Activity Enhancement of a Catalyst System for the Selective Trimerization of Ethene to 1-Hexene by Modification of the Chromium to Chloride to Aluminium Ratio

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Polyethylene is currently the largest volume polymer in the world. Linear low-density polyethylene (LLDPE) has penetrated almost all the traditional markets for polyethylene but is mainly used for plastic foils, as it allows the use of a lower thickness of the foils. It is a substantially linear polymer with significant numbers of short branches, commonly prepared by copolymerization of ethene with short-chain alpha-olefins (for example, 1-butene, 1-hexene, and 1-octene), therefore causing a growing commercial demand for comonomer-grade linear alpha-olefins (LAOs). The conventional method to obtain LAOs was derived from ethene oligomerization processes, and resulted in a mathematical product distribution of alpha-olefins like the Schulz–Flory or Poisson,[1] which do not match the market demands. Therefore, there is a high industrial interest in selective oligomerization reactions that lead to certain alpha-olefins.

Quite a number of catalyst systems oligomerizing ethene to 1-hexene or 1-octene have been reported.[1] In general, these are complex systems that consist of a transition metal, a ligand, and mostly of an aluminium alkyl as co-catalyst. There was no lack of effort to elucidate mechanistic details of the selective reactions. A metallacycle mechanism, which was proposed initially by Manyik et al.[2] and expanded later by Briggs[3] is widely accepted.

Up to now, only one trimerization system made its way towards commercialization. In 2003, a process based on a catalyst system developed by Chevron Phillips went on

stream in Qatar. This system comprises chromium(III) tris(2-ethylhexanoate), 2,5-dimethylpyrrole, and a mixture of the co-catalysts triethylaluminium and diethylaluminium chloride.[4]

Recently, we described a promising selective catalyst system for the trimerization of ethene based on $[CrCl_3(thf)_3]$ as a chromium source, the ligand $Ph_2PN(iPr)P(Ph)N(iPr)H$, and triethylaluminium as co-catalyst in toluene.[5,6,7] By testing chlorine-free alternative chromium sources and by the addition of ammonium or phosphonium chlorides as modifiers, it became obvious that chlorine must be an essential part of the catalytically active species. Furthermore, a screening of different aluminium alkyls revealed the outstanding relevance of triethylaluminium for activity and selectivity of the described catalytic system. Whereas many attempts have been made to explain the selectivity by interaction of the ligand with the transition metal or the oxidation state of the metal, there are less investigations on the role of the co-catalyst and of the supporting ligands.

The development of Chevron Phillips selective trimerization technology took over 20 years and revolutionized the alpha-olefin technology. The mixture of triethylaluminium and diethylaluminium chloride implies the importance of chlorine for the catalysis. Luo et al. reported about an improvement of the catalytic activity by using triethylaluminium as co-catalyst and hexachloroethane as additive.[1,8] A deeper understanding of this "chlorine-effect" was given by Gambarotta and co-workers, who used 2,3,4,5-tetrahydro-1H-carbazole as ligand.[9]

Together with $[CrCl_3(thf)_3]$ and triethylaluminium, they were able to isolate a single crystal of a compound in which chlorine acts as a bridging ligand between two metals. They postulated an active species in which the pyrrole motif is metalated with a diethylaluminium fragment and π-bonded to chromium. Chloride acts as a bridging ligand between chromium and aluminium (Figure 1).

We recently described a highly selective ethene trimerization reaction using an aminodiphosphanoamine with a secondary amine function $Ph_2PN(iPr)P(Ph)N(iPr)H$. Additionally, we reported on the general coordination chemistry[10] and the reaction of the ligand with aluminiumalkyles.[11] The kinetics of the catalytic reaction was examined with [CrCl₃-

