

A Selective Chromium Catalyst System for the Trimerization of Ethene and Its Coordination Chemistry

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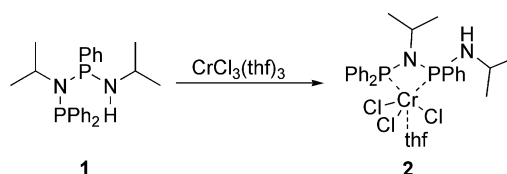
In this paper a novel ligand of the type [PNPNH] is presented for the application in a new homogeneous highly selective ethene trimerization system for the formation of 1-hexene, which consists of the chromium source $\text{CrCl}_3(\text{thf})_3$, the ligand $\text{Ph}_2\text{PN}(\text{iPr})\text{P}(\text{Ph})\text{N}(\text{iPr})\text{H}$ (**1**), and Et_3Al as an activator in toluene. The excellent characteristics of this new system, e.g. very high selectivity to C_6 with highest purity of the C_6 frac-

tion (>99 % 1-hexene), activity on a constant level on a long timescale, use of small amounts of Et_3Al as a cheap activator, and only very low production of PE, make it to a hot candidate for industrial application. Its organometallic background gives an indication of the nature of the active catalyst species.

Introduction

Linear α -olefins (LAOs) are useful and versatile intermediates for many industrially important substances like comonomers for HDPE or LLDPE, alcohols, aldehydes, carboxylic acids or sulfonates. Conventional full-range producers of LAOs, which obtain a wide product distribution, have to meet a formidable challenge to match the market demand.^[1] Conventional technologies, such as the SHOP (Shell Higher Olefin Process) or the α -Sabin process, are based on an ethene insertion/ β -elimination mechanism by chain growth, resulting in a Schulz–Flory distribution. Thus, the selective production of the economically most viable LAOs, i.e. comonomer-grade 1-hexene and more recently 1-octene, appears highly desirable.^[2] For selective ethene trimerization, instead of the chain-growth pathway, a metallacycle mechanism is generally accepted. In this process, two ethene units coordinate at the catalytically active site and form a metallacyclopentane by oxidative coupling. Insertions of further ethene units result in larger metallacycles. Through β -elimination/reductive elimination, LAOs are formed.^[3,4]

In this paper we describe the synthesis of the novel ligand **1** of the type [PNPNH], its complexation (Scheme 1) and metalation as well as its application as a new homogeneous selective trimerization system to 1-hexene consisting of the chromium source $\text{CrCl}_3(\text{thf})_3$, the ligand $\text{Ph}_2\text{PN}(\text{iPr})\text{P}(\text{Ph})\text{N}(\text{iPr})\text{H}$ (**1**) and Et_3Al as an activator in toluene.^[5]



Scheme 1. Formation of complex **2** from ligand **1**.

Results and Discussion

For easier access to kinetic parameters and mechanistic observations, the average productivity of this new trimerization system was held constant at around 5200 g/(g_{Cr}·h) (determined after 2 h), but with some smaller modifications an increase up to 27000 g/(g_{Cr}·h) and more was achieved.^[5c]

The results of a typical ethene oligomerization experiment^[6] concerning selectivity are given in Table 1. In various experiments it could be shown that the activity, the achieved selectivity to C_6 , and the purity of the C_6 fraction (>99 wt.-% of 1-hexene) of this new trimerization catalyst system are very promising. The high purity within the C_6 fraction has the advantage that it can be used without further purification in co-polymerization. Additionally, due to

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the high catalytic stability, the productivity stays at a constant level for a long time in comparison to other systems.^[2i–2l,2q–2s] Also, the use of Et₃Al as activator is advantageous, due to lower costs and its more precise specification compared to MAO (methylalumoxane). Only low ratios of co-catalyst/Cr are necessary to activate the new system, whereas for many other catalyst systems molar ratios of Al/Cr up to 850 are employed.^[2i–2l] Moreover, a very low amount of PE (polyethylene) is produced during the catalytic trimerization reaction. Given the advantages, this novel trimerization catalyst system competes very well with comparable systems, especially in view of a potential implementation in a technical process. In particular, the moderate average activities may allow for a relatively simple design on a technical scale, due to easier control of the heat release of the exothermal reaction.

