DOI: 10.1002/chem.201001936

VIP

Activation and Deactivation by Temperature: Behavior of $Ph_2PN(iPr)P(Ph)N(iPr)H$ in the Presence of Alkylaluminum Compounds Relevant to Catalytic Selective Ethene Trimerization

Stephan Peitz,[a] Normen Peulecke,[a] Bhaskar R. Aluri,[a] Bernd H. Müller,[a] Anke Spannenberg,[a] Uwe Rosenthal,*[a] Mohammed H. Al-Hazmi,[b] Fuad M. Mosa,[b] Anina Wöhl,[c] and Wolfgang Müller*[c]

Abstract: Coordination, deprotonation, rearrangement, and cleavage of $Ph_2PN(iPr)P(Ph)N(iPr)H$ (**1**) by trialkylaluminum compounds R_3Al (R = Me, Et) are reported that are relevant to the selective ethene trimerization system consisting of the ligand **1**, $CrCl_3(THF)_3$ and Et_3Al that produces 1-hexene in more than 90% yield and highest purity. With increasing temperature and residence time first the formation of an adduct $[Ph_2PN(iPr)P(Ph)N(iPr)H][AlR_3]$ (**2**), second the aluminum amide $[Ph_2PN(iPr)P(Ph)(AlR_3)N(iPr)][AlR_2]$ (**3**) and third its rearrangement to the cyclic compound $[N(iPr)P(Ph)P(Ph_2)N(iPr)][AlR_2]$ (**4**) were observed. The cleavage of **3** by an excess of R_3Al into an amidophosphane and an iminophosphane could be the reason for its rearrangement to complex **4**, as well as to the cyclic dimer $[R_2AlN(iPr)P(Ph)_2]_2$ (**5**). The chemistry of ligand **1** in the presence of alkylaluminum compounds gives hints on possible activation and deactivation mechanisms of **1** in trimerization catalysis.

Keywords: aluminum · amides · complexes · homogeneous catalysis · oligomerization · rearrangement

Introduction

Having a profound knowledge about the role of alkylaluminum compounds in the chromium-catalyzed selective trimerization reaction of ethene to 1-hexene is of great importance for the understanding of the active catalyst species. In many cases only one special aluminum activator is suitable for the desired ethene conversion in terms of activity and selectivity.[1,2] Additionally, the molar ratio of co-catalyst to chromium has a great influence on the outcome of the trimerization reaction.[3a] Up to now this has not been fully rationalized. Thus, it is rather complicated to find a new catalytic system that contains, besides a suitable ligand and metal source, an appropriate activator, all together showing the desired catalytic characteristics. Several aspects concerning this problem have been elucidated so far. It is known that the alkylaluminum co-catalyst can fulfill different tasks in the oligomerization reaction like alkylation,[1,4,5a,b] reduction of the chromium center,[1,2,3b,4,5a,d] formation of a cationic complex,[3b,4a,5b,6] and a counterion,[4a,6,7] where applicable dehalogenation,[5] deprotonation,[2,3] and C–H activation,[2] as well as acting as scavenger for impurities in the system.[6] Nevertheless, further investigation on the role of the alkylaluminum activator in this special catalytic transformation is absolutely necessary.

Our group recently published the first results of a new homogeneous chromium-based trimerization catalyst for the transformation of ethene to 1-hexene,[8,9a] including complexation,[9b] deprotonation,[10] comprehensive kinetic investigations,[11a] and modeling,[11b] as well as heterogenization,[12] using a new type of P,N donor ligand in conjunction with $CrCl_3(THF)_3$ and Et_3Al that produces co-monomer grade 1-hexene in more than 90% yield. New ideas about mechanis-

[a] S. Peitz, Dr. N. Peulecke, Dr. B. R. Aluri, Dr. B. H. Müller, Dr. A. Spannenberg, Prof. Dr. U. Rosenthal
Leibniz-Institut für Katalyse an der Universität Rostock e.V.
Albert-Einstein-Str. 29A, 18059 Rostock (Germany)
Fax: (+49) 381-1281 51176
E-mail: Uwe.rosenthal@catalysis.de

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

[c] Dr. A. Wöhl, Dr. W. Müller
Linde AG, Linde Engineering Division
Dr.-Carl-von-Linde-Str. 6–14, 82049 Pullach (Germany)
Fax. (+49) 89-744 54981
E-mail: Wolfgang.mueller@linde-le.com

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001936.

tic differences between tri- and tetramerization of ethene were also issued in recent times.[13]

Herein, we describe in more detail the organometallic characteristics of $Ph_2PN(iPr)P(Ph)N(iPr)H$ (**1**) in presence of trialkylaluminum compounds R_3Al. These complexes show what effect alteration of the ligand in catalysis can have, which is of major interest concerning activation and deactivation in catalysis. Thus, a better understanding of the behavior and reactivity of this type of aminodiphosphanoamine ligand in the catalytic system, especially in terms of temperature dependence and residence time, is feasible.

