)**	**0.2 (99+)**	**5.5**	**2.45**
11 (**4**)*	toluene	60	77	74.1	0.7	94.1 (99.9)	0.3 (99+)	4.9	0.38
12 (**4**)*	dichlorobenzene	60	88	84.6	0.6	92.2 (99.9)	0.3 (99+)	6.9	2.20
13 (**4**)*[A]	toluene	90	60	38.5	1.0	94.6 (99.8)	0.5 (99+)	3.9	0.9
14 (**4**)*[B]	toluene	60	15	14.4	2.1	92.2 (99.8)	0.9 (99+)	4.8	10.0
15 (**4**)*[C]	toluene	90	40	25.7	1.1	93.4 (99.7)	0.3 (99+)	5.2	0.25
16 (4)*[D]	**toluene**	**30**	**80**	**153.9**	**0.8**	**95.4 (99.8)**	**0.3 (99+)**	**3.5**	**0.57**
17 (**5**)	toluene	60	0	0.0	n.d.	n.d	n.d.	n.d.	-
18 (**5**)	chlorobenzene	60	45	43.3	2.8	30.6 (59)	57.9 (98)	8.7	0.7
19 (**6**)	toluene	25	80	184.3	0.6	94.1 (99.9)	0.4 (99+)	4.9	1.20

C4, C6, C8, C10+ wt% in the liquid fraction; standard reaction conditions are: p_{ethene} = 30 bar, T = 50 °C, co-catalyst = 4.0 mL MMAO-3A (7 wt% Al in *n*-heptane), 96.0 mL solvent, [Cr] = 0.002 mmol/L, [Ligand]/[Cr] = 1.5, [Al]/[Cr] = 375 *ligand with Cl/Br-isomers. A) 30°C, B) 75 °C, C) 15 bar, D) 40 bar.

The polar aprotic solvent increases the S_N2 reaction rate as it stabilizes the nucleophilic character of the intermediate. Thus the reaction temperature could be dramatically decreased from 140 °C for **1**[13] without solvent down to 60 °C for **2** and **3** in DMF and it was possible to isolate them in moderate yields. To investigate the effect of varying the surrounding at the nitrogen, compound **5** was prepared as published by Rosenthal *et al*.[12a]

The molecular structure of **1**, **4** and **5** could be obtained and were discussed in a former publication.[12a] Neither the increase of the sterical demand at the phosphorus atoms nor the insertion of space filling substituents at the nitrogen center led to a smaller P-N-P angle when compared to **1**. Both angles (Scheme 1 ligand **4** and **5**) are obviously widened.

All compounds **1**-**5** were tested in oligomerization reaction of ethene according to a standard procedure (see experimental part). Table 2 presents the results of the catalyzed selective oligomerization under different parameters (p, T, solvents).

In toluene ligand **1** does not show any activity at all. Switching the solvent to chlorobenzene could effect an increase in activity and leads to a mixture of C6 (26.4 %, 48.0 % 1-C6) and C8 (50.6 %, 98.4 % 1-C8).

With respect to prior investigations the sterical demand of one substituent at the phosphorus was raised and its effect on the catalysis reaction was examined. Thereby it was possible to observe a correlation between the catalyst´s structure and the product distribution of the oligomerization reaction.

Whereas the $(PPhCl)_2NMe$ (**1**) shows nearly no activity and accordingly leads to a product mixture of C6/C8 in chlorobenzene (exp. no. 2), the insertion of even *ortho*-methyl groups at the P-aryl substituent (**2**) causes a tripling of the 1-C6 percentage (in chlorobenzene from 26.4 up to 89.4 %) as well as a sixfold activity (from 19.2 kg/g_{Cr}*h up to 115.4 kg/g_{Cr}*h) and a remarkable increase in the purity of the 1-olefin fraction (48.0 % up to 89.4 % 1-C6).

