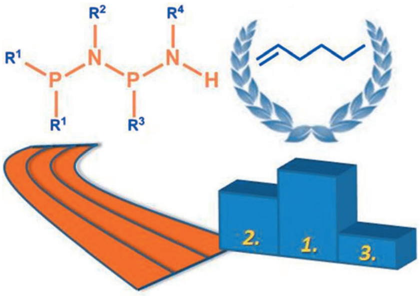
FULL PAPERS

A family competition between selected ligands with a PNPN–H motive turns out to be a neck-and-neck race. A highly selective trimerization catalyst for ethylene is optimized through fine-tuning of structural and electronic properties.



*S. Heinig, A. Wöhl, W. Müller,**
M. H. Al-Hazmi, B. H. Müller, N. Peulecke,
*U. Rosenthal**

■■ – ■■

The Effect of Substituents in PNPN–H Ligands on Activity and Selectivity of a Chromium-Based Catalyst System for Highly Selective Ethylene Trimerization

DOI: 10.1002/cctc.201300324

The Effect of Substituents in PNPN–H Ligands on Activity and Selectivity of a Chromium-Based Catalyst System for Highly Selective Ethylene Trimerization

Stefan Heinig,[a] Anina Wöhl,[a] Wolfgang Müller,*[a] Mohammed H. Al-Hazmi,[b]
Bernd H. Müller,[c] Normen Peulecke,[c] and Uwe Rosenthal*[c]

The influence of ligand substituents on a highly selective homogeneous catalyst system for the trimerization of ethylene to 1-hexene consisting of chromium(III) acetylacetonate, a ligand with a PNPN–H backbone, tetraphenylphosphonium chloride as chlorine source, and triethyl aluminum as activator was investigated. These N-modified and P-modified ligands, which differ strongly in their electronic and steric properties of the substituents, were tested in the ethylene trimerization at three temperatures (50, 70, and 90 °C). Interestingly, the substituents at the N atoms of the PNPN–H-backbone had only little effect on the catalytic activity, on 1-hexene selectivity, and on thermal stability of the catalyst system, whereas the substituents at the P atoms significantly influenced the efficiency of the system. This is even more surprising as the PNP ligand from SASOL for ethylene tetramerization is much more sensitive against substituent variation at its N atom.

Introduction

Linear α-olefins are versatile intermediates for the petrochemical industry. Their application is strongly dependent on their chain length. Whereas 1-butene, 1-hexene, and 1-octene are used as comonomers in the production of polyethylene (HDPE, LLDPE), longer chain olefins are converted to surfactants, plasticizers, or lubricants.[1] Each market segment has a different size and growth rate. Thus, it is difficult to cover the market with the conventional full-range processes, such as the Shell Higher Olefin Process or the α-Sablin technology.[2] The comonomer market segment has the highest growth rate with 5–6%/a, whereas the market for long-chain olefins is expected to grow only by 3% per annum in the years 2009–2014.[1] Owing to the market imbalance, the interest in selective routes leading to the high-value comonomer fractions (C_6 and C_8) has increased drastically. In recent years, a multitude of different ethylene tri- and tetramerization catalyst systems have been published.[3] The main focus has been on homogeneous chromium-based catalyst systems, often in combination with mixed P and N donors and an aluminum alkyl (e.g., TEA:triethyl aluminum and MAO:methyl aluminoxane) as activator.[3]

In previous publications by our group, the utilization of novel PNPN–H ligands in a chromium-based catalyst system has been described, which converts ethylene to comonomer-grade 1-hexene with more than 90% yield.[4] For the ligand $Ph_2PN(iPr)P(Ph)N(iPr)$–H (**L0**), we reported on detailed kinetic data and modeling studies,[5] investigated its coordination behavior,[6] and conducted organometallic studies with relevance to activation and deactivation of the catalyst system[7] as well as its heterogenization.[8] Some disadvantages such as the comparatively low catalytic activity (4–8 $kg\,g_{Cr}^{-1}\,h^{-1}$) of the original system, which was based on $CrCl_3(THF)_3$ as chromium precursor, could be eliminated by these modifications.[9] The modified catalyst system, which consisted of the chlorine-free chromium(III) acetylacetonate, $Cr(acac)_3$, instead of the expensive and sensitive $CrCl_3(THF)_3$, reached activities of 40–60 $kg\,g_{Cr}^{-1}\,h^{-1}$ if combined with an additional chlorine source (e.g., ammonium or phosphonium chlorides), the PNPN–H ligand, and TEA. Depending on the precise reaction conditions, this modification led to an approximately tenfold increase in activity over that of the previous system.

Based on these earlier results, our objective was to investigate the influence of various N and P substituents of the ligand on the activity and selectivity of the catalyst during the oligomerization reaction. In a recent publication,[10] we reported on the preparation and characterization of several ligands, which were now tested in catalysis with the objective to assess the effects of steric and/or electronic changes in the ligand structure on the activity, selectivity, and thermal stability. The ten ligands investigated were divided into two groups: first, the N-modified ligands and, second, the P-modified ligands (Figure 1).