Results and Discussion

This work describes, as a detailed extension of a short communication,[9a] the reactivity, coordination chemistry, and cleavage pathways of the novel aminodiphosphanoamine $Ph_2PN(iPr)P(Ph)N(iPr)H$ (**1**; PNPNH hereafter), used in selective ethene trimerization, in the presence of trialkylaluminium compounds. Naturally, the question arises as to which factors of the PNPNH-ligand are essential for the high selectivity towards 1-hexene in the catalytic trimerization of ethene. It could be shown that, besides the usage of chromium as the metal, the PNPN structure and in particular the terminal secondary amine function are crucial for C6-selectivity.[9a] Exclusively, Et_3Al shows considerable activity and selectivity as an activator for the "Cr-PNPNH" system.

An important aspect, regarding the elucidation of the catalytically active site, deals with the question of what kind of alteration the ligand undergoes in the catalytic system, where, due to its high complexity, several organometallic reactions could occur.

As the secondary amine function of **1** is essential for catalytic selectivity to 1-hexene, we concluded that deprotonation most likely to occur in the real catalytic system.[9a] This could be supported by detailed deprotonation–metalation studies of **1** with different organometal bases.[10]

To start with a simplified examination of the catalytic system, we investigated the chemistry of the trimerization ligand **1** in conjunction with the aluminum alkyls Me_3Al and Et_3Al. Their reactions with **1** can give an important insight into possible reaction activation and deactivation pathways of **1** in catalysis. Therefore, stoichiometric experiments under different thermal conditions were conducted.

To follow the reactions, ^{31}P NMR spectroscopy studies were carried out. Ligand **1** was dissolved in toluene, mixed with R_3Al, and heated at different temperatures. As reported previously,[9a] different species depending on reaction temperature and time could be identified. Here we expand these investigations to have a complete overview of the reactivity pattern of the ligand in conjunction with aluminum alkyls.

Complexation of Me_3Al led, even at room temperature, to a chemical shift of the ligand's two phosphorus atoms at $\delta = 46$ and 70 ppm (Figure 1b, compound **2a**), contrary to the chemical shift of **1** at $\delta = 41$ and 68 ppm (Figure 1a).

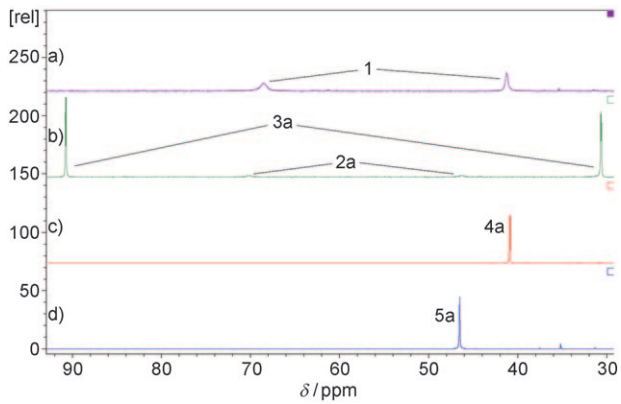


Figure 1. ^{31}P NMR spectroscopy results of: a) Compound **1** without any Me_3Al being present; b) Formation of **2a** and **3a** after heating a **1**/Me_3Al mixture for 4 h at 50 °C; c) Isolated **4a** after heating a **1**/Me_3Al mixture for 22 h at 85 °C; d) Isolated **5a** after heating a **1**/Me_3Al mixture for 5 days at 85 °C.

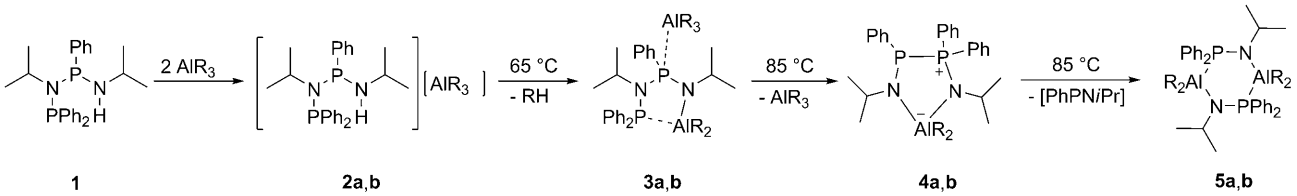
Upon heating the mixture to 50 °C for 26 h, two new NMR spectroscopy signals were observed at $\delta = 31$ and 91 ppm, respectively (Figure 1b, compound **3a**), whereas the adduct **2a** was completely consumed during that time. When this mixture was heated for a further 22 h to nearly 100 °C, the signals changed completely (Figure 1c, **4a**).