The successive increase of sterical bulk at the aryl substituents provokes a continuous shift towards 1-C6 which climaxes in a maximum for ligand **4** in exp. no. 9, 10 and 16. Ligand **4** seems

to act as part of a very active catalyst which procures C6 percentages up to 95.4 % and purities up to 99.9 % 1-C6.
According to NOVA Chemicals there must be at least one chlorine bound to at least one phosphorus center to be essential for the trimerization reaction.[8] Due to the very similar product contributions (in range of 92.2 to 95.4 % C6) and purities within the C6 fractions (1-C6 > 99.7 %) when using mixed halides (**4***) we claim an *in situ* conversion of the N,N-bis{chloro(aryl)-phosphino}-amines into the methylated species due to the large excess of cocatalyst (MMAO). These N,N-bis{methyl(aryl)-phosphino}-amines would belong to the actually active catalyst species in the oligomerization reaction of ethene.

4 **6**

Scheme 2. Preparation of **6** by reacting **4** with a methyl Grignard reagent.[11]

To prove this hypothesis ligand **6** was prepared directly by the reaction of **4** with the methyl Grignard (see Scheme 2). It was tested using the standard procedure and showed a very similar product contribution (94.1 % C6) and purities (99.9 % 1-C6) within the C6 fractions when compared to ligand **4**.
Compared to the dichloro compound **4** the corresponding ^{31}P NMR resonances of the methylated analogue **6** are round about 100 ppm highfield shifted (from 140/138 to 49/41 ppm).
When adding some MMAO - as it is used in the standard procedure – to **4**, we are able to observe an equivalent highfield shift (see Figure 1) what might be caused by the reaction with the cocatalyst MAO. Due to the inhomogeneous nature of MAO especially MMAO-3A (modified MAO containing differently alkylated species) there exist different alkylated species of **4**. Both, the broadening and shifting of the signals (when compared to pure **6** in deuterated solvent) ought to be a consequence of coordination to the aluminium centers as it can be shown by adding some MMAO to **6**.

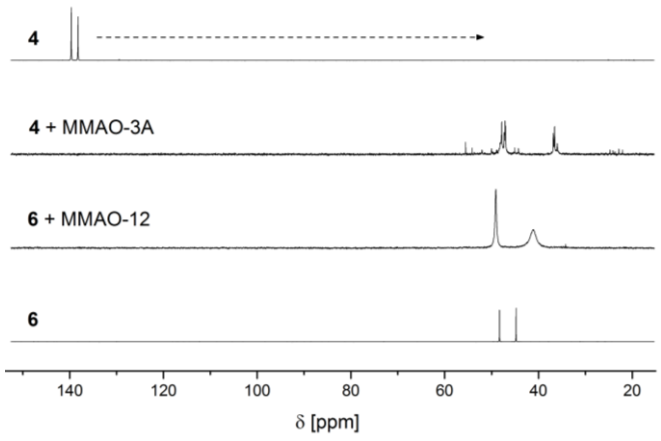


Figure 1. Comparison of the ^{31}P NMR spectra of **4** and **6**, respectively (with and without addition of MMAO).

These data as well as the very similar results in the oligomerization reaction support our assumption of the *in situ* methylation.
The activities exhibits a larger range (from 14.4 to 153.9 kg/(g_{Cr}*h)) when using **4** or **4*** in the oligomerization reaction. This probably depends on several parameters e.g. on the solvent, temperature or the halides within the catalytic system. Chlorinated solvents generally lead to somewhat higher activities, what has already been investigated as a halide effect. Suitable halide compounds could significantly enhance both, the selectivity towards 1-C6 and the catalytic activity.[14] Furthermore chlorides do obviously show a more positive effect on the catalytic activity than their corresponding bromides or iodides.