---

[a] S. Heinig, Dr. A. Wöhl, Dr. W. Müller
Linde AG, Linde Engineering Division
Dr.-Carl-von-Linde-Str. 6-14, 82049 Pullach (Germany)
Fax: (+49) 8974454981
E-mail: Wolfgang.mueller@linde-le.com

[b] Dr. M. H. Al-Hazmi
Saudi Basic Industries Corporation,
P.O. Box 42503, Riyadh 11551 (Saudi Arabia)

[c] Dr. B. H. Müller, Dr. N. Peulecke, Prof. Dr. U. Rosenthal
Leibniz-Institut für Katalyse an der Universität Rostock e.V.
Albert-Einstein-Str. 29A, 18059 Rostock (Germany)
Fax: (+49) 381128151176
E-mail: Uwe.rosenthal@catalysis.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300324.

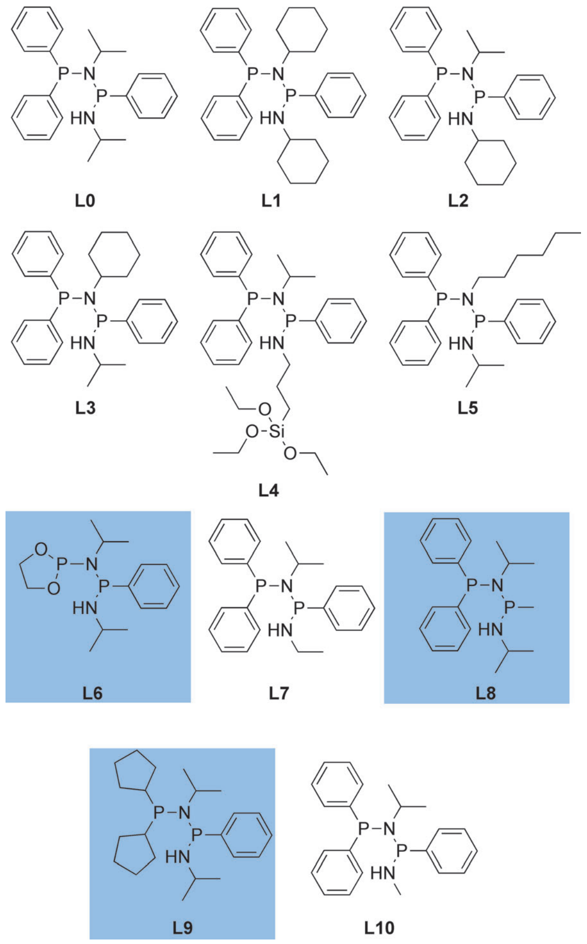


Figure 1. Structures of all investigated N-modified ligands (clear). Structures of all investigated P-modified ligands (blue).

Results and Discussion

All ligands (**L0**–**L10**) were investigated at 50, 70, and 90 °C, whereas all other parameters were kept constant. The objective was to examine their thermal deactivation behavior and to determine typical catalyst performance parameters such as selectivity, 1-hexene purity (i.e., 1-hexene selectivity with respect to the total C_6 fraction), and activity. The temperatures were chosen based on previous studies,[5] which showed that the original catalyst system with ligand **L0** starts to deactivate at elevated temperatures ($>60\,^{\circ}C$). This deactivation is most likely associated with ligand deprotonation and subsequent rearrangement of the ligand in the presence of the co-catalyst TEA.[7] The evaluation of the results for ligands with varying substituents can give information on the deactivation of the respective catalyst.

Ligand screening at optimized reaction conditions

All ligands (N- and P-modified) were first tested under previously optimized standard conditions at 50 °C (Table 1). Interestingly, the average activity was strongly affected by the location of the substituent modification. For example, the activities of N-modified ligands were approximately as high as those of the original ligand **L0**, whereas modifications at the P atoms led to dramatic drops in activity.[1] Nevertheless, all investigated ligands with the PNPN–H backbone (except ligand **L9**) exhibited a selectivity >85 wt % towards 1-hexene. 1-Hexene selectivities of more than 90 wt % could be obtained with ligands **L0**, **L1**, **L2**, and **L3**, with 1-butene selectivities ranging between 2.5 and 3.1 wt %. Notably, the C_{10} fraction consisted of several branched C_{10} isomers, indicating a formation mechanism that involves the incorporation of a 1-hexene molecule into the metallacycle. Only the ligand **L9** with cyclopentyl groups at the terminal P atom exhibited a relatively poor selectivity of >60 wt %. From the GC pattern it was suggested that a nonselective catalyst was formed through decomposition of the ligand, producing an underlying Schulz–Flory distribution. This might be also the reason for the enhanced C_8 formation in this case. In addition, the relative amount of formed polymer increased if the P atoms were modified and no phenyl substituents stabilized the phosphorus atom.

Table 1. Average activities and selectivities of the trimerization system $Cr(acac)_3$/***LX***/$[Ph_4P]Cl/AlEt_3$. Runs were conducted at 50 °C, 30 bar, $[Cr]=0.3$ or $1.0\ mmol\,L^{-1}$, $t=1$ h, $[L]/[Cr]=1.3$, $[Al]/[Cr]=25$, $[Cl]/[Cr]=5$; all ratios in molar units.

Ligand	Activity[a] $[kg\,g_{Cr}^{-1}\,h^{-1}]$	Selectivity [wt %] C_4	C_6	1-C_6	C_8	C_{10}	PE
L0	44.9	2.5	92.5	99.0	0.4	4.2	0.3
L1	44.5	2.1	93.1	99.0	0.4	4.3	0.1
L2	42.0	2.9	92.1	98.9	0.4	4.0	0.1
L3	38.0	3.1	92.4	99.0	0.4	3.6	0.1
L4	42.1	3.0	87.3	98.9	0.8	8.5	0.1
L5	21.7	7.4	86.8	98.7	1.8	3.4	0.4
L6	3.1	3.8	88.3	96.8	2.7	3.5	4.5
L7	36.2	4.2	86.8	98.8	0.9	7.6	0.2
L8	14.2	3.4	88.6	97.8	1.4	6.3	0.6
L9	3.2	2.9	62.3	95.4	13.1	18.3	3.9
L10	34.1	4.0	85.9	98.7	1.1	8.6	0.3

[a] Average activity over 1 h.