The same reaction sequence was observed by employing Et_3Al. The adduct **2b** that was formed at room temperature showed signals in the ^{31}P NMR spectrum at $\delta = 47$ and 70 ppm, respectively. Deprotonation at 65 °C shifted the phosphorus signals to $\delta = 31$ and 92 ppm (**3b**). Heating at 95 °C for 26 h resulted again in a shift of the P signals to $\delta =$ 36.8 and 41.5 ppm in an AB-pattern, indicating two similar phosphorus atoms bound together (**4b**).

The results of these NMR investigations led to the following reaction pathway: First, the formation of an adduct $[Ph_2PN(iPr)P(Ph)N(iPr)H][AlR_3]$ (**2a**: R = Me; **2b**: R = Et) takes place. Due to the high reactivity of the aluminum alkyls, isolation has not been possible so far.

Second, the alumination of the N–H function with liberation of the corresponding alkane to give an aluminum amide $[Ph_2PN(iPr)P(AlR_3)(Ph)N(iPr)][AlR_2]$ (**3a**: R = Me; **3b**: R = Et) and third its rearrangement to the cyclic compound $[N(iPr)P(Ph)P(Ph_2)N(iPr)][AlR_2]$ (NPPN hereafter) (**4a**: R = Me, **4b**: R = Et) by transamidation occurs (Scheme 1).

Deprotonation of **1** at 65 °C in the presence of Me_3Al and Et_3Al, respectively, leads to the formation of complexes **3a** and **3b**. Interestingly, in complexes **3a** and **3b** a second molecule R_3Al is implemented, respectively. This could be proven by X-ray analysis of **3a** and combustion analysis of **3a** and **3b**. The molecular structure of **3a** is depicted in Figure 2. The terminal amide function forms a covalent bond with the metal and the P2 atom acts as a donor giving a chelating $[PNPN]^-$ fragment at the aluminum center. The additionally coordinating molecule Me_3Al is located at the central phosphorus atom of the ligand backbone with a distance of 2.5831(10) Å. One can discuss whether this second



Scheme 1. Stepwise reaction of $Ph_2PN(iPr)P(Ph)N(iPr)H$ (**1**) with R_3Al to give the adduct $[Ph_2PN(iPr)P(Ph)N(iPr)H][AlR_3]$ (**2a**, **2b**), alumination leading to $[Ph_2PN(iPr)P(AlR_3)(Ph)N(iPr)][AlR_2]$ (**3a**, **3b**), rearrangement to $[N(iPr)P(Ph)P(Ph_2)N(iPr)][AlR_2]$ (**4a**, **4b**) and cleavage to give $[Ph_2PN(iPr)AlR_2]_2$ (**5a**, **5b**) (a: R = Me; b: R = Et).

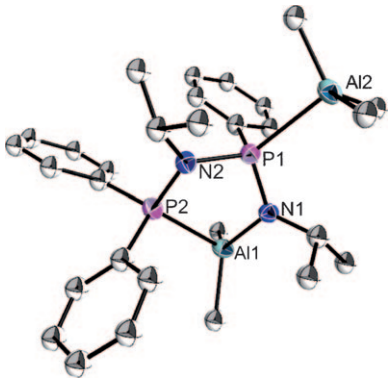


Figure 2. Molecular structure of **3a** with thermal ellipsoids set at 50% probability.[9a] The asymmetric unit contains two molecules, only one is depicted. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–P1 1.653(2), P1–N2 1.740(2), N2–P2 1.684(2), N1–Al1 1.879(2), P2–Al1 2.5093(10), P1–Al2 2.5831(10), N2-P1-N1 105.08(10), P2-N2-P1 113.71(10), P2-Al1-N1 85.36(6).

