Ethylene Tri- and Tetramerization with Borate Cocatalysts: Effects on Activity, Selectivity, and Catalyst Degradation Pathways

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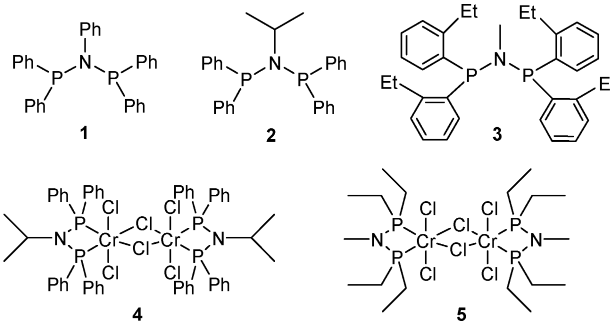
Summary: Chromium-based ethylene tri- and tetramerization catalysts have been evaluated with a combination of trialkylaluminium and borate cocatalyst activation. A remarkable effect on activity and selectivity has been observed and studied, and a cocatalyst-induced degradation pathway has been identified.

Introduction

In recent years the chromium-catalyzed oligomerization of ethylene to linear α-olefins (LAOs) has been extensively studied both in industry and in academia, due in part to increased demand for LAOs, particularly the co-monomers 1-hexene and 1-octene. Recent work includes the development of increasingly more active systems for full-range oligomerization,[1] a variety of Cr-based ethylene trimerization systems,[2−4] and the first example of selective ethylene tetramerization to 1-octene.[5] The cocatalyst typically employed in the tetramerization reaction, MAO, is normally thought to implicate a formally cationic active species, and as such we were interested in exploring the effect of more well-defined counterions on the tetramerization reaction. The use of only alkyl aluminum, AlR_3, is ineffectual, presumably due to the low Lewis acidity of these compounds. In contrast, activation of olefin polymerization catalysts with combinations of AlR_3 (alkylating agent) and the well-known alkyl-abstracting agents $B(C_6F_5)_3$ and $Ph_3C-B(C_6F_5)_4$ (BAr^F_3 and $[Ph_3C][BAr^F_4]$) is now well established.[6] Herein we report on investigations on the use of BAr^F_3 and $[Ph_3C][BAr^F_4]$ in ethylene tetramerization and the surprising shift in catalyst properties that these cocatalysts can produce.

Scheme 1



Results and Discussion

The ligands/complexes tested in this study are shown in Scheme 1 and were prepared as reported previously[5a] or via similar procedures. Complex **5** was prepared such that the effects of differing ligand sterics on the reaction could be studied (see below). Crystals of this complex suitable for X-ray analysis were grown from toluene, and the molecular structure of the complex is shown in Figure 1. A chloride-bridged dimeric structure is displayed, as has been found previously for an aryl-substituted PNP ligand.[5a] The chromium centers of the binuclear complex display a distorted octahedral geometry, enforced by the tight chelate bite angle of the PNP ligand [66.62(5)°]. The Cr−Cr distance of 3.543(2) Å is indicative of little or no metal−metal bonding.

As shown in Table 1, treatment of chromium/ligand combinations or preformed complexes with trialkylaluminium and stoichiometric BAr^F_3 or $[Ph_3C][BAr^F_4]$ leads to active catalysts for ethylene trimerization and tetramerization. In general, activation with the boranes leads to greatly lower activities compared to when MAO is employed, and a greater and somewhat variable polymer content results. Within the liquid fraction, the distribution of oligomers is very similar to that obtained with MAO.[5] In particular, tetramerization to 1-octene

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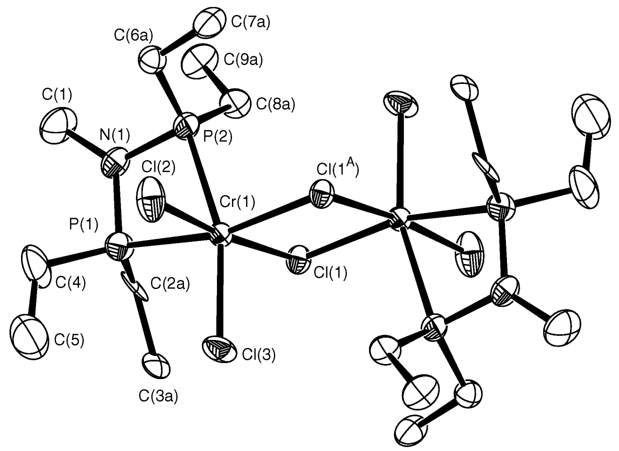