A similar behavior was observed if the 1-hexene selectivity in the C_6 fraction, that is, the 1-hexene purity, was considered. Although all N-modified ligands exhibited purities of approximately 99 wt %, the P-modified ligands (**L6**, **L8**, **L9**) exhibited significantly reduced purities down to 95.4 wt %.

The 1-hexene purity is of central importance for every technical-scale processes using one of these catalyst systems. The reason for this is the necessity to achieve very high 1-hexene purities through the intrinsic chemical properties of the system, so as to avoid any need for a superfractionation of the C_6 cut.

Regarding the ethylene uptake curve in Figure 2, the experiments with ligands **L0**–**L5**, which were all modified at the N-atoms, exhibited approximately constant ethylene consump-

---

[1] *For simplicity, we refer here to the "activity of the ligand" meaning, of course, the activity of the respective catalyst system using this particular ligand and comprising all necessary catalyst components, namely Cr source, ligand, modifier, and activator. The same holds for other catalytic key figures such as catalyst stability, selectivity, and product purity.*

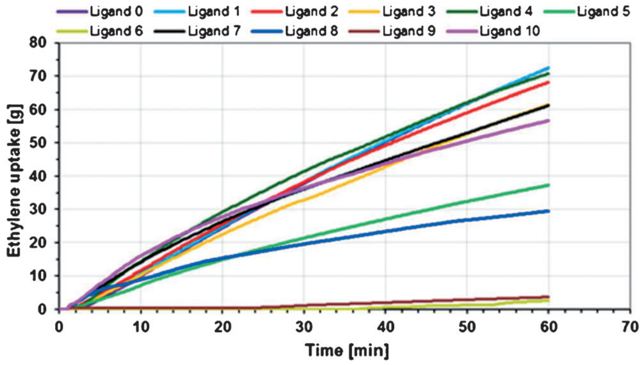


Figure 2. Ethylene uptake curves of all investigated ligands of the trimerization system $Cr(acac)_3/L\mathbf{\mathit{X}}/[Ph_4P]Cl/AlEt_3$. Runs were conducted at 50 °C, 30 bar, $[Cr]=0.3\ mmol\,L^{-1}$, $t=1$ h, $[L]/[Cr]=1.3$, $[Al]/[Cr]=25$, $[Cl]/[Cr]=5$.

tion over time, meaning that the catalyst was not deactivated. As a result, a shift from the isopropyl (**L0**) to the cyclohexyl group at one of the N atoms (**L2** and **L3**) or at both N atoms (**L1**) had only a minor influence on the catalytic performance, although the cyclohexyl substituent was more bulky. Nevertheless, the spatial demand was on a similar level for isopropyl and cyclohexyl.

Interestingly, the ligand with the substituent $(EtO)_3Si(CH_2)_3$ at the terminal N atom (**L4**) exhibited an ethylene uptake that was similar to that of the standard ligand, although this catalyst system started to deactivate earlier. Owing to the fact that a higher amount of branched decenes was formed with this ligand, one can conclude that this system was more susceptible to incorporation of 1-hexene into the metallacycle. This led to a lower ethylene consumption rate caused by high 1-hexene concentrations in the reaction liquid, thereby blocking the active center of the catalyst. In contrast, the catalyst systems with the ligands **L5**, **L7**, and **L10**, having *n*-alkyl substituents at one N atom, exhibited uptake curves with a detectable curvature after short reaction times, indicating an additional deactivation process or an increased susceptibility of the catalyst complex to product inhibition. Although thermal deactivation at 50 °C by ligand deprotonation and subsequent rearrangement was unlikely, it could not be excluded that the change in ligand structure shifted the deactivation temperature.

In the case of an *n*-hexyl group at the internal N atom (**L5**), the activity was halved relative to that of the standard ligand (**L0**). The long freely rotatable alkyl chain seemed to inhibit the reaction at the catalytic center.

In contrast, short alkyl substituents (ethyl and methyl) at the terminal N atom (**L7** and **L10**) resulted only in a minor decrease in activity compared to the isopropyl group. Clearly, the reduced space requirements of the methyl and ethyl groups relative to that of the isopropyl group of the standard ligand induced no significant positive effect on the catalyst performance. These results confirm the assumption that small changes in the ligand structure, for example, an expansion of an alkyl group by one methylene group, do not influence the catalytic behavior significantly. However, long-chain alkyl substituents and the position of the N atom, that is, internal or terminal, seems to influence the activity reduction verifiably. The P-modified ligands **L6**, **L8** and **L9** all exhibited very low ethylene consumption rates, suggesting that they were much less active than the N-modified ligands. Owing to the low activity, the P-modified ligands were investigated at a higher chromium concentration of $1.0\ mmol\,L^{-1}$. The results are discussed below.

Thermal stability of the N-modified ligands

Already at a reaction temperature of 70 °C a thermal deactivation of the catalyst system could be observed for all ligands, induced by ligand deprotonation and subsequent rearrangement.[7] This was clarified by a strong curvature of the ethylene uptake curves as exemplified by the curves of ligand **L1** with cyclohexyl groups at both N atoms (Figure 3). After a short initial phase in which the reaction rate was faster as a consequence of the elevated temperature (Arrhenius behavior), the thermal deactivation predominated and slowed down the reaction rate, an effect that was even more pronounced at 90 °C.