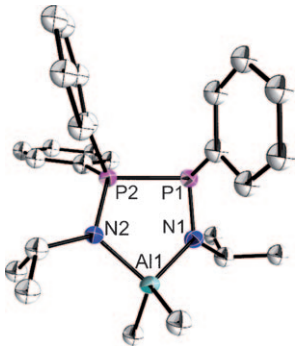


Figure 3. Molecular structure of **4a** with thermal ellipsoids set at 50% probability.[9a] All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.2178(4), N1–P1 1.6645(10), P2–N2 1.6191(10), N1–Al1 1.8796(11), N2–Al1 1.9303(10), N1-Al1-N2 95.79(4).

molecule R_3Al is of importance for catalytic activity in selective trimerization.

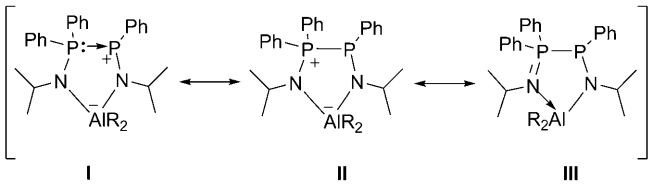
It was possible to reverse the formation of the PNPN-Al compounds **3a** and **3b** back to **1** by hydrolysis with equimolar amounts of ammonium chloride or even with water. By heating **3a** and **3b** for several hours in toluene at 85 °C rearrangement to **4a** and **4b** takes place, respectively. Both compounds could be crystallized and analyzed by X-ray diffraction. The molecular structure of compound **4a** is depicted in Figure 3.

A similar molecule to **4a** and **4b** was described previously by Chivers et al.,[14] which was obtained by reaction of DippN(H)PhPNRCR′NR (Dipp = 2,6-$iPrC_6H_3$) (NPNCN hereafter) with Me_3Al.

As illustrated in Scheme 2, complexes **4a** and **4b** can be viewed in terms of three resonance structures: phosphane–phosphenium aluminate I, phosphonium–aluminate II or amidophosphane–phosphazene–aluminum complex III.[14,15]

Resonance structure I is suggested by the P1–P2 bond length of 2.2178(4) Å, which is in the same range as Chivers' molecule and at the upper limit of the range of published values for phosphane–phosphenium cation complexes.[16] Interestingly, in **4a** the P–N bond from the four coordinated phosphorus center (P2–N2) is 0.045 Å shorter than P1–N1 with the three coordinated phosphorus atom, as observed for the metalation of acylic NPNCN. The aluminum center is coordinated more strongly to N1 than to N2, which is consistent with the suggestion that the P2–N2 side has a larger degree of ionicity. Accordingly, the resonance forms II and III cause a contribution to the structure. Comparison of bond lengths and angles shows the similarities of the solid state structures of **4a** and **4b** (Table 1).

A rather astonishing difference between **4a** and **4b** is observed in the ^{31}P NMR spectra of these complexes. Though



Scheme 2. Resonance structures of $R_2Al[N(iPr)P(Ph)P(Ph)_2N(iPr)]$ (**4**).

Table 1. Summary of important bond lengths [Å] and angles [°].

Complex	Ligand backbone	Al–N	R_2Al–P	N-Al-N
3a	$PNPN^-$	1.879(2)	2.5093(10)	–
4a	$NPPN^-$	1.8796(11) 1.9303(10)	–	95.79(4)
4b	$NPPN^-$	1.886(2) 1.928(2)	–	95.90(8)
5a	PN^-	1.8768(12)	2.4783(5)	–

the two adjacent P nuclei are chemically very different they cause similar shifts. Therefore, one would expect an AB-pattern in the spectra. For **4b** this is true, but the spectrum of **4a** shows at first glance two very similar signals that are overlapping. This was unexpected and we attribute this to the nearly identical shifts of both phosphorus atoms at room temperature beginning to form an A_2-pattern. Nevertheless, to exclude dynamic processes, e.g., shift of a Ph group from one P to the other, that might produce identical nuclei on the NMR time scale, we performed variable temperature (VT)-NMR measurements. If it was a dynamic process, increased temperature should lead to total overlapping of both signals. Interestingly, the NMR spectra show a different behavior. At higher temperatures the chemical shifts of both phosphorus atoms, besides a slight shift downfield, start to disperse, thus resulting in the expected AB-pattern with a strong roof effect of the four peaks at a final temperature of 347 K. The missing symmetry of the molecule, indicated by the three different Ph groups that were observed in VT-NMR, and constancy of line shape in the applied temperature range are additional characteristics. These exclude a dynamic process and clarify the temperature dependence of the chemical shifts of both P nuclei in **4a**, that is, apparently, leading to nearly identical shifts at room temperature. One reason could be a small but effective difference in ring size or ring planarity.