Figure 1. Molecular structure of complex **5**. Selected bond distances (Å) and angles (deg): Cr(1)−P(1) 2.4152(13); Cr(1)−P(2) 2.4775(15); Cr(1)−Cl(1) 2.3741(13); Cr(1)−Cl(1A) 2.4191(12); Cr(1)−Cl(2) 2.2839(14); Cr(1)−Cl(3) 2.3168(13); P(1)−N(1)−P(2) 106.32(19); P(1)−Cr(1)−Cl(1) 94.28(5); P(1)−Cr(1)−Cl(2) 88.43(5); P(2)−Cr(1)−Cl(1A) 99.11(5).

is accompanied by trimerization to 1-hexene along with methyl- and methylenecyclopentane.

The use of $AlEt_3$ as an alkylating agent along with BAr^F_3 was far more effective than $AlMe_3$ (entries 1 and 2). The productivity was further improved by lowering the temperature from 65 °C to 45 °C (entry 3), and all subsequent runs are at this lower temperature. The amount of $AlEt_3$ employed has a pronounced effect on productivity, as shown by entries 4−6. Productivity is highest with between 30 and 50 equiv of $AlEt_3$, while 100 equiv led to an order of magnitude drop in productivity. The best result in terms of combined selectivity and activity was obtained with the catalyst derived from **2**/Cr with 50 equiv of $AlEt_3$ (entry 5), which gave only 2% polyethylene.

The preformed complex **4** was also activated by $AlEt_3/BAr^F_3$ (entries 7 and 8), although the productivity was considerably lower than found in comparable in-situ runs. Such a trend was also observed when MAO activation was employed[5] and may relate to the dimeric and highly insoluble nature of the complexes. The addition of a large excess of $AlEt_3$, along with a concomitant increase in the amount of BAr^F_3 to 5 equiv, did not improve the results (entry 8).

We have previously shown that the introduction of steric bulk on the PNP ligands leads to a dramatic selectivity shift toward 1-hexene.[4] For instance ligand **3** gives over 90% selectivity to 1-hexene under activation with MAO. The same result was observed when **3**/Cr was activated with $AlEt_3/BAr^F_3$ (entry 9), although again a greater proportion of polymer was formed. It seems the selectivity within the oligomeric fraction is relatively unaffected by the cocatalyst, whether MAO or BAr^F_3, and remains controlled by the ligand. This suggests that the environment at the active Cr center is the same in each case. As such, the high polymer content may be a consequence of a separate and distinct chromium species that is formed under conditions of activation with AlR_3/BAr^F_3.

The cocatalyst $[Ph_3C][BAr^F_4]$ also resulted in active tetramerization catalysts, again with reduced productivity and, in some cases, a high proportion of polymer (entries 10 and 11). This cocatalyst seemed somewhat more tolerant to excess $AlEt_3$ than BAr^F_3 was, and the use of 100 equiv of $AlEt_3$ (entry 11) did not result in the same deactivation profile as observed when using AlR_3/BAr^F_3 (e.g., entry 6).

In all of the above runs it was noted that activity was initially quite high, as judged by ethylene uptake, but a rapid catalyst deactivation occurred. This was more pronounced when $AlMe_3$ was employed as an alkylating agent or when a large excess of AlR_3 was present. A deactivation pathway caused by trialkylaluminium seems likely. Such catalyst deactivation has been noted for $Cp_2MR_2/[Ph_3C][BAr^F_4]/AlR_3$ polymerization systems, prompting Bochmann to study the interaction of AlR_3 with BAr^F_3 and $BAr^F_4{}^-$.[7] This work showed that reaction of $AlMe_3$ with $[Ph_3C][BAr^F_4]$ or BAr^F_3 can lead to degradation of the borane compound through alkyl−C_6F_5 exchange, resulting in mixtures of $BAr^F_{3-x}Me_x$ and $AlMe_{3-x}Ar^F_x$ ($x = 1-3$). While $AlAr^F_3$ has been shown to be an effective cocatalyst,[8] mixed $AlR_{3-x}Ar^F_x$ species are expected to be much less so. It was also shown that this can lead to catalyst deactivation through transfer of Ar^F to the electrophilic catalyst metal center.[7] Increasing the concentration of AlR_3 will both accelerate this scrambling process and push the equilibrium toward increased alkylation of the borane. The observation that increased amounts of trialkylaluminium lead to deactivation thus supports such a mode of catalyst degradation.