This could explain the lower activities when using the mixed halogenated ligand **4**. Furthermore the *in situ* methylation of the different halides (**4** and **4***) might take place with different reaction rates and yields what can impact the concentration of the active catalyst species ant therefor on the activity.
An enlargement of the steric bulk at the nitrogen´s substituent has already been discussed to have an effect on the alpha selectivity or even to increase 1-C6 selectivity.[15] In order to compare the effect of increasing the bulkiness at the phosphorus (**1**-**4**, **6**) to that at the nitrogen, compound **5** was prepared and tested in the oligomerization reaction. As depicted in Table 2 **5** shows no activity all when the catalysis is performed in toluene. If the same experiment was run in dichlorobenzene it results in a C6/C8 (30.6 % C-6/ 57.9 % C-8) mixture with low activity. These values resemble the C6/C8 ratios and activity of exp. 2 when applying the unsubstituted ligand **1**. Accordingly, the more space filling N-substitution could not be identified to be responsible for the product distribution in the oligomerization experiment.
Furthermore, the ability of the PNP ligands to bridge two metal centers was postulated to allow a binuclear mechanism which would be reasonable for the tetramerization of ethene by Rosenthal[16] and Gambarotta *et al*.[17] Due to the large sterical demand of the herein reported ligands there might be not enough space to allow a binuclear catalyst species and leads to C6 instead. McGuinness and coworkers presented a mono- and bis-ethylene route: the increasing demand of the ligands hinders the coordination of further ethene monomers what rather leads to 1-hexene.[7, 18]

Conclusion

In contrast to other publications which discuss a necessity of a hemilabile donor ligand (oMe etc.) in *ortho* position of the P-aryl group,[4, 6b] the presence of two space filling *ortho* substituted aryl substituents at the phosphorus centers[6a] or a chlorine bound at least to one phosphorus[8] we could reveal that one sterically demanding substituent per phosphorus center is sufficient for excellent 1-C_6 selectivity. Even the chlorine does not have to be bonded to the phosphorus as it could be shown by means of the catalyzed trimerization reaction under use of the methylated ligand **6** as well as the mixed halide species **4***. Besides the very similar activities of **4**, **4*** and **6** indicates an *in*

situ methylation and thus, the N,N-bis{methyl(aryl)-phosphino}-amines to be part of the active species in the catalysis reaction.

Experimental part

All synthetic work was carried out under oxygen- and moisturefree conditions using standard Schlenk and Glovebox techniques. THF, *n*-hexane and toluene were purified with a Grubbs type column system Pure Solv MD-5. Deuterated solvent C_6D_6 was dried over Na/benzophenone and freshly distilled prior to use. Other chemical reagents and solvents were obtained from commercial sources and used without further purification. *NMR:* $^{31}P\{^1H\}$, $^{13}C\{^1H\}$- and ^1H-NMR spectra were recorded on BRUKER spectrometers AVANCE 300 and AVANCE 400, respectively. The ^1H and ^{13}C NMR chemical shifts were referenced to the solvent signals (C_6D_6). The ^{31}P NMR chemical shifts are referred to H_3PO_4 (85%). *Elemental analysis*: C, H, N: Leco TruSpec Micro CHNS Elementaranalysator. P: ICP-OES Varian/Agilent 715-ES. *IR*: Bruker Alpha FT-IR. *MS*: Thermo Electron MAT 95-XP (CI, EI). *Melting Points* are uncorrected (Mettler Toledo MP70). Heating-rate 3 °C min^{-1} (unless otherwise stated the clearing points are reported.)