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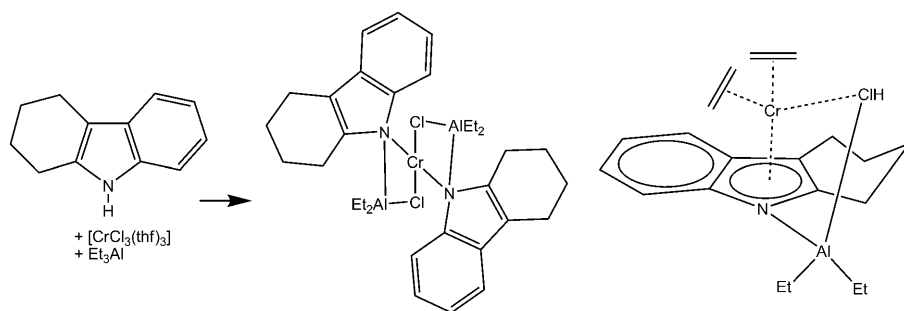
Figure 1. Isolated compound and active trimerization species postulated by Gambarotta and co-workers.

[Ph$_4$P]X (X = Cl, Br, I) were used as modifiers. The activities increase in the sequence I, Br, Cl whereas the selectivities increase in reverse order. What is remarkable here, is the lower formation of branched decenes in the case of iodide. Although the analogous tetra-*n*-butyl-phosphonium- and ammonium chlorides result in comparable
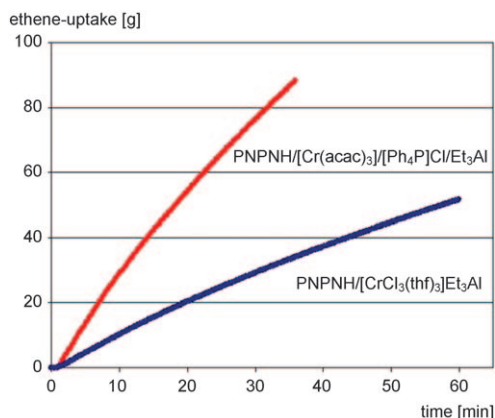
(thf)$_3$] as chromium source and triethylaluminium as co-catalyst.[12,13] The trimerization experiments were carried out in toluene as solvent. In contrast to the Chevron Phillips system, our system is not inhibited by aromatic solvents. Varying the ratios chromium/ligand/aluminium has a big impact on the activity but less influence on the selectivity of the reaction. Naturally, the ratio chromium/chloride was always fixed to 1:3 by using [CrCl$_3$(thf)$_3$].

Surprisingly, with chloride-free chromium sources (e.g., chromium(III) tris(2-ethylhexanoate) and chromium(III) acetylacetonatealmost no ethene consumption was observed. The use of diethylaluminium chloride or organic σ-bonded chloro-compounds as additives results in moderate activation, often accompanied by slightly enhanced polymer formation. Therefore, we substituted [CrCl$_3$(thf)$_3$] by a 1:3 mixture of [Cr(acac)$_3$] and modifiers which contain chloride, halides, or a tetrafluoroborate anion. The results are summarized in Table 1. A halide is essential for catalyst activation. So an ammonium salt with a BF$_4^-$ ion shows, for example, nearly no activity at all (Table 1, entry 5).

Compared with the standard system consisting of [CrCl$_3$-(thf)$_3$] (Table 1, entry 12), separating the chromium and the chloride source (Table 1, entry 2) results in a big impact on the activity while the selectivity remains largely unaffected (Figure 2). Table 2 exemplifies the importance of the halide.

Figure 2. Ethene-uptake curve for System No. **1** (red) and System No. **11**. (blue) (runs conducted at 50 °C, 30 bar, [Cr] = 1 mmol L^{-1}).

activities, there is an influence of the countercation revealed by the results reported in Tables 1 and 3. We attribute this effect to the different solubilities of the modifiers. These considerations are confirmed by trimerization experiments with varying solvents (Table 4). Nevertheless, after addition of the co-catalyst we always obtained homogeneous solutions.