This reaction likely occurs through dimeric Al−B intermediates, and as such, it was reasoned that a sterically encumbered trialkylaluminium reagent may slow the process. Al^iBu_3 was therefore tested as an alkylating agent with both BAr^F_3 and $[Ph_3C][BAr^F_4]$ (Table 1, entries 12 and 13) and led to the highest productivities in each case. Unfortunately, the high productivity was also accompanied by very high polymer production (ca. 50%).

Attempts to optimize the system resulted in the amount of $[Ph_3C][BAr^F_4]$ being increased to 5 equiv. To our surprise this led to a remarkable increase in activity and an equally dramatic change in selectivity from tri-/tetramerization to a Schulz−Flory

Table 1. Ethylene Tri- and Tetramerization with 1−4[a]

entry	cat	AlR_3 (equiv)	cocatalyst (equiv)	*T* (°**C**)	*P* (bar g)	PE (wt %)	C_6 (wt %) ($1-C_6$)	C_8 (wt %) ($1-C_8$)	prod (g/g Cr)[b]
1	**1**/Cr	$AlEt_3$ (40)	BAr^F_3 (1)	60	45	6.6	20.4 (65.1)	44.4 (93.4)	1930
2	**1**/Cr	$AlMe_3$ (50)	BAr^F_3 (1)	60	45	17.7	26.8 (71.4)	51.7 (83.3)	200
3	**1**/Cr	$AlEt_3$ (40)	BAr^F_3 (1)	45	50	31.3	12.8 (44.7)	41.2 (95.0)	5075
4	**2**/Cr	$AlEt_3$ (30)	BAr^F_3 (1)	45	50	13.0	16.0 (69.0)	62.1 (98.3)	6280
5	**2**/Cr	$AlEt_3$ (50)	BAr^F_3 (1)	45	50	2.0	28.0 (73.0)	67.0 (99.0)	7110
6	**2**/Cr	$AlEt_3$ (100)	BAr^F_3 (1)	45	50	25.2	21.4 (73.3)	47.6 (96.9)	587
7	**4**	$AlEt_3$ (40)	BAr^F_3 (1)	45	50	22.0	19.0 (69.0)	53.0 (98.0)	1930
8	**4**	$AlEt_3$ (250)	BAr^F_3 (5)	45	50	7.0	21.0 (50.0)	40.0 (95.0)	570
9	**3**/Cr	$AlEt_3$ (40)	BAr^F_3 (1)	45	50	14.7	79.3 (99.3)	4.8 (100)	5580
10	**2**/Cr	$AlEt_3$ (50)	$Ph_3CBAr^F_4$ (1)	45	40	15.8	17.3 (71.4)	62.2 (98.9)	2595
11	**2**/Cr	$AlEt_3$ (100)	$Ph_3CBAr^F_4$ (1)	45	40	trace	19.6 (69.2)	70.8 (98.3)	2540
12	**2**/Cr	Al^iBu_3 (30)	BAr^F_3 (1)	45	50	50.6	7.7 (66.5)	34.6 (98.6)	14 790
13	**2**/Cr	Al^iBu_3 (30)	$Ph_3CBAr^F_4$ (1)	45	50	45.1	8.0 (66.3)	39.0 (98.7)	10 540

[a] 10 μmol of $CrCl_3(thf)_3$, 12 μmol of ligand, 100 mL of toluene as solvent, 30 min. [b] Productivity expressed in g(total product)·g(Cr)$^{-1}$.

Table 2. Ethylene Oligomerization with 5 equiv of $[Ph_3C][BAr^F_4]^a$

entry	cat	AlR_3 (equiv)	PE wt %	olig wt %	*K*	prod (g/g Cr)
1	**2**/Cr	$AlEt_3$ (50)	<0.1	99.9	0.55	59 825
2	**2**/Cr	$AlEt_3$ (200)	0.4	99.6	0.53	78 850
3	**4**	$AlEt_3$ (200)	0.2	99.8	0.54	34 300
4	**4**	$AlMe_3$ (200)	1.0	99.0	0.49	38 222
5	**3**/Cr	$AlMe_3$ (200)	6.3	93.7	0.51	34 410
6	**5**	$AlEt_3$ (50)	3.4	96.6	0.52	13 065
7	Cr	$AlEt_3$ (50)	1.0	99.0	0.60	25 450

[a] 10 μmol of Cr, 12 μmol of ligand, 45 °C, 40 bar g, 100 mL of toluene, 30 min.