Synthesis of $C_{12}H_{12}Cl_2NP_2$ (1): The synthesis was done according to Jefferson *et al*.[13] For description and characterization see Rosenthal *et al*.[12a]

Synthesis of $C_{17}H_{21}Cl_2NP_2$ (2): The reaction was held in several steps. 1) 2-chloro-1.3-dimethylbenzene (3.000 g. 0.021 mol) and 1.1 eq. of magnesium (0.563 g. 0.023 mol) were refluxed in THF (50.0 mL) for 1 day. 2) After cooling to room temperature the resulting solution was filtered via cannula to a cooled solution (-78°C) of 10 eq. of PCl_3 (18.4 mL. 0.210 mol) in THF. The resulting solution was allowed to warm up to room temperature overnight. After removing the solvent in vacuum the resulting residue was extracted with *n*-hexane. Afterwards the Ar-PCl_2 could be crystallized from *n*-hexane. Yield: 3.203 g (0.015 mol, 74 %). 3) The isolated Ar-PCl_2 was added to a solution of 0.5 eq. of $MeN(SiMe_3)_2$ (1.7 mL. $7.77\cdot10^{-3}$ mol) in DMF and heated at 60°C. After 3 days the DMF was removed in vacuum. The resulting residue was dissolved in hot *n*-hexane, filtrated and cooled to -78°C. A white solid precipitated and could be isolated. It was recrystallized from *n*-hexane. Compound **2** was obtained as a diastereomeric mixture (ratio 39:61). Yield (NMR): 76 %; yield (isolated): 1.670 g ($4.51\cdot10^{-3}$ mol, 58 %). Yield overall: 1.670 g ($4.51\cdot10^{-3}$ mol, 42 %). ^1H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) 6.99-6.91 (m, 2H, *p*-Ar*H*), 6.81-6.74 (m, 4H, *m*-Ar*H*), 2.69 (t, $^2J_{HP}$ = 6.0 Hz, 3H, NCH_3, major isomer), 2.69 (t, $^2J_{HP}$ = 5.5 Hz, 3H, NCH_3, minor), 2.58 (br s, 12H, *o*-ArCH_3, minor), 2.55 (br s, 12H, *o*-ArCH_3, major). ^{13}C (100 MHz, C_6D_6, 298 K): δ (ppm) 143.2 (*i*-Ar*C*), 133.2 (*o*-Ar*C*), 131.3 (*m*-Ar*C*, minor), 131.2 (*m*-Ar*C*. major), 130.4 (*p*-Ar*C*), 35.8 (NCH_3), 23.5 (*o*-ArCH_3, minor), 23.3 (*o*-ArCH_3. major). ^{31}P (162 MHz, C_6D_6, 298 K) δ (ppm) 139.6 (minor), 139.3 (major). IR (neat, cm^{-1}, 298 K): ν = 2867 (w), 2928 (w), 2969 (w), 2997 (w), 3052 (w). MS (CI): *m/z* 323 $[C_{16}H_{18}ClNP_2+2]^+$, 171 $[C_8H_9ClP]^+$. Element. Anal. Calcd. for $C_{17}H_{21}Cl_2NP_2$ (372.21 g/mol): C 54.86, H 5.69, N 3.76, P 16.64. Found: C 54.83, H 5.69, N 3.82, P 16.78. M.p.: 147 °C.