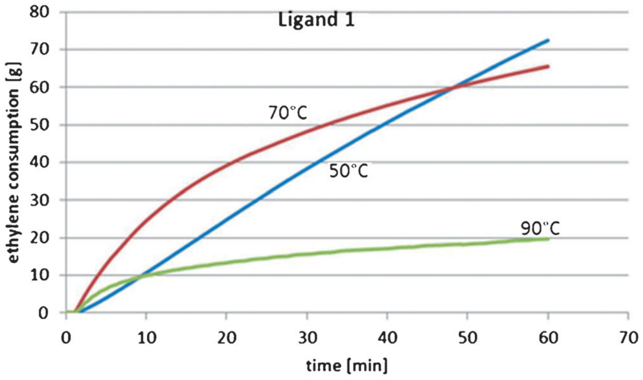


Figure 3. Ethylene consumption of the trimerization system $Cr(acac)_3/$ $\mathbf{L1}/[Ph_4P]Cl/AlEt_3$ at different temperatures. Runs conducted at 50/70/90 °C, 30 bar, $[Cr]=0.3\ mmol\,L^{-1}$, $t=1$ h, $[L]/[Cr]=1.3$, $[Al]/[Cr]=25$, $[Cl]/[Cr]=5$.

Clearly, a purely qualitative interpretation of the temporal deactivation characteristics as shown, for example, for the 70 °C curve in Figure 3 could, in principle, lead to an entirely different conclusion regarding the deactivation mechanism. This alternative interpretation would hint at an enhanced 1-hexene incorporation into the metallacycle as a competing mechanistic pathway to the incorporation of ethylene, thereby slowing down the overall reaction rate and leading to a higher amount of long-chain oligomers such as C_{10}. However, taking the full picture from parameter studies and kinetic modeling work into consideration, this mechanism can largely be ruled out.[5] Parameter studies with varying temperatures and otherwise constant conditions showed clearly that a high 1-hexene selectivity and a constantly low selectivity to C_{10} isomers was maintained throughout the temperature regime of the investigation (50–90 °C, additional experiments given in the Supporting Information). Consequently, the observed deactivation could not be attributed to product inhibition. Moreover, kinetic modeling work for this type of catalytic oligomerization reaction indicated that the observed deactivation time characteristics could not be explained by either irreversible or reversible product inhibition. This, in turn, was strongly supported by the observation of elevated levels of 1-hexene having no significant influence on the productivity.[5,7]

This latter observation is a key factor for the transfer of these catalyst systems into a viable technology, because continuous technical-scale process based on these systems has to tolerate very high steady-state 1-hexene levels in the reaction phase without discernible deterioration of the productivity.

The degree of thermal deactivation differed slightly with different substituents, which became clear for the average activities (determined after 1 h) at different temperatures in Figure 4.

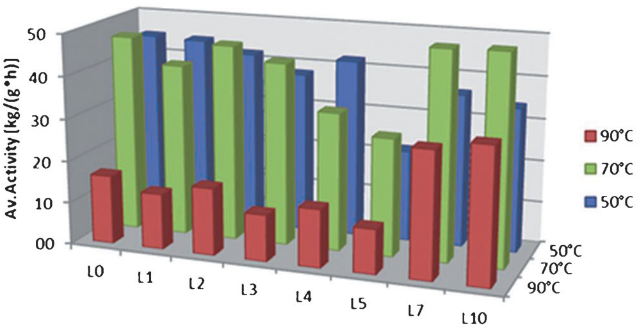


Figure 4. Average activities of the trimerization system $Cr(acac)_3/L\mathit{X}/[Ph_4P]Cl/AlEt_3$ at different temperatures with different N-modified ligands. Runs conducted at 50/70/90 °C, 30 bar, $[Cr] = 0.3\ mmol\,L^{-1}$, $t = 1$ h, $[L]/[Cr] = 1.3$, $[Al]/[Cr] = 25$, $[Cl]/[Cr] = 5$.

In the case of the cyclohexyl group at the terminal N atom (**L2**), a similar temperature-dependent behavior was observed to that of the ligand with isopropyl (**L0**) substituent. The substituent $(EtO)_3Si(CH_2)_3{-}$ in **L4** reduced the thermal stability of the catalyst complex already at 70 °C. Either the space requirement of this substituent influenced the stability negatively or the ligand had a higher tendency to decompose. As the Si substituent is very sensitive, it is possibly decomposed or attacked by TEA at high temperatures. In contrast, if the substituent at the terminal atom was replaced by a short alkyl group (**L7** and **L10**), the thermal stability was slightly enhanced. In conclusion, the following thermal stability sequence for the substituents at the terminal N atom (isopropyl substituent at the center N atom) was proposed:

methyl (**L10**) > ethyl (**L7**) > isopropyl (**L0**), cyclohexyl > $(EtO)_3Si(CH_2)_3{-}$ (**L4**)

For the center N atom, a slightly enhanced thermal stability was observed with the cyclohexyl substituent. The ligand **L5** with the hexyl group, which already exhibited a relatively low activity at 50 °C, had a higher average activity at 70 °C. At 90 °C its activity was similar to that of **L3**, which means that this catalyst system decomposed not as fast as the other systems. Consequently, the following sequence for the center N-atom could be derived:

cyclohexyl (**L3**) > hexyl (**L5**) > isopropyl (**L0**)

However, exchanging both substituents of the N atoms by cyclohexyl substituents resulted in a faster deactivation of the catalyst system.