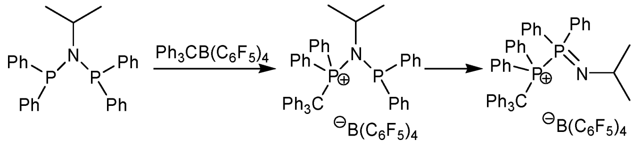
distribution of α-olefins (Table 2).[9] For instance, with a combination of $CrCl_3(thf)_3$ and **2**, activated with 50 equiv of $AlEt_3$ and 5 equiv of $[Ph_3C][BAr^F_4]$, a productivity of 59 825 g/g Cr resulted (Table 2, entry 1). At the start of this run, an exotherm occurred that took the temperature from 45 °C to 80 °C upon pressurizing with ethylene, the temperature being brought back to 45 °C over ca. 4 min with internal cooling of the reactor. Likewise, all experiments listed in Table 2 required continued cooling throughout the run to maintain the temperature. The shift to Schulz−Flory oligomerization in these examples was accompanied by a large reduction in the amount of polymer formed, and the α-content in each olefin fraction was generally above 99%.

Subsequent experiments showed that this selectivity change occurs regardless of the amount of trialkylaluminium (entry 2), whether the catalyst is preformed (entry 3) or whether $AlMe_3$ is employed in place of $AlEt_3$ (entry 4). The sole deciding factor appears to be the amount of $[Ph_3C][BAr^F_4]$ employed. Additionally, the rapid catalyst deactivation observed in the tetramerization runs when a single equivalent of cocatalyst was used was not evident when 5 equiv of this activator was used.

Evidently, a very different catalytic species is forming under these conditions, and we were intrigued to study this further, in particular to establish if the olefin distribution could be shifted to more interesting (higher) *K* values. The introduction of increased steric bulk at the metal center has been shown to increase the molecular weight distribution in both ethylene oligomerization and polymerization. The more bulky PNP ligand **3** was therefore tested along with 5 equiv of $[Ph_3C][BAr^F_4]$. This ligand was expected to affect the Schulz−Flory distribution, especially given the pronounced shift in selectivity that occurs in the tri-/tetramerization reaction when **2** and **3** are compared. Surprisingly however, **3** led to no change in the *K* value (entry 5). To further explore this, complex **5**, which contains the compact alkyl-substituted PNP ligand, was also tested. The low steric demand of this ligand is evident from the crystal structure, but nonetheless when tested for oligomerization the olefin distribution was effectively unchanged (entry 6).

These observations are somewhat unexpected if the ligand mediates oligomerization on Cr and leads to the conclusion that the ligand may not be involved when a Schulz−Flory distribution is observed. To test for this, $CrCl_3(thf)_3$ was tested without PNP ligand present, as an approximation of "naked" Cr (entry 7). This led to an uncontrollable exotherm to 110 °C, which was slowly brought back to 45 °C with cooling of the reactor. Although the *K* value obtained was modestly higher than the PNP-containing catalyst's, it can be concluded that unligated Cr leads to catalysis very similar to the PNP system's, and there appears to be very little ligand influence when 5 equiv of $[Ph_3C][BAr^F_4]$ is present. A ligand abstraction by excess $[Ph_3C][BAr^F_4]$ seems likely, and the interaction between the PNP ligands and $[Ph_3C][BAr^F_4]$ was therefore studied by NMR spectroscopy.

Scheme 2



When a C_6D_6 solution of **2** (^{31}P: 50 ppm) was treated with an equimolar amount of $[Ph_3C][BAr^F_4]$, some precipitation occurs and the singlet gives way to two coupled doublets (J = 65 Hz) at 65 and 47 ppm, along with two weaker resonances at 53 and 22 ppm (the signals are quite weak due to low solubility of the products). After some hours the signals at 53 and 22 ppm are predominant. After sitting overnight, the C_6D_6 was decanted from the precipitate and the product taken up in $CDCl_3$, in which only the peaks at 53 and 22 ppm are observed. There is no change to the $BAr^F_4{}^-$ anion, as shown in the ^{19}F NMR spectrum. The ^{31}P, ^1H, and ^{19}F NMR are all consistent with the reaction sequence shown in Scheme 2. Unfortunately, attempts to isolate this product resulted in a sticky solid that could not be further purified.

A further experiment shows that excess $[Ph_3C][BAr^F_4]$ can abstract the PNP ligands from an alkylated Cr center. The methylated complex $CrCl_2Me(\mathbf{1})(thf)$ (**6**) was prepared from $CrCl_2Me(thf)_3$ and ligand **1** in toluene. When this was treated with 3.5 equiv of $[Ph_3C][BAr^F_4]$ in $CDCl_3$, the ^1H NMR spectrum clearly shows the expected formation, through alkyl abstraction, of 1,1,1-triphenylethane. The reaction also cleanly affords two signals in the ^{31}P NMR spectrum at 37 and 22 ppm (free ligand 70 ppm), consistent with the iminophosphine.