Table 1. Selectivity of the trimerization system CrCl₃(thf)₃, **1**, Et₃Al in toluene at 65 °C and 30 bar ethene pressure.^[a]

Oligomer ^[b]	C ₄	1-C ₄	C ₆	1-C ₆	C ₈	1-C ₈	C ₁₀	1-C ₁₀	Polymer
wt.-%	4.7	88.2	90.7	99.3	1.3	84.1	3.4	10.9	0.09

[a] Standard conditions: loading 0.1 mmol of CrCl₃(thf)₃, 0.175 mmol of Ph₂PN(*i*Pr)P(Ph)N(*i*Pr)H, 7.0 mmol of Et₃Al, 100 mL of toluene as solvent, 2 h of reaction time, 55 g ethene uptake. [b] Selectivity for 1-alkene (1-C_n) as percentage of total C_n fraction.

To obtain an idea of the nature of the active site and its required structural characteristics for C₆ selectivity, different model compounds were isolated from relevant mixtures of the single components of the system and investigated by X-ray structure analysis.

For the synthesis of the desired [PNPNH] ligand two different synthetic methods were elaborated. According to these procedures, Ph₂PN(*i*Pr)P(Ph)N(*i*Pr)H (**1**) was synthesized and characterized by X-ray analysis (see Supporting Information).

The coordination chemistry of this ligand was investigated in detail for the (monoligand)chromium trichloride complex [Ph₂PN(*i*Pr)P(Ph)N(*i*Pr)H]CrCl₃(thf) (**2**), which was prepared according to Scheme 1.

Interestingly, the intact undeprotonated N–H function of the [PNPNH] ligand does not coordinate to the metal atom. Instead, the ligand is coordinated through both phosphorus atoms to the metal center (Figure 1). This coordination mode is already known from the Sasol-type [PNP] ligands.^[2i]

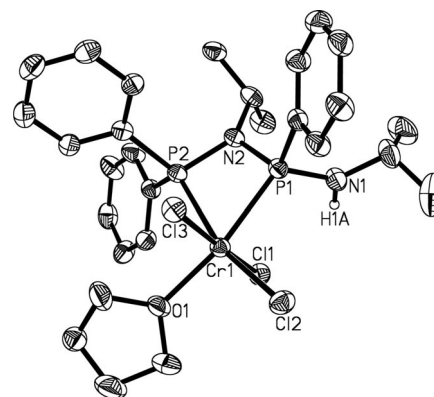


Figure 1. Molecular structure of **2** with thermal ellipsoids set at 30% probability. The asymmetric unit contains (besides solvent molecules) two molecules of **2**; only one molecule is depicted. Hydrogen atoms, except H1A, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–P1 1.644(4), N2–P2 1.694(4), N2–P1 1.717(4), Cr1–P1 2.3975(14), Cr1–P2 2.5161(14); N1–P1–N2 110.9(2), P2–N2–P1 104.9(2), P1–Cr1–P2 66.73(4).^[7]

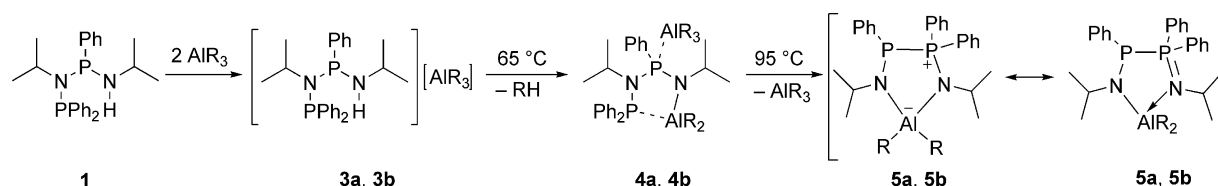
One has to consider that during the reaction metalation of the N–H group by aluminum (or chromium after alkylation) forming an amide [PNPN][–] should occur in the herein presented new catalytic ethene trimerization system, consisting of CrCl₃(thf)₃, the ligand **1** and Et₃Al. Since compounds of the structure [PNPNR₂] are totally inactive in catalysis, it seems that the N–H group is essential for trimerization activity.

To come to a closer look at the real catalytic system, we investigated the reaction of **1** with Et₃Al and Me₃Al, respectively. By NMR investigations, we found three different steps of interaction of **1** with Et₃Al.

The first step is the formation of an adduct [Ph₂PN(*i*Pr)P(Ph)N(*i*Pr)H][AlEt₃] (**3a**), the second step is the aluminatation of the N–H function by liberation of ethane to the aluminum amide, which additionally coordinates Et₃Al to give the complex [Ph₂PN(*i*Pr)P(AlEt₃)(Ph)N(*i*Pr)][AlEt₂] (**4a**), and the third step is the rearrangement of **4a** to the cyclic compound **5a** by transamidation at higher temperature (Scheme 2).

Compound **5a** was characterized by X-ray analysis, and its molecular structure is shown in Figure 2.