Thermal stability of the P-modified ligands

Owing to the low activity of the three tested P-modified ligands, the chromium concentration was increased to achieve higher ethylene consumption rates at a residence time of 1 h. Already at 50 °C, the ethylene uptake behavior and, hence, the catalytic performance of the catalyst systems differed with different P substituents (Figure 5). For example, the ligand **L8** with a methyl group instead of a phenyl group at the internal P atom exhibited the highest ethylene uptake rate of the three P-modified ligands, but at a significantly reduced activity compared to that of the standard **L0**. However, the distinct shape of the ethylene uptake curve, indicating a deactivation process of **L8** at this temperature, was surprising. Clearly, the smaller size (steric effect) and the different electronic structure of the methyl group was responsible for this behavior.

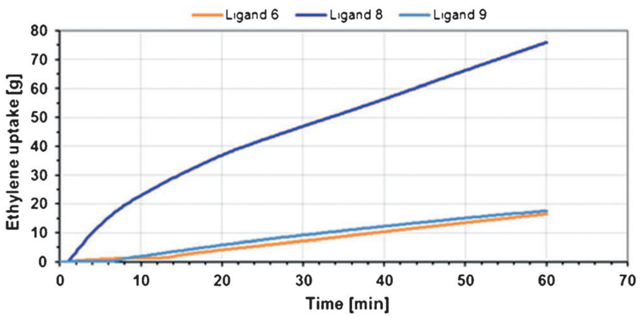


Figure 5. Ethylene consumption of the trimerization system $Cr(acac)_3/$ **L6**, **L8**, **L9**$/[Ph_4P]Cl/AlEt_3$ at 50 °C. Runs conducted at 50 °C, 30 bar, $[Cr] = 1.0\ mmol\,L^{-1}1$, $t = 1$ h, $[L]/[Cr] = 1.3$, $[Al]/[Cr] = 25$, $[Cl]/[Cr] = 5$.

Modifications of the substituents at their terminal P atom (**L6** and **L9**) led to similar ethylene consumption characteristics at a low constant reaction rate. Moreover, the induction period, that is, the time between ethylene pressurization and start of ethylene consumption, was considerably pronounced with these two ligands.

The low activity and the poor selectivity caused by the ligand **L9**, carrying two cyclopentyl rings, was somehow surprising because these rings had a similar size to the phenyl rings of the standard ligand **L0**. Therefore, this result confirms the hypothesis that the phenyl substituents with their π-electron system are necessary to stabilize the active catalysts.[11] The phenyl substituents increased the electron density of the chromium catalyst complex, resulting in a catalytically more active complex. It is also interesting that the heterocycle of **L6** did not decrease the activity more than the cyclopentyl groups, although the substituent was not freely rotatable.

However, it is also possible that additional ligand substituent effects may influence the catalytic performance. Especially the changed spatial demand of the substituents and the changed donor properties of the P atoms have a minor influence on the performance of the catalytic species.[3e]

In the case of increased temperature regimes (70 and 90 °C), all catalyst systems exhibited approximately the same or enhanced average activities compared to those at 50 °C (Figure 6). This suggests that the P-modified ligands are much more temperature-stable than their N-modified counterparts, despite their comparatively low activity. However, ligand **L9** with cyclopentyl substituents was more sensitive to the temperature increase than **L6** with the heterocycle. Interestingly, the kinetic behavior of **L8** changed at higher temperatures (see the Supporting Information). The ethylene consumption was nearly linear at 70 °C and had no curvature as it was observed at 50 °C. At 90 °C, a deactivation process could be observed. An explanation of this effect was not possible without further investigations.

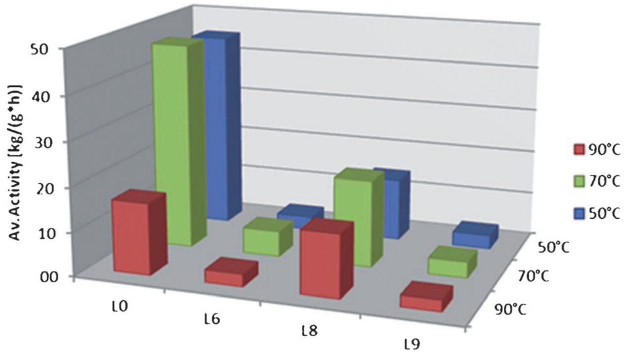


Figure 6. Average activities of the trimerization system Cr(acac)$_3$/L***X***/[Ph$_4$P]Cl/AlEt$_3$ at different temperatures with different P-modified ligands. Runs conducted at 50/70/90 °C, 30 bar, [Cr] = 1.0 mmol L^{-1}, t = 1 h, [L]/[Cr] = 1.3, [Al]/[Cr] = 25, [Cl]/[Cr] = 5.

In general, small substituents such as methyl (**L8**) or isopropyl (**L6**) instead of bulky substituents such as phenyl (**L0**) or cyclopentyl (**L9**) at one of the two P atoms led to the observed deactivation at 50 °C. Further investigations are necessary to understand the low-temperature deactivation effect. Furthermore, the P-modified **L8** reached the activity level of the N-modified ligands (activity level of **L0**) at 90 °C. It is therefore proposed that each variation of the substituents at the P atoms of the PNPN–H backbone significantly reduces the activity of the catalyst system. Furthermore, the phenyl substituents at both P atoms of the standard ligand were identified as important structural function blocks for high catalyst performances.