Probably the most important advantage of using a mixture of [Cr(acac)$_3$] together with a modifier versus [CrCl$_3$(thf)$_3$] is the degree of freedom concerning the [Cl]/[Cr] ratio. Excluding the observed influence of the cation, the modifier, the solvent, the temperature, the pressure, etc. on the catalytic reaction, herein we concentrated our work on a defined system. The defined system consisted of [Cr-(acac)$_3$], the modifier [Ph$_4$P]Cl, and toluene as solvent; we focused the investigation on the [Cr]/[Cl]/[Al] ratio. Figure 3 and Figure 4 illustrate the effect on activity of different [Cl]/[Cr] ratios at a given [Al]/[Cr] ratio, respectively, at a given [Al]/[Cl] ratio. The average activity depends on the [Cl]/[Cr] ratio and on the [Al]/[Cr] ratio (Figure 3). In fact, the catalyst system showed its best performance at a chloride/chromium ratio of 5 and an aluminium/chromium ratio of about 25. Now, it was to prove that the catalyst performance depends on the alu-
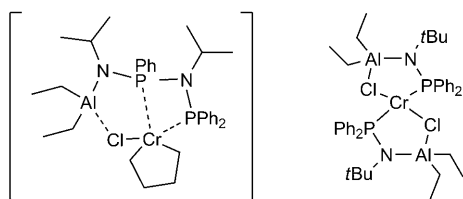
Table 1. Average activity and selectivity of the trimerization system [Cr(acac)$_3$]/modifier/PNPNH/AlEt$_3$ (runs conducted at 50 °C, 30 bar, [Cr] = 1 mmol L^{-1}, t = 1 h, [L]/[Cr] = 1.75, [Al]/[Cr] = 25, [modifier]/[Cr] = 3).

	System No.	Modifier	Average activity [kg g$_{Cr}^{-1}$ h^{-1}]	Selectivity [wt %]				
				C4	C6	1-C6	C8	C10
1	**0**	–	0.0	–	–	–	–	–
2	**1**	[Ph$_4$P]Cl	26.7	1.2	93.0	99.0	0.3	5.3
3	**2**	[Et$_4$N]Br	12.2	1.1	94.8	99.1	0.4	3.6
4	**3**	[Et$_4$N]Cl	16.5	1.2	93.4	99.0	0.3	4.9
5	**4**	[Et$_4$N]BF$_4$	0.6	4.4	84.4	98.3	1.5	8.6
6	**5**	[HN(Et)$_3$]Cl	2.7	1.0	93.2	98.9	0.4	5.2
7	**6**	[H$_3$N(*i*Pr)]Cl	7.0	0.4	93.8	99.0	0.2	5.3
8	**7**	[Pr$_4$N]Cl	12.5	2.2	91.7	99.0	0.5	5.5
9	**8**	*p*-toluidine hydrochloride	2.4	1.4	93.4	99.0	0.3	4.5
10	**9**	[RR′$_3$P]Cl[a]	17.8	1.6	92.8	99.0	0.3	4.1
11	**10**	[R$_2$R′$_2$N]Cl[b]	14.9	1.9	91.4	98.9	0.4	6.0
12	**11**	[CrCl$_3$(thf)$_3$] (reference)	8.1	2.0	92.7	98.9	0.3	4.9
13	**12**	Cr-(2-ethylhexanoate)$_3$+ [Ph$_4$P]Cl (3 equiv)	3.1	6.4	84.1	97.5	1.6	7.5

[a] (Tri-*n*-butyl)*n*-tetradecylphosphonium chloride. [b] Dimethyldistearylammonium chloride.

Figure 5. Predicted[5] and by Gambarotta and co-workers[14] isolated structures containing N-Al-Cl-Cr interactions.

Table 2. Average activities and selectivities of the trimerization system [Cr(acac)₃]/modifier/PNPNH/AlEt₃ (runs conducted at 50°C, 30 bar, [Cr]=0.25 mmol L⁻¹, t=1 h, [L]/[Cr]=1.75, [Al]/[Cr]=25, [modifier]/[Cr]=3).