It is evident from the above that excess $[Ph_3C][BAr^F_4]$ can result in ligand loss from Cr. At the very least, this reaction would destroy the bidentate coordination mode of the ligand and may even lead to complete dissociation. It seems that the alkyl group must be abstracted from Cr preferentially, as with 1 equiv of $[Ph_3C][BAr^F_4]$ an active tetramerization catalyst results. However, with excess trityl cation present, an essentially unligated Cr species is formed that is highly active for Schulz−Flory oligomerization.

Summary and Conclusion

We have shown that fluorinated borane and borate cocatalysts, in combination with an alkylating agent, give rise to active trimerization and tetramerization catalysts with Cr/PNP combinations. Liquid fraction selectivities are similar to when MAO is used; however productivities are much reduced and a higher proportion of polymer is formed. The requirement for known alkyl-abstracting reagents in catalysis points toward a formally cationic metal center in the tetramerization reaction.[10] A dramatic shift in activity and selectivity that occurs when excess $[Ph_3C][BAr^F_4]$ is employed is likely due to ligand abstraction from the Cr, rather than a mechanism mediated by the PNP ligand. This result cautions that careful selection of catalyst/cocatalyst ratios may be required when highly Lewis acidic activators are employed in olefin oligomerization and polym-

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(9) The Schulz−Flory distribution is characterized by the *K* value; $K = \mathrm{mol}(C_{n+2})/\mathrm{mol}(C_n)$.

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erization reactions. We have also demonstrated that reports on the development of Cr-based ethylene oligomerization catalysts must be evaluated with reference to the high intrinsic activity of unligated Cr for Schulz−Flory oligomerization and a need to establish genuine ligand effects on catalysis.

Experimental Section

All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox, using solvents purified and dried by standard procedures. Oligomerization of ethylene was performed as described previously.[2b] The preparation of ligands **1**−**3** has been reported previously.[5a] Complexes **4** and **5** were prepared by heating a toluene solution of the ligand and $CrCl_3(thf)_3$ to 90 °C, as described in ref 5a. Complex **4**: Anal. Calcd for $C_{27}H_{27}P_2NCrCl_3$ (found): C, 55.36 (55.19); H, 4.64 (4.87); N, 2.39 (2.29). Complex **5**: Anal. Calcd. for $C_9H_{23}P_2NCrCl_3$ (found): C, 29.57 (29.62); H, 6.34 (6.45); N, 3.83 (3.87). μ_{eff}: 3.86 μ_B/Cr (5.46/dimer). Complex **6** was prepared from $CrCl_2Me(thf)_3$ and ligand **1** in toluene: Anal. Calcd. for $C_{35}H_{36}P_2ONCrCl_2$ (found): C, 62.60 (62.37); H, 5.40 (5.23); N, 2.08 (1.95). μ_{eff}: 3.59 μ_B.

X-ray Crystallography of 5. $C_{18}H_{46}N_2P_4{-}Cl_6Cr_2$. $M = 731.15$, blue platelet, crystal size 0.10 × 0.05 × 0.01 mm, monoclinic, $P2_1/n$, $a = 10.443(4)$ Å, $b = 12.753(3)$ Å, $c = 12.657(5)$ Å, $\beta = 106.366(6)°$, $V = 1617.3(11)$ Å^3, $Z = 2$, $D_{calcd} = 1.501$ Mg m^{-3}; Mo Kα radiation (confocal optic, $\lambda = 0.71073$ Å), $\mu = 1.378$ mm^{-1}, $T = 93(2)$ K, 11 742 data (2887 unique, $R_{int} = 0.0346$, $2.75° < \theta < 25.351°$) were collected on a Rigaku MM007/Saturn CCD diffractometer and were corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL, Bruker AXS Madison WI, 2001, version 6.1) to give $wR = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.1110$, conventional $R = 0.0502$ for F values of reflections with $F_o^2 > 2\sigma(F_o^2)$ [2486 observed reflections], $S = 1.099$ for 191 parameters. Disorder in the ethyl arms was resolved into different orientations of 50% occupancy, except for the C4/C5 arm, which was not disordered. All $P{-}CH_2$ distances were treated with a restraint. Residual electron density extremes were 0.517 and −0.388 e Å^{-3}.

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Supporting Information Available: Crystallographic data for **5**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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