Synthesis of $C_{19}H_{25}Cl_2NP_2$ (3): The synthesis was done in three steps. 1) Mes-Br (7.59 g. 0.038 mol) was added to a stirred suspension of 1.1 eq. Mg (1.000 g. 0.040 mol) in THF (40.0 mL). The resulting mixture was stirred until the magnesium chips have almost vanished. 2) The grey green coloured solution was filtered via cannula to a cooled solution (-78 °C) of 10 eq. PCl_3 (33.30 mL. 0.380 mol) in THF (40.0 mL). The stirred solution became yellow and was allowed to warm to room temperature overnight. Afterwards the THF was removed in vacuum and the resulting residue was extracted with *n*-hexane to get rid of the magnesium salt. After evaporation of the *n*-hexane. the intermediate product, Mes-PXY (X= Cl, Br. Y= Cl, Br), was redissolved in THF. In order to isolate the chlorinated product, a halogen exchange was done by adding an excess of $ZnCl_2$ (12.000 g. 0.088 mol). It was stirred overnight at 60 °C before the THF was removed and the residue was extracted with *n*-hexane. After removing the solvent in vacuum the product was purified by distillation ($1\cdot10^{-2}$ mbar. 250 °C) (Yield: 2.240 g. 0.001 mol. 26 %). 3) The Mes-PCl_2 (2.240 g. 0.010 mol) was dissolved in DMF (50.0 mL). 0.5 eq. of $MeN(SiMe_3)_2$ (0.860 g. 0.005 mol) was added. The solution was stirred for 2 days at 50 °C before the solvent was removed in vacuum. The residual oil was extracted twice with *n*-hexane and the product was precipitated as a white solid at – 78°C. Compound **3** was obtained as a diastereomeric mixture (ratio 41:59). Yield (isolated): 1.038 g ($2.60\cdot10^{-3}$ mol, 52 %). Yield overall: 1.038 g ($2.60\cdot10^{-3}$ mol, 7 %).^1H NMR (300 MHz, C_6D_6, 298 K): δ (ppm) 6.65-6.59 (m, 4H, *m*-Ar*H*), 2.78 (t, $^2J_{HP}$ = 5.9 Hz, 3H, NCH_3. major), 2.72 (t, $^2J_{HP}$ = 5.7 Hz, 3H, NCH_3. minor), 2.62 (br s, 12H, CH_3, *o*-ArCH_3, minor), 2.59 (br s, 12H, CH_3, *o*-ArCH_3, major), 1.99 (br s, 6H, CH_3, *p*-ArCH_3). ^{13}C (75 MHz, C_6D_6, 298 K): δ (ppm) 143.2 (*i*-Ar*C*), 141.3 (Ar*C*H), 141.1 (Ar*C*H), 131.2 (*p*-Ar*C*), 35.6 (NCH_3), 23.4 (CH_3), 20.9 (CH_3). ^{31}P (121 MHz. C_6D_6, 298 K): δ (ppm) 140.6 (minor), 139.9 (major). IR (neat, cm^{-1}, 298 K): ν = 2869 (w), 2922 (m), 2961 (m), 2995 (w), 3022 (w). MS (CI): *m/z* 400 $[C_{19}H_{25}Cl_2NP_2]^+$, 384 $[C_{18}H_{22}Cl_2NP_2]^+$, 364 $[C_{19}H_{25}ClNP_2]^+$, 216 $[C_{10}H_{14}ClNP+2]^+$, 180 $[C_{10}H_{14}NP+1]^+$. Element. Anal. Calcd. for $C_{19}H_{25}Cl_2NP_2$ (399.08 g/mol): C 57.01, H 6.30, N 3.50, P 15.48. Found: C 57.09, H 6.28, N 3.51, P 15.34. M.p.: 120 °C.

Synthesis of $C_{19}H_{25}Cl_2NP_2$ (4/4*): For synthesis and characterization see Rosenthal *et al*.[12a] **4*** is the crude product before the halogen exchange with $ZnCl_2$.

Synthesis of $C_{18}H_{28}Cl_2NP_2$ (5): For synthesis and characterization see Rosenthal *et al*.[12a]