Detailed thermal behavior of L7

Ligand **L7** (and also **L10**) exhibited a higher thermal stability than the other investigated ligands. Therefore, the ligand was measured also at 110 °C. In the following the behavior of typical catalyst performance parameters as a function of temperature is shown. In Figure 7 the change of the product distribution (selectivities) with temperature is visualized.

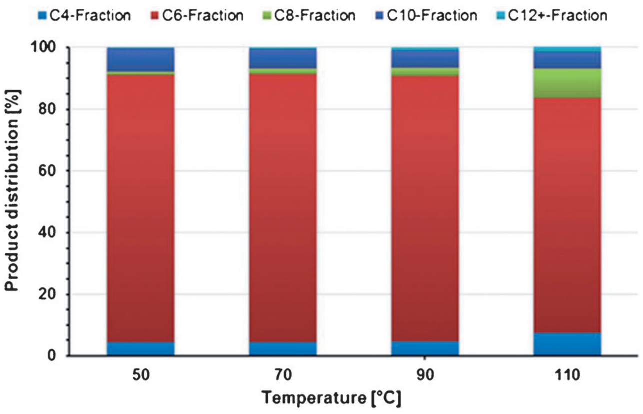


Figure 7. Product distribution of the trimerization system Cr(acac)$_3$/**L7**/[Ph$_4$P]Cl/AlEt$_3$ at different temperatures. Runs were conducted at 50/70/90/110 °C, 30 bar, [Cr] = 0.3 mmol L^{-1}, t = 1 h, [L]/[Cr] = 1.3, [Al]/[Cr] = 25, [Cl]/[Cr] = 5.

The formation of all main and side products are coupled through the metallacycle mechanism[12] and each of these reactions has its own rate constant with an individual temperature dependency. The proportions of the C_4 fraction (mainly 1-butene) and the C_6 fraction (mainly 1-hexene) were almost constant at temperatures between 50 and 90 °C, which is a unique feature of ligands **L7** and **L10**. All other ligands exhibited a significantly changed product composition already at 90 °C (compared with 50 °C/70 °C, see the Supporting Information). At 110 °C, the C_6 selectivity was reduced by approximately 10 wt % and the C_4 selectivity was increased by approximately 2.6 wt %, whereas simultaneously the amount of the C_8 (up to 10 wt %) and C_{12} fractions was significantly increased. The higher formation rate of 1-butene can be explained by a preferred β-hydride elimination of 1-butene from the metallacyclopentane complexes at higher temperatures. But it is also possible that through thermal decomposition of the catalyst system new active species were formed, leading to a non-selective production of linear α-olefins. This would lead to a superposition of a Schulz–Flory distribution and the usual selective trimerization product distribution.

In Figure 8 the important parameters such as average activity, 1-hexene purity, and polymer formation are summarized as a function of temperature. As discussed above, ligand **L7** exhibited the highest thermal stability of all tested ligands. The catalyst system using **L7** was still active at 110 °C. Presumably, the ligand substituent of **L7** and also of **L10** prevented or, at least, slowed down the rearrangement of the ligand at high temperatures in the catalyst complex. It is also possible that the rearranged complex had a better activity than the complex of the other ligands.

The purity of the C_6 fraction decreased with increasing temperature. It can be concluded that higher temperatures lead to