At ratios larger than 1:1 (R_3Al/**1**), which is the case under catalytic conditions, parallel to the formation of **4** other compounds are observed in ^{31}P NMR spectra. They are formed by addition of an excess of R_3Al to a solution of **1**, heating to 85 °C for several days. As before, in the beginning of the reaction deprotonation of the ligand's amine function and later rearrangement of **1** are observed. After 24 h heating additional signals show up in the ^{31}P NMR spectra. After five days **3** and **4** are consumed totally to form new phosphorus-containing compounds as indicated by NMR spectroscopy (^{31}P NMR spectrum of **5a** shown in Figure 1d).

Cooling the reaction solution of former **3** to room temperature leads to the formation of colorless crystals. NMR spectroscopy and elemental analysis confirmed a uniform material. By X-ray analysis it could be shown that the cyclic complex $[Me_2Al\text{-}N(i\text{Pr})\text{-}PPh_2]_2$ (**5a**) (Figure 4) was formed.[17] The other P-containing compound in the oily reaction mixture could not be identified so far, but it should contain the missing part [PhP-N*i*Pr] of the original ligand backbone.

With Et_3Al much more time (11 days at 85 °C) was needed to complete the cleavage reaction. So far no crystals could be obtained, but the ^{31}P NMR spectrum clearly shows the analogous signals for the complex $[Et_2Al\text{-}N(i\text{Pr})\text{-}PPh_2]_2$ (**5b**).

Compound **5a** could be isolated previously from the reaction of lithiated $Ph_2PN(i\text{Pr})H$ with Me_2AlCl but was not crystallographically characterized.[18] Compound **5b** was synthesized before by direct alumination of $Ph_2PN(i\text{Pr})H$[19] and it was reported to be the trimeric compound $[Et_2Al\text{-}N(i\text{Pr})\text{-}PPh_2]_3$. Isolation of **5b** out of the reaction mixture of **1** with Et_3Al (5 equiv) was not successful so far. Thus, it could not be proven whether **5b** is dimeric in the solid state like **5a** or trimeric as claimed in ref. [19].

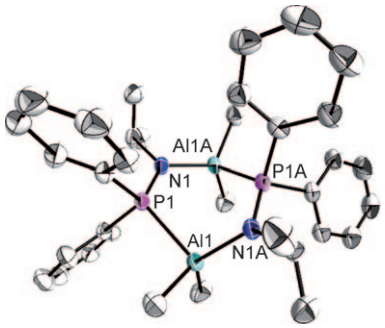
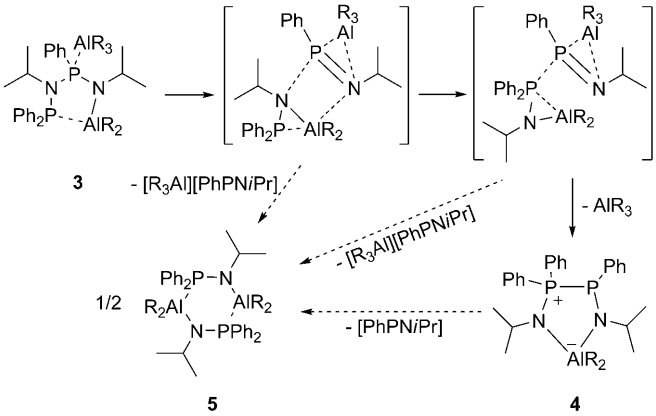


Figure 4. Molecular structure of **5a** with thermal ellipsoids set at 50% probability. All hydrogen atoms have been omitted for clarity. Important bond lengths [Å] and angles [°]: N1–P1 1.6479(12), N1–Al1A 1.8768(12), Al1–P1 2.4783(5), P1-N1-Al1A 120.78(7), N1-Al1A-P1A 104.72(4), N1-P1-Al1 119.09(4).

The cleavage of the PNPN moiety by R_3Al into an amidophosphane and a supposed iminophosphane, as shown in Scheme 3, could be the reason for its rearrangement to complex **4**, as well as to the cyclic dimer **5**. Accordingly, besides **5** an iminophosphane-AlR_3 compound must be left in solution, which could not be isolated so far.



Scheme 3. Possible pathways for rearrangement and cleavage of the PNPN backbone.