By using Me₃Al instead of Et₃Al, we were not only able to crystallize the rearrangement product **5b** but also the aluminated ligand **4b** as an intermediate (Figure 3). From this molecular structure it becomes obvious that a molecule of Me₃Al coordinates to the central phosphorus atom.



Scheme 2. Stepwise reaction of **1** with R₃Al to afford adduct [Ph₂PN(*i*Pr)P(Ph)N(*i*Pr)H][AlR₃] (**3**), aluminatation to form [Ph₂PN(*i*Pr)P(AlR₃)(Ph)N(*i*Pr)][AlR₂] (**4**) and rearrangement by transamidation to give [N(*i*Pr)P(Ph)–(Ph)₂PN(*i*Pr)][AlR₂] (**5**) (a: R = Et; b: R = Me).

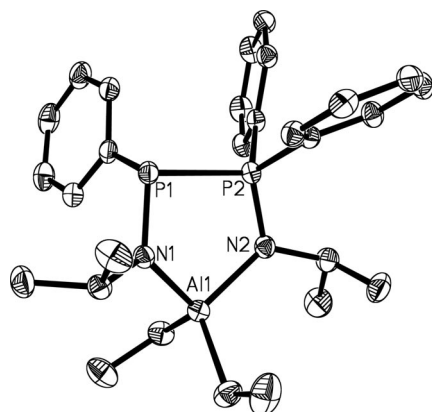


Figure 2. Molecular structure of **5a** with thermal ellipsoids set at 30% probability. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.2262(7), N1–P1 1.668(2), P2–N2 1.614(2), N1–Al1 1.886(2), N2–Al1 1.928(2); N1–Al1–N2 95.90(8).

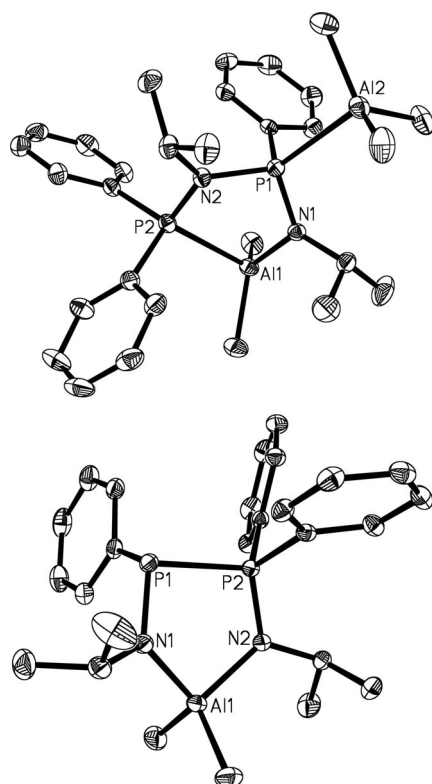


Figure 3. Molecular structures of **4b** and **5b** with thermal ellipsoids set at 30% probability. The asymmetric unit of **4b** contains two molecules; only one is depicted. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: **4b**: N1–P1 1.653(2), P1–N2 1.740(2), 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); **5b**: 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).

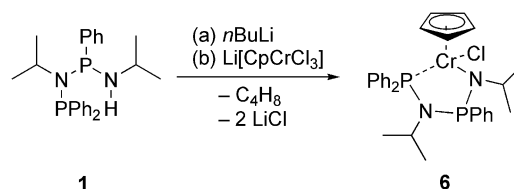
Complexes **5a** and **5b** bear an $N(i\text{Pr})\text{P}(\text{Ph})\text{--P}(\text{Ph})_2\text{N}(i\text{Pr})$ ligand N,N' -chelated to the metal center. A quite similar complex $\text{Me}_2\text{Al}[\text{N}(\text{dipp})\text{P}(\text{Ph})\text{--P}(\text{Me})\text{PhN}(\text{dipp})]$ {dipp = 2,6- $(i\text{Pr})_2\text{C}_6\text{H}_3$ } was published before, having a comparable

NPPN ligand backbone. It can be described in terms of resonance structures of a phosphane–phosphonium complex or a phosphane–phosphazene cation.^[8] According to these investigations, compounds **5a** and **5b** can be interpreted analogously (Scheme 2).

Catalytic tests with complexes **4a** and **4b** in the presence of $\text{CrCl}_3(\text{thf})_3$ and Et_3Al at 65 °C show comparable activities to the in situ system concerning the slope of the ethene-uptake curve after the initiation of the reaction, indicating the aluminated ligand to be a precursor or a part of the catalytic system. A trimerization experiment with the pure rearranged ligand **5a**, $\text{CrCl}_3(\text{thf})_3$, and Et_3Al complex showed no activity at all. A catalytic run with the in situ system at 90 °C indicates **5a** to be responsible for the decline in ethene consumption (for more details see Supporting Information). This is why we regard **5a** as the main species causing derogation of catalysis at higher temperatures.