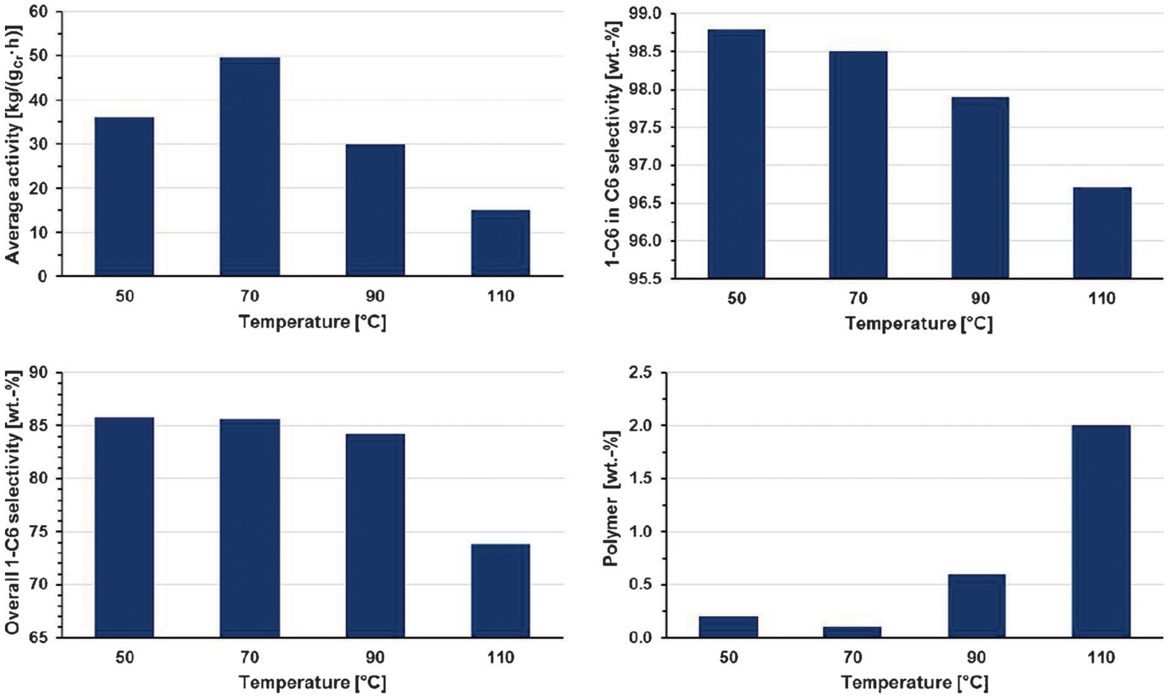


Figure 8. Average activity, 1-hexene purity, overall 1-hexene selectivity, and polymer formation depending on temperature of the trimerization system Cr(acac)$_3$/**L7**/[Ph$_4$P]Cl/AlEt$_3$. Runs were conducted at 50/70/90/110 °C, 30 bar, [Cr] = 0.3 mmol L^{-1}, t = 1 h, [L]/[Cr] = 1.3, [Al]/[Cr] = 25, [Cl]/[Cr] = 5.

the formation of more hexene isomers. This can be traced back to an acceleration of isomerization reactions at higher temperatures in the presence of AlEt$_3$.

The polymer-to-product ratio was nearly constant at temperatures between 50 and 70 °C. At higher temperatures, the polymer fraction was strongly increased up to 2 wt%. It appears that elevated temperatures supported the polymer formation by an insertion mechanism. Another possibility is that the catalyst complex was partially decomposed under release of a polymerization catalyst (TEA + "naked" chromium).

Comparison of substituent influences in diphosphinoamine and PNPN–H ligands

A direct comparison of the effects of substituents on the catalytic performance to other similar systems is considerably difficult. Only for the distantly related Sasol ethylene tetramerization system, which uses diphosphinoamine (PNP) ligands, several studies with various substituents at the PNP ligands at two different sets of reaction conditions were conducted.[13] In these studies, different substituents at the N atom and different aromatic substituents at the P-atoms were tested. In general, activity and selectivity seemed to be strongly dependent on the ligand substituents especially at the N atom.[13] This dependency was by far not as pronounced for the PNPN–H ligand in our study.

Furthermore, an extension of the π-electron system using naphthyl and biphenyl substituents resulted in a profound increase of the activity relative to that with phenyl substituents.[13a] This result confirmed the assumption that π-electron systems of aromatic substituents activate the catalyst complex. Nonaromatic substituents, in contrast, reduce the activity significantly.

Conclusions

It is desirable to investigate a larger variety of substituents at the inner N atom to allow for more unique conclusions regarding the relative importance of the substitution variation at the N versus the P atoms. Furthermore, ligands with identical substituents at both N atoms could be investigated to extend the scope of possible conclusions regarding individual influences.

Unfortunately, we were not able to synthesize and/or characterize all of the desired compounds with further N substituents that could introduce larger electronic changes. However, keeping in mind that even very small changes in the N-atom substitution of Sasol's diphosphinoamine (PNP) system causes dramatic effects, it appears remarkable that our current PNPN–H system was by far less susceptible to analogous variations at the central N atom.[13b]

Furthermore, the range of investigated ligand modifications allowed for a comparison with the standard, or "reference", ligand **L0** with phenyl substituents at the P atoms.

Therefore, for the restricted number of ligands investigated in this study, one can conclude that the phenyl groups at the P atoms are essential for a high catalytic activity. In addition, the side-product selectivities were less temperature-sensitive if phenyl substituents were bound to the P atoms. Furthermore, comparison with **L0** revealed that the substitution of the isopropyl at the terminal N atom by a methyl or ethyl group improved the thermal stability significantly. Moreover, α-branched (isopropyl or cyclohexyl) substituents at the N atoms promoted high 1-hexene selectivities, whereas the ligands were less temperature-stable. Long alkyl chains such as *n*-hexyl at the internal N-atom led to a reduction of activity and to high amounts of C_4 (50 °C).

In summary, it was very surprising that the ethylene trimerization system based on the PNPN–H ligand was less sensitive towards variation of substituents at the N atom of the ligand than Sasol's PNP tetramerization system. Consequently, it is very unlikely to achieve an extraordinary activity increase or significant change of the selectivity only by variation of N substituents.

It is still questionable if the general kinetic behavior of the catalyst system can be influenced by variation of the ligand substituents. This pertains to, for example, the influence of the catalyst composition (Al/Cr ratio, ligand/chromium ratio) or pressure effects on the overall kinetics. These aspects will be covered in a further publication.

Experimental Section

A detailed description of the experimental setup, the catalyst preparation and additional experimental results are given in the Supporting Information.

Acknowledgements

The authors thank Linde Engineering and SABIC for the permission to publish this work. Furthermore, we wish to thank Linde Engineering's R&D department for their valuable contributions as well as the analytical service and the technical staff at LIKAT.

Keywords: homogeneous catalysis · ligand design · N,P ligands · oligomerization · substituent effects

[1] a) E. O. C. Greiner, Y. Inoguchi, *CEH Marketing Research Report LINEAR ALPHA-OLEFINS*, The Chemical Economics Handbook, SRI International, **2010**; b) E. Burridge, Chemical Profile: *Alpha Olefins*, ICIS Chemical Business, **2008**.

[2] A. Meiswinkel, A. Wöhl, W. Müller, H. V. Bölt, F. M. Mosa, M. H. Al-Hazmi, *Oil Gas* **2012**, *38*, 103–106.