Synthesis of $C_{33}H_{55}NP_2$ (6): 0.56 mL ($1.68\cdot10^{-3}$ mol) MeMgCl (3M in THF) was added at 0°C to a stirred solution of 0.475 g ($0.84\cdot10^{-3}$ mol) of **4** in THF (10.0 mL). The solution was stirred for 48 hrs at room temperature and afterwards all volatiles were removed in vacuum. *N*-Pentane was added to precipitate $MgCl_2$. After filtration, the supernatant was stored at - 40°C for several days to give 0.222 g ($0.42\cdot10^{-3}$ mol) of colourless crystals of **6**. Compound **6** was obtained as a diastereomeric mixture (ratio 48:52). Yield: 0.222 g ($0.42\cdot10^{-3}$ mol, 50 %). ^1H NMR (300 MHz, C_6D_6, 298 K): δ (ppm) 7.15-7.05 (m, 8H, Ar*H*), 4.32-4.15 (m, 8H, iPr-C*H*), 3.31-3.21 (m, 2H, iPr-C*H*, minor), 2.81-2.65 (m, 2H, iPr-C*H*, major), 2.64 (t, $^3J_{HP}$ = 3.7 Hz, 3H, N-CH_3, minor), 2.62 (t, $^3J_{HP}$ = 6.8 Hz, 3H, N-CH_3, major), 1.71 (t, $^2J_{HP}$ = 5.4 Hz, 3H, P-CH_3, major), 1.57 (t, $^2J_{HP}$ = 5.1 Hz, 3H, P-CH_3, minor), 1.36-1.23 (m, 48H, ^{i}Pr-CH_3), 1.20-1.15 (m, 24H, ^{i}Pr-CH_3). ^{13}C (100 MHz, C_6D_6, 298 K) δ (ppm) 154.7 (*o*-Ar*C*, t, $^2J_{CP}$ = 8.0 Hz, major), 154.6 (*o*-Ar*C*, t, $^2J_{CP}$ = 7.9 Hz, minor), 150.4 (*p*-Ar*C*, major), 150.3 (*p*-Ar*C*, minor), 133.5 (*i*-Ar*C*, s, minor), 133.4 (*i*-Ar*C*, s, major), 122.2 (*m*-Ar*C*, s, minor + major), 34.9 (NCH_3, t, $^2J_{CP}$ = 5.0 Hz, minor), 32.3 (NCH_3, t, $^2J_{CP}$ = 6.2 Hz, major), 34.7 (iPr*C*H, br s, minor + major), 30.9 (*iPrC*H, t, $^3J_{CP}$ = 11.2 Hz,), 30.5 (*iPrC*H, t, $^3J_{CP}$ = 12.6 Hz, minor), 25.6 (iPrCH_3, br s), 25.4 (iPrCH_3, br s), 25.2 (iPrCH_3, br s), 24.9 (iPrCH_3, br s), 24.2-24.0 (iPrCH_3, m), 15.4 (t, $^1J_{CP}$ = 5.1 Hz, PCH_3, minor) 15.0 (t, $^1J_{CP}$ = 5.4 Hz, PCH_3, major). ^{31}P (121 MHz. C_6D_6, 298 K): δ (ppm) 48.3 (minor), 44.8 (major). IR (neat, cm^{-1}, 297 K): ν = 2798 (w), 2841 (w), 2841 (w), 2869 (m), 2930 (m), 2957 (s), 3040 (w). MS (CI): *m/z* 528 $[C_{33}H_{55}NP_2]^+$, 512 $[C_{32}H_{52}NP_2]^+$, 484 $[C_{30}H_{48}NP_2]^+$, 324 $[C_{18}H_{32}NP_2]^+$, 278 $[C_{17}H_{29}NP]^+$. Element. Anal. Calcd. for $C_{33}H_{55}NP_2$ (527,76 g/mol): C 75.10, H 10.50, N 2.65, P 11.74. Found: C 74.88, H 10.51, N 2.65, P 11.47. M.p.: 96 °C.

Standard Ethene Oligomerization Reaction was carried out as follows: A 300 ml pressure reactor, equipped with a dip tube, thermowell, gas entrainment stirrer, cooling coil, and control units for temperature, pressure and stirrer speed (all hooked up to a data acquisition system) was inertized with dry argon. The isobaric ethene supply was maintained by an aluminum pressurized gas cylinder on a balance to monitor the ethene consumption over time by means of a computerized data acquisition system. For the catalyst preparation, the suitable amounts of the ligands and the chromium precursor according to the molar ratios given in Table 2 were weighed and charged to a Schlenk tube under an