To arrive at a chromium complex with the amide-bonded ligand, we tried $\text{CrCl}_3(\text{thf})_3$, the preferred chromium source in catalysis, to react with the aluminum amides **4a** and **4b** to obtain a dimetallic complex that could be active in catalysis. Unfortunately, all efforts in this direction failed so far.

Reaction of **1** with n -butyllithium and $\text{Li}[\text{CpCrCl}_3]$ instead of $\text{CrCl}_3(\text{thf})_3$ as chromium source causes elimination of butane and 2 equiv. of LiCl and leads to the formation of $\text{CpCrCl}[\text{N}(i\text{Pr})\text{P}(\text{Ph})\text{N}(i\text{Pr})\text{PPh}_2]$ (**6**) (Scheme 3), which bears a chromium–amide bond (Figure 4).



Scheme 3. Formation of **6**.

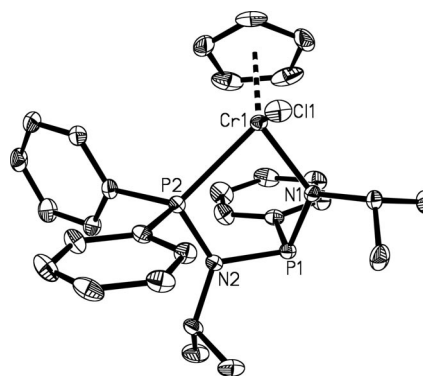


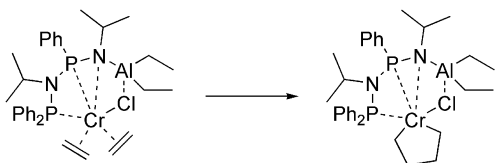
Figure 4. Molecular structure of **6** with thermal ellipsoids set at 30% probability. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–P1 1.6671(13), P1–N2 1.7558(14), N2–P2 1.6786(14), N1–Cr1 1.9650(13), P2–Cr1 2.5081(5); N2–P1–N1 102.74(7), P2–N2–P1 118.08(7), P2–Cr1–N1 82.68(4).

This complex can serve as a model compound for the interaction of the metallated ligand with the chromium atom. It was also tested in the selective oligomerization of

ethene with Et_3Al as activator, but it generates 1-butene as the main product. With MAO as a co-catalyst only PE is produced. This different selectivity compared to the original system is explained by the influence of the Cp ligand.

The lithiated ligand was also tested in trimerization and shows nearly identical ethene consumption compared to the other systems, again being proof for the involvement of a deprotonated ligand species in catalysis (see Supporting Information).

As a result of all these experiments, we are sure that the catalytically active species is a complex, in which the deprotonated [PNPNH] ligand causes C_6 selectivity. With regard to the fact that an organoaluminum and a chloride compound are present in the system, bridged dimetallic compounds (Scheme 4) must be considered, which fits very well with the results recently published by Gambarotta et al.^[9a,9b] and Hor et al.^[9c] for other systems.



Scheme 4. Dinuclear model for the catalytic active species.

Conclusions

We have reported the development of a new system for the chromium-catalyzed selective trimerization of ethene, accompanied by its organometallic background, which gives an indication of the nature of the active catalyst species. The excellent characteristics of this new trimerization system, e.g. high selectivity to C_6 with highest purity of the C_6 fraction (>99% of -hexene), activity on a constant level on a long timescale, use of small amounts of Et_3Al as a cheap activator and only very low production of PE, make it a hot candidate for industrial application with many advantages compared to other systems.

Experimental Section

All air- and moisture-sensitive compounds were handled under argon by using standard Schlenk techniques or in a glove box. Triethylamine (99% purity), isopropylamine (99% purity), *n*-butyllithium solution (2.5 M in heptanes) were obtained from Acros Organics and used as received. Chlorodiphenylphosphane (98% purity), $\text{CrCl}_3(\text{thf})_3$ (97% purity), Et_3Al (1.9 mol/L in toluene) and Me_3Al (1.0 M Me_3Al in toluene) were obtained from Sigma-Aldrich and used without further purification. Toluene (>99.9% purity), thf and *n*-hexane were obtained from Acros Organics, dried with sodium/benzophenone and then distilled under argon. Argon 5.0 and ethene 3.0 were purchased from Linde Gas and used as received.

Supporting Information (see footnote on the first page of this article): Experimental details for the preparation of all new compounds (including detailed analytical data); detailed procedures and results

for trimerization reactions with important complexes and crystallographic information.

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