Testing of all the complexes described above in ethene oligomerization showed expected results (Table 2). Complexes **3a** and **3b** exhibited similar results to the in situ system[9a] in terms of selectivity. This is a clear indication that the aluminated ligand is part of the active trimerization species. Employing **3a** and **3b** in catalytic experiments leads to a linear ethene uptake for at least two hours, respectively. Interestingly, with **1** a different curvature is observed. After 20 min the uptake is also linear (and parallel to the catalytic curves of **3a** and **3b**) but prior to that the activity is much higher. This leads to the kink-curvature described before and an all-in-all higher activity.[9a] Up to now, we attribute this behavior to the formation of two different trimerization

Table 2. Oligomerization results with compounds **1**, **3a**, **3b**, **4a**, **4b**, **5a**, and the **5b** mixture.[a]

Compound	Activity [$g\,g_{Cr}^{-1}\,h^{-1}$]	Oligomer fraction [mol%] C4	C6[b]	C8	C10+	Polymer [g]
1	5200	4.7	90.7 (99.3)	1.3	3.4	0.09
3a	1890	3.6	89.5 (97.8)	1.7	4.6	0.16
3b	2750	3.6	90.1 (98.0)	1.5	4.8	0.11
4a	80	33.4	45.0	15.3	5.8	0.27
4b	140	34.1	37.5	18.2	10.2	0.68
5a	980	14.9	32.8	21.8	30.5	0.67
5b[c]	980	23.2	29.8	23.2	23.8	0.82

[a] Conditions: $T=65\,°C$, 30 bar ethene, 1 h reaction time, total volume toluene (100 mL), $CrCl_3(THF)_3$ (0.1 mmol), compound (0.175 mmol), $AlEt_3$ (7 mmol). [b] In brackets: percentage of 1-hexene of total C6 fraction. [c] Non-isolated complex employed.

species. One of these is obviously consumed after 20 min. Complexes **3a** and **3b** instead directly seem to lead to the second active species, which produces 1-hexene on a constant level with very high selectivity.

The rearranged products **4a** and **4b** show nearly no activity in ethylene oligomerization. This supports the idea that the rearranged ligand, or a chromium complex thereof, is responsible for the decline of activity in trimerization catalysis at temperatures higher than 90 °C.[9,10] Most ethene (>67%) consumed under these conditions is transformed into polyethylene in both cases. The very small oligomer amounts are nonselectively distributed with many isomers in every fraction, meaning 1-alkenes are not always the favored products.

Complex **5a** and the reaction mixture comprising **5b** give very low activity also yielding a nonselective distribution of oligomers. The activities and product distributions caused by the two complexes are quite similar even though **5b** was only available in an oily product mixture. It is worth mentioning that each oligomer fraction consists of several isomers.

These catalytic results clearly reveal that the special backbone of **1** (PNPNH) comprising a *sec*-amino function is absolutely necessary for selective ethene trimerization.

Complex formation of the presented Al-complexes **3a**, **3b**, **4a**, **4b**, **5a**, and **5b** with $CrCl_3(THF)_3$, the preferred chromium salt in catalysis,[9a] is currently under investigation.

Conclusion

We herein presented results showing coordination, deprotonation, rearrangement and cleavage of $Ph_2PN(iPr)P(Ph)N(iPr)H$ (**1**) by trialkylaluminum compounds R_3Al (R = Me, Et). These reactions are relevant for activation and deactivation of the new selective ethene trimerization system consisting of the ligand **1**, $CrCl_3(THF)_3$, and Et_3Al that produces 1-hexene in more than 90% yield and high purity. The formation of an adduct $[Ph_2PN(iPr)P(Ph)N(iPr)H][AlR_3]$ (**2**) and the aluminum amide $[Ph_2PN(iPr)P(AlR_3)(Ph)N(iPr)][AlR_2]$ (**3**) are processes involved in the activation of the system, whereas the rearrangement of **3** to the cyclic compound $[N(iPr)P(Ph)P(Ph_2)N(iPr)][AlR_2]$ (**4**) leads to its deactivation. The cleavage of **3** by an excess of R_3Al could be the reason for its rearrangement to complex **4**, as well as to the cyclic dimer $[R_2AlN(iPr)P(Ph)_2]_2$ (**5**). In conclusion, this chemistry of **1** in the presence of alkylaluminum compounds gives many hints on possible activation and deactivation mechanisms in catalysis, which are of great importance for understanding the interaction of the aluminum alkyl activator with the ligand in the corresponding catalytic selective trimerization system.