inert atmosphere. A volume of 95.0 ml anhydrous solvent was added and the solution was stirred by means of a magnetic stirrer. After dissolving the Cr-compound and ligand, the appropriate amount of a solution of MMAO-3A (7 wt% Al in heptane) was added. The solution was immediately transferred to the reactor and the reaction was started. The reaction was stopped either when the maximum uptake of ethene (80.000 g) was reached or after a predefined time (60 min) by closing the ethene inlet valve, cooling to room temperature, depressurizing and opening the reactor. The liquid product mixture was quenched with diluted HCl and analyzed using gas chromatography. The sideproduct solids (waxes, polyethylene) were filtered, dried and weighed. Before conducting an experiment, the reactor was heated to 100 °C at reduced pressure for several hours to eliminate traces of water, oxygen and oxygenated impurities.

Acknowledgements

The authors acknowledge the financial support of Saudi Arabian Basic Corporation (SABIC) and Linde Engineering Division, Pullach, Germany.

Keywords: oligomerization • ethene • chromium • diphosphinoamine • bulky

[1] a) J. T. Dixon, M. J. Green, F. M. Hess, D. H. Morgan, *J. Organomet. Chem.* **2004**, *689*, 3641–3668; b) U. Rosenthal, B. H. Müller, N. Peulecke, S. Peitz, A. Wöhl, W. Müller, in *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Three Volumes, Vol. Third Edition* (Eds.: B. Cornils, W. A. Herrmann, M. Beller, R. Paciello.), Wiley-VCH Verlag GmbH & Co. KGaA, **2017**.

[2] R. M. Manyik, W. E. Walker, T.P. Wilson, Union Carbide Corporation, USA, **1967**.

[3] a) S. Tang, Z. Liu, X. Yan, N. Li, R. Cheng, X. He, B. Liu, *Appl. Catal. A* **2014**, *481*, 39-48; b) Y. Yang, Z. Liu, R. Cheng, X. He, B. Liu, *Organometallics* **2014**, *33*, 2599-2607.

[4] A. Carter, S. A. Cohen, N. A. Cooley, A. Murphy, J. Scutt, D. F. Wass, *Chem. Commun.* **2002**, 858-859.

[5] A. Bollmann, K. Blann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. S. McGuinness, D. H. Morgan, A. Neveling, S. Otto, M. Overett, A. M. Z. Slawin, P. Wasserscheid, S. Kuhlmann, *J. Am. Chem. Soc.* **2004**, *126*, 14712-14713.

[6] a) K. Blann, A. Bollmann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. H. Morgan, A. Neveling, S. Otto, M. J. Overett, *Chem. Commun.* **2005**, 620-621; b) M. J. Overett, K. Blann, A. Bollmann, J. T. Dixon, F. Hess, Esna Killian, H. Maumela, D. H. Morgan, A. Neveling, S. Otto, *Chem. Commun.* **2005**, 622–624.

[7] G. J. P. Britovsek, D. S. McGuinness, A. K. Tomova, *Catal. Sci. Technol.* **2016**, *6*, 8234–8241.

[8] G. Xiaoliang, C. C. A. Garret, in *PCT* (Ed.: N. Chemicals), **2012**.

[9] S. Härzschel, F. E. Kühn, A. Wöhl, W. Müller, M. H. Al-Hazmi, A. M. Alqahtani, B. H. Müller, N. Peulecke, U. Rosenthal, *Catal. Sci. Technol.* **2015**, *5*, 1678–1682.

[10] D. S. McGuinness, *Chem. Rev.* **2011**, *111*, 2321-2341.

[11] A. Wöhl, U. Rosenthal, B. H. Müller, N. Peulecke, S. Peitz, W. Müller, H. Böldt, A. Meiswinkel, B. R. Aluri, M. AlHazmi, M. Al-Masned, K. Al-Eidan, F. M. Mosa, Linde A.-G., Germany; Saudi Basic Industries Corporat, **2010**.