System No.	Modifier	Average activity [kg g$_{Cr}^{-1}$ h⁻¹]	C4	C6	1-C6	C8	C10
1 **1**	[Ph₄P]Cl	26.7	1.2	93.0	99.0	0.3	5.3
2 **13**	[Ph₄P]Br	20.7	0.9	95.0	99.2	0.4	3.6
3 **14**	[Ph₄P]I	3.5	1.4	96.2	98.9	0.5	1.7

Table 3. Average activities and selectivities of the trimerization system [Cr(acac)₃]/modifier/PNPNH/AlEt₃ (runs conducted at 50°C, 30 bar, [Cr]=1 mmol L⁻¹, t=1 h, [L]/[Cr]=1.75, [Al]/[Cr]=25, [modifier]/[Cr]=3).

System No.	Modifier	Average activity [kg g$_{Cr}^{-1}$ h⁻¹]	C4	C6	1-C6	C8	C10
1 **15**	[(nBu)₄P]Br	11.2	1.2	93.9	99.1	0.5	4.1
2 **16**	[(nBu)₄N]Br	13.3	1.2	93.8	99.1	0.6	4.0

Table 4. Average activities and selectivities of the ethene trimerization reaction catalyzed by the [Cr(acac)₃]/[PPh₄]Cl/PNPNH/AlEt₃ catalyst system (Runs conducted at 50°C, 30 bar, [Cr]=0.3/0.5/1 mmol L⁻¹, t=1 h, [L]/[Cr]=1.75, [Al]/[Cr]=25, [modifier]/[Cr]=3).

System No.	Solvent	Average activity [kg g$_{Cr}^{-1}$ h⁻¹]	C4	C6	1-C6	C8	C10
1 **1**	toluene	26.7	1.2	93.0	99.0	0.3	5.3
2 **17**	1-hexene	4.8	2.5	87.9	92.5	0.3	8.9
3 **18**	cyclohexane	4.9	2.6	91.7	99.0	1.5	4.1

Figure 3. Average activities of the ethene trimerization reaction catalyzed by the [Cr(acac)₃]/[PPh₄]Cl/PNPNH/AlEt₃ catalyst system (Runs conducted at 50°C, 30 bar, [Cr]=0.3 mmol L⁻¹, t=1 h, [L]/[Cr]=1.75, [Al]/[Cr]=5–100, [modifier]/[Cr]=3 or 5).
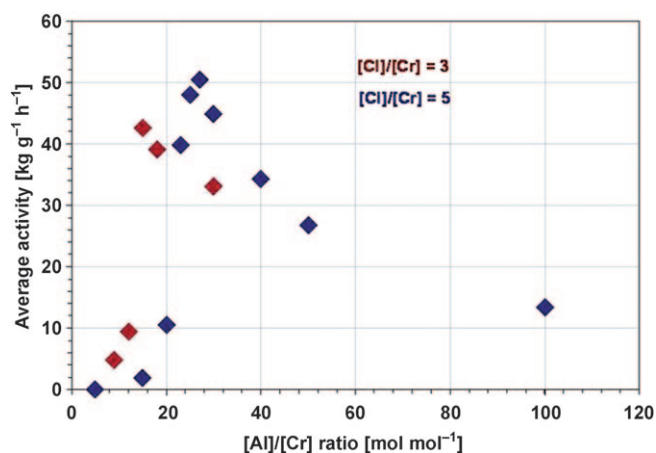
Figure 4. Average activities of the ethene trimerization reaction catalyzed by the [Cr(acac)₃]/[PPh₄]Cl/PNPNH/AlEt₃ catalyst system (Runs conducted at 50°C, 30 bar, [Cr]=0.3 mmol L⁻¹, t=1 h, [L]/[Cr]=1.75, [Al]/[Cl]=1–20, [modifier]/[Cr]=3 or 5).

minium/chloride ratio. Therefore, another test series was conducted (Figure 4). In both test series the signal in the average activity arises at an aluminium/chloride ratio of around 5.

From a mechanistic perspective, it was not well understood that the [Cr(acac)₃] catalyst system has its highest activity at a chloride/chromium ratio of 5. We assume that chromium and aluminium are competitors for chloride anions. However, in any case the activity of the trimerization system [Cr(acac)₃]/[PPh₄]Cl/PNPNH/AlEt₃ can be improved to 50 kg g$_{Cr}^{-1}$ h⁻¹ at the given conditions (50°C, 30 bar) by an optimized [Cr]/[Cl]/[Al] ratio.