Experimental Section

All air and moisture sensitive compounds were handled under argon atmosphere by using standard Schlenk techniques or in a glove box. Prior to use, nonhalogenated solvents (including deuterated solvents $[D_6]$benzene and $[D_8]$THF) were freshly distilled from sodium tetraethylaluminate and stored under argon. All other chemical reagents and solvents were obtained from commercial sources and were used without further purification. The following spectrometers were used, for mass spectra: MAT 95-XP and Finnigan Polaris Q and for NMR spectra: Bruker AV300, AV400, and AMX400 spectrometers. Chemical shifts (^1H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of the used solvent: $[D_6]$benzene ($\delta_H=7.16$, $\delta_C=128.0$) and $[D_8]$THF ($\delta_H=2.73$, $\delta_C=25.2$). Chemical shifts for ^{31}P are given relative to 85% H_3PO_4. The spectra were assigned with the help of DEPT. Melting points were carried out using sealed capillaries on Büchi 535 apparatus. Elemental analyses were carried out using a Leco CHNS-932 elemental analyzer. Diffraction data were collected on a STOE IPDS II diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The structure of **5a** was solved by direct methods (SHELXS-97)[20a] and refined by full-matrix least-squares techniques on F^2 (SHELXL-97).[20a] DIAMOND[20b] was used for graphical representations.

Compounds **1**, **3a**, **3b**, **4a**, and **4b** were prepared according to published literature procedures.[9a]

Oligomerization experiments were conducted as described previously.[21] In all cases $CrCl_3(THF)_3$ (0.1 mmol), **3a**, **3b**, **4a**, **4b**, or **5a** (1.75 equiv) were weighed in and dissolved in toluene (100 mL) and Et_3Al (7 mmol) was added. For oligomerization with **5b** 0.090 g (≈0.3 mmol of **5b**) of the oily product were applied together with the corresponding amounts of $CrCl_3(THF)_3$ and Et_3Al given above.

Preparation of $[Ph_2PN(iPr)AlMe_2]_2$ (5a): $Ph_2PN(iPr)P(Ph)N(iPr)H$ (1.50 g, 3.675 mmol) was dissolved in toluene (10 mL). Me_3Al (5.6 mL, 2.0 M Me_3Al in toluene, 11.0 mmol) was added to the solution, which was heated at 85 °C. After a color change from colorless to yellow and back to colorless in a time scale of 120 h the reaction was completed. The solution was kept at room temperature until colorless crystals precipitated. The precipitate was filtered and washed three times with pentane (5 mL). The remaining solvent was removed in vacuum to give a colorless powder (0.444 g; 30% yield). M.p. 215 °C; ^1H NMR ($[D_8]$THF): $\delta=7.36$–7.49 (m, 8H, Ar-H), 7.17–7.29 (m, 12H, Ar-H), 3.32 (sept, $J=6.6$ Hz, 2H, $CHCH_3$), 0.91 (d, $J=6.6$ Hz, 12H, $CHCH_3$), −0.72 ppm (d, $J=1.1$ Hz, 12H, $AlCH_3$); ^{13}C NMR ($[D_8]$THF): $\delta=144.9$, 144.7, 133.3, 133.1, 128.3, 128.0 (4×6C, arom.), 50.30 (d, $CHCH_3$), 27.44 (d, $CHCH_3$), −6.45 ppm ($AlCH_3$); $^{31}P\{H\}$ NMR ($[D_8]$THF): $\delta=46.5$ ppm; MW: 598.65 g mol^{-1} $[C_{34}H_{46}Al_2N_2P_2]$; elemental analysis calcd (%) C 68.21, H 7.74, N 4.68; found: C 68.25, H 7.51, N 4.78.

Preparation of $[Ph_2PN(iPr)AlEt_2]_2$ (5b): $Ph_2PN(iPr)P(Ph)N(iPr)H$ (2.0 g, 4.896 mmol) was dissolved in toluene (10 mL). Et_3Al (12.88 mL, 1.9 M Et_3Al in toluene, 24.5 mmol) was added to the solution, which was heated to 85 °C. After a color change from colorless to yellow and back to colorless in a time scale of 11 days the reaction was complete. After removal of the solvent in vacuum a colorless oil remains. $^{31}P\{H\}$ NMR

([D$_8$]THF): $\delta = 46.9$ ppm; unidentified side product: $\delta = 44.7$ ppm (ratio 1:1).

Acknowledgements

The authors would like thank Linde Engineering and SABIC for the permission to publish this work. The analytical and technical staff at LIKAT is thankfully acknowledged.