[12] a) M. Höhne, M. Joksch, K. Konieczny, B. H. Müller, A. Spannenberg, N. Peulecke, U. Rosenthal, *Chem. Eur. J.* **2017**, *23*, 4298 – 4309; b) Among the other compounds of this type PhP(Cl)-N(Me)-P(Cl)Ph (**1**) was synthesized and published with its molecular structure in [11a]. Later the same compound was obtained and characterized independently by the group of J. Weigand: S. Yogendra, F. Hennersdorf, J. J. Weigand, *Inorg. Chem.* **2017**. Accepted Manuscript. DOI: 10.1021/acs.inorgchem.7b00141.

[13] R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat, L. Stobbs, *Dalton Trans.* **1973**, 1414-1419.

[14] a) H.-K. Luoa, D.-G. Li, S. Li, **2004**, *221*, 9-17; b) B. H. Müller, N. Peulecke, S. Peitz, B. R. Aluri, U. Rosenthal, M. H. Al-Hazmi, F. M. Mosa, A. Wöhl, W. Müller, *Chem. Eur. J.* **2011**, *17*, 6935-6938; c) S. Heinig, A. Wöhl, W. Müller, M. H. Al-Hazmi, B. H. Müller, N. Peulecke, U. Rosenthal, *ChemCatChem* **2014**, *6*, 514-521.

[15] a) K. Blann, A. Bollmann, H. d. Bod, J. T. Dixon, E. Killian, P. Nongodlwana, M. C. Maumela, H. Maumela, A. E. McConnell, D. H Morgan, M. J. Overett, M. Prétorius, S. Kuhlmann, P. Wasserscheid, *J. Catal.* **2007**, *249*, 244-249; b) N. Cloete, H. G. Visser, I. Engelbrecht, M. J. Overett, W. F. Gabrielli, A. Roodt, *Inorg. Chem.* **2013**, *52*, 2268−2270.

[16] S. Peitz, B. R. Aluri, N. Peulecke, B. H. Müller, A. Wöhl, W. Müller, M. H. Al-Hazmi, F. M. Mosa, U. Rosenthal, *Chem. Eur. J.* **2010**, *16* 7670-7676.

[17] Y. Shaikh, K. Albahily, M. Sutcliffe, V. Fomitcheva, S. Gambarotta, I. Korobkov, R. Duchateau, *Angew. Chem. Int. Ed.* **2012**, *51*, 1366 –1369.

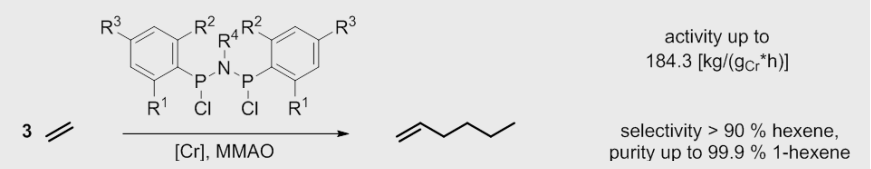
[18] G. J. P. Britovsek, D. S. McGuinness, *Chem. Eur. J.* **2016**, *22*, 16891 – 16896.

10.1002/cctc.201700448

WILEY-VCH

Layout 2:

FULL PAPER



Different N,N-bis{chloro(aryl)-phosphino}-amines were found to form highly active and selective trimerization catalysts which lead to purities of the hexene fraction up to 99.9 % of 1-hexene. Furthermore, an *in situ* methylation of the chlorinated ligands into the N,N-bis{methyl(aryl)-phosphino}-amines is supposed.

*Martha Höhne, Normen Peulecke, Katharina Konieczny, Bernd H. Müller and Uwe Rosenthal**

Page No. – Page No.

Chromium Catalyzed Highly Selective Oligomerization of Ethene to 1-Hexene with N,N-bis{chloro(aryl)-phosphino}-amine Ligands