In conclusion, the important role of chloride in the described chromium catalyst system for selective trimerization of ethene to form 1-hexene is elucidated. As predicted[5] and in accordance with results of Gambarotta and co-workers[14] for related systems, it is most likely that the active catalytic species contains chloride (Figure 5).

It is still an open question whether the assumed active bimetallic Cr−Al species should be regarded as a chromium chloride coordinated by the co-catalyst or as a chromium complex with a coordinating chlorinated aluminium species. We assume a reduced Cr²⁺ species as an intermediate,[15] which is considered either as a chloroaluminate-complex with a chromium monochloride cation {[CrCl]⁺[Cl-Al(Me)₂-N(iPr)P(Ph)N(iPr)PPh₂-P,P']⁻}₂ or as an aluminium-coordinated chromium dichloride {CrCl₂[Me₂Al-N(iPr)P(Ph)N-(iPr)PPh₂-P,P']}₂—these options are difficult to distinguish.[15] The above mentioned observation of the competi-

tion of Cr and Al interacting with Cl is important, and by this fact the influence of the ratio of pre-catalyst to the activator (Cr to Al and hence Cr/Al/Cl), in agreement with the findings of earlier parameter studies.[12] This suggests an entangled equilibrium between the strong Lewis acids Cr^{n+} and Al^{3+} and the strong Lewis base chloride. The independent use of a chromium source, like chromium acetylacetonate, an aluminiumalkyl and a chloride-containing modifier offers a promising opportunity to enhance catalytic activity of the described trimerization system. We assume that this principle of optimized Cr/Al/Cl ratios can be extended to other selective ethene oligomerization systems.[7]

Experimental Section

Ph₂PN(iPr)P(Ph)N(iPr)H was prepared according to a published method.[5,6,16] [Ph₄P]Cl, p-toluidine hydrochloride (ACROS), [HN(Et)₃]Cl (Fluka), [H₃N(iPr)]Cl (TCI), [Et₄N]Br, [Et₄N]Cl, [Et₄N]BF4, [Pr₄N]Cl, (tri-n-butyl)n-tetradecylphosphonium chloride, and dimethyldistearylammonium chloride (Alfa Aesar) were used as received. [CrCl₃(thf)₃] (97% purity) and a solution of AlEt₃ in toluene (1.9 mol L⁻¹) were obtained from Sigma–Aldrich and used without further purification; toluene (>99.9% purity) was obtained from Merck Chemicals and was dried over sodium with benzophenone and was then distilled in an inert gas atmosphere (Ar); argon 5.0 and ethene 3.0 were purchased from Linde Gas and used as received.

For the oligomerization of ethene an apparatus described earlier[12] was used. Before conducting an experiment, the reactor was heated to 100°C at reduced pressure for several hours to eliminate traces of water and oxygen. For the catalyst preparation, the suitable amounts of the PNPNH-ligand, chromium precursor [CrCl₃(thf)₃]/[Cr(acac)₃], and the modifier were weighed in and charged to a Schlenk tube under inert atmosphere. A volume of 100 mL anhydrous toluene was added and the solution was stirred by means of a magnetic stirrer. After dissolving the Cr-compound, ligand and modifier, the required amount of a 1.9 mol L⁻¹ solution of TEA in toluene was added. The solution was immediately transferred to the reactor and the reaction was started by opening the ethene supply.

After the residence time, the reaction in the liquid phase was quenched by transferring the liquid inventory by means of the ethene pressure to a glass vessel filled with water (ca. 100 mL). The mass balance of the experiment was determined via quantification and GC-FID analysis of the gaseous and liquid product separately, followed by comparison with the ethene uptake data. Through the closed mass balance selectivity of 1-hexene could be easily determined, when 1-hexene was used as solvent. Based on the measured data, the overall yields and selectivities were determined.

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