[1] J. T. Dixon, M. J. Green, F. M. Hess, D. H. Morgan, *J. Organomet. Chem.* **2004**, *689*, 3641–3668.
[2] a) J. Zhang, A. Li, T. S. Andy Hor, *Organometallics* **2009**, *28*, 2935–2937; b) D. S. McGuinness, A. J. Rucklidge, R. P. Tooze, A. M. Z. Slawin, *Organometallics* **2007**, *26*, 2561–2569.
[3] a) D. S. McGuinness, P. Wasserscheid, D. H. Morgan, J. T. Dixon, *Organometallics* **2005**, *24*, 552–556; b) D. S. McGuinness, D. B. Brown, R. P. Tooze, F. M. Hess, J. T. Dixon, A. M. Z. Slawin, *Organometallics* **2006**, *25*, 3605–3610.
[4] a) R. D. Köhn, D. Smith, M. F. Mahon, M. Prinz, S. Mihan, G. Kociok-Köhn, *J. Organomet. Chem.* **2003**, *683*, 200–208; b) W. Janse van Rensburg, J.-A. van den Berg, P. J. Steynberg, *Organometallics* **2007**, *26*, 1000–1013; c) A. Jabri, C. B. Mason, Y. Sim, S. Gambarotta, T. J. Burchell, R. Duchateau, *Angew. Chem.* **2008**, *120*, 9863–9867; *Angew. Chem. Int. Ed.* **2008**, *47*, 9717–9721.
[5] a) A. Jabri, C. Temple, P. Crewdson, S. Gambarotta, I. Korobkov, R. Duchateau, *J. Am. Chem. Soc.* **2006**, *128*, 9238–9247; b) C. Temple, A. Jabri, P. Crewdson, S. Gambarotta, I. Korobkov, ; R. Duchateau, *Angew. Chem.* **2006**, *118*, 7208–7211; R. Duchateau, *Angew. Chem.* **2006**, *118*, 7208–7211; *Angew. Chem. Int. Ed.* **2006**, *45*, 7050–7053; c) C. Temple, S. Gambarotta, I. Korobkov, R. Duchateau, *Organometallics* **2007**, *26*, 4598–4603; d) A. Jabri, S. Gambarotta, I. Korobkov, R. Duchateau, *Organometallics* **2006**, *25*, 715–718.
[6] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391–1434.
[7] W. Janse van Rensburg, C. Grove, J. P. Steynberg, K. B. Stark, J. J. Huyser, P. J. Steynberg, *Organometallics* **2004**, *23*, 1207–1222.
[8] 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**.
[9] 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) 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, U. Rosenthal, *Dalton Trans.* **2010**, 7911–7920.
[10] 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.
[11] 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.
[12] 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*, DOI: 10.1021/om100371f.
[13] 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.
[14] a) T. Chivers, M. C. Copsey, M. Parvez, *Chem. Commun.* **2004**, 2818–2819; b) T. Chivers, M. C. Copsey, C. Fedorchuk, M. Parvez, M. Stubbs, *Organometallics* **2005**, *24*, 1919–1928.
[15] M. C. Copsey, T. Chivers, *Dalton Trans.* **2006**, 4114–4123.
[16] N. Burford, P. J. Ragogna, R. McDonald, M. J. Ferguson, *J. Am. Chem. Soc.* **2003**, *125*, 14404–14410.
[17] Crystal data of **5a**: $C_{46}H_{58}Al_2N_2P_2$, $M_r = 754.84$, monoclinic, space group $C2/c$, $a = 13.3852(3)$, $b = 14.3122(4)$, $c = 22.6901(5)$ Å, $\beta = 91.151(2)°$, $V = 4345.9(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.154$ g cm^{-3}, $\mu = 0.173$ mm^{-1}, $T = 200$ K, 35642 reflections collected, 5005 independent reflections ($R_{int} = 0.04$), of which 3930 were observed [$I > 2\sigma(I)$], final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0370$, $wR_2 = 0.1035$, R indices (all data): $R_1 = 0.0498$, $wR_2 = 0.1074$, 227 refined parameters. Compound **5a** crystallizes together with two solvent molecules of benzene in the asymmetric unit, which is not depicted in Figure 4. CCDC-783641 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.
[18] J. A. Labinger, J. N. Bonfiglio, D. L. Grimmett, S. T. Masuo, E. Shearin, J. S. Miller, *Organometallics* **1983**, *2*, 733–740.
[19] D. F. Clemens, H. H. Sisler, W. S. Brey, Jr., *Inorg. Chem.* **1966**, *5*, 527–533.
[20] a) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122; b) K. Brandenburg, M. Berndt, *DIAMOND*, Crystal Impact GbR, Bonn, Germany, **1999**.
[21] A. Wöhl, W. Müller, N. Peulecke, B. H. Müller, S. Peitz, D. Heller, U. Rosenthal, *J. Mol. Catal. A* **2009**, *297*, 1–8.

Received: July 8, 2010
Published online: October 7, 2010