[3] a) D. S. McGuinness, *Chem. Rev.* **2011**, *111*, 2321–2341, and refs. cited therein; b) T. Agapie, *Coord. Chem. Rev.* **2011**, *255*, 861–880, and refs. cited therein; c) P. W. N. M. van Leeuwen, N. D. Clement, M. J. L. Tschan, *Coord. Chem. Rev.* **2011**, *255*, 1499–1517, and refs. cited therein; d) D. F. Wass, *Dalton Trans.* **2007**, 816–819; e) Y. Wang, C. Yang, J. Chen, *Adv. Mater. Res.* **2011**, *317–319*, 1797–1800; f) G. P. Belov, P. E. Matkovskii, *Neftekhimiya* **2010**, *50*, 296–302; g) J. T. Dixon, M. J. Green, F. M. Hess, D. H. Morgan, *J. Organomet. Chem.* **2004**, *689*, 3641–3668.

[4] a) S. Peitz, N. Peulecke, B. R. Aluri, S. Hansen, B. H. Müller, A. Spannenberg, U. Rosenthal, M. H. Al-Hazmi, F. M. Mosa, A. Wöhl, W. Müller, *Eur. J. Inorg. Chem.* **2010**, 1167–1171; b) P. M. Fritz, H. Bölt, A. Wöhl, W. Müller, F. Winkler, A. Wellenhofer, U. Rosenthal, M. Hapke, N. Peulecke, B. H. Müller, M. H. Al-Hazmi, V. O. Aliyev, F. M. Mosa, (Linde AG/SABIC), WO 2009/006979 A2, **2009**.

[5] a) A. Wöhl, W. Müller, S. Peitz, N. Peulecke, B. R. Aluri, B. H. Müller, D. Heller, U. Rosenthal, M. H. Al-Hazmi, F. M. Mosa, *Chem. Eur. J.* **2010**, *16*, 7833–7842; b) W. Müller, A. Wöhl, S. Peitz, N. Peulecke, B. R. Aluri, B. H. Müller, D. Heller, U. Rosenthal, M. H. Al-Hazmi, F. M. Mosa, *ChemCatChem* **2010**, *2*, 1130–1142; B. H. Müller, D. Heller, U. Rosenthal, M. H. Al-Hazmi, F. M. Mosa, *ChemCatChem* **2010**, *2*, 1130–1142.

[6] B. R. Aluri, N. Peulecke, S. Peitz, A. Spannenberg, B. H. Müller, S. Schulz, H.-J. Drexler, D. Heller, M. H. Al-Hazmi, F. M. Mosa, A. Wöhl, W. Müller, *Dalton Trans.* **2010**, *39*, 7911–7920.

[7] a) S. Peitz, N. Peulecke, B. R. Aluri, B. H. Müller, A. Spannenberg, U. Rosenthal, M. H. Al-Hazmi, F. M. Mosa, A. Wöhl, W. Müller, *Organometallics* **2010**, *29*, 5263–5268; b) S. Peitz, N. Peulecke, B. R. Aluri, B. H. Müller, A. Spannenberg, U. Rosenthal, M. H. Al-Hazmi, F. M. Mosa, A. Wöhl, W. Müller, *Chem. Eur. J.* **2010**, *16*, 12127–12132; c) 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; d) S. Peitz, N. Peulecke, B. H. Müller, A. Spannenberg, H.-J. Drexler, U. Rosenthal, M. H. Al-Hazmi, K. Al-Eidan, A. Wöhl, W. Müller, *Organometallics* **2011**, *30*, 2364–2370.

[8] N. Peulecke, B. H. Müller, S. Peitz, B. R. Aluri, U. Rosenthal, A. Wöhl, W. Müller, M. H. Al-Hazmi, F. M. Mosa, *ChemCatChem* **2010**, *2*, 1079–1081.

[9] N. Peulecke, B. H. Müller, 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.

[10] M. Gongoll, B. H. Müller, S. Peitz, B. R. Aluri, N. Peulecke, A. Spannenberg, U. Rosenthal, M. H. Al-Hazmi, A. Wöhl, W. Müller, *Phosphorus Sulfur Silicon Relat. Elem.* **2013**, DOI: 10.1080/10426507.2013.807257.

[11] T. J. M. de Bruin, L. Magna, P. Raybaud, H. Toulhoat, *Organometallics* **2003**, *22*, 3404–3413.

[12] J. R. Briggs, *J. Chem. Soc. Chem. Commun.* **1989**, 674–675.

[13] a) 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; b) K. Blann, A. Bollmann, H. de 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; c) S. Kuhlmann, K. Blann, A. Bollmann, J. T. Dixon, E. Killian, M. C. Maumela, D. H. Morgan, M. Prétorius, N. Taccardi, P. Wasserscheid, *J. Catal.* **2007**, *245*, 279–284; d) E. Killian, E. Blann, A. Bollmann, J. T. Dixon, S. Kuhlmann, M. C. Maumela, H. Maumela, D. H. Morgan, P. Nongodlwana, M. J. Overett, M. Prétorius, K. Höfener, P. Wasserscheid, *J. Mol. Catal. A* **2007**, *270*, 214–218; e) N. Cloete, H. G. Visser, I. Engelbrecht, M. J. Overett, W. F. Gabrielli, A. Roodt, *Inorg. Chem.* **2013**, *52*, 2268–2270.

Received: April 29, 2013
Revised: June 12, 2013