Cocatalyst Influence in Selective Oligomerization: Effect on Activity, Catalyst Stability, and 1-Hexene/1-Octene Selectivity in the Ethylene Trimerization and Tetramerization Reaction

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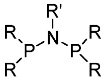
The trimerization and tetramerization of ethylene to 1-hexene and 1-octene with a Cr/PNP/$AlEt_3$ catalyst system, in combination with a variety of cocatalysts, has been investigated. The cocatalysts $B(C_6F_5)_3$ (**1**), $Al(OC_6F_5)_3$ (**2**), $[(Et_2O)_2H][Al(OC_6F_5)_4]$ (**3**), $[Ph_3C][Ta(OC_6F_5)_6]$ (**4**), $(Et_2O)Al\{OCH(C_6F_5)_2\}_3$ (**5**), $(Et_2O)Al\{OC(CF_3)_3\}_3$ (**6**), $[Ph_3C][Al\{OC(CF_3)_3\}_4]$ (**7**), $[Ph_3C][AlF\{OC(CF_3)_3\}_3]$ (**8**), $[Ph_3C][\{(F_3C)_3CO\}_3Al{-}F{-}Al\{OC(CF_3)_3\}_3]$ (**9**), and $[Ph_3C][CB_{11}H_6Br_6]$ (**10**) have been evaluated. The relative selectivity to 1-hexene and 1-octene obtained shows a strong dependence on the nature of the cocatalyst, and a range of selectivities from <5% C_8 (90% C_6) to 72% C_8 have been observed. The stability of several cocatalysts toward $AlEt_3$ has been studied, and the poor performance of **1** and **2** is linked to degradation of the cocatalyst through ethyl group exchange with $AlEt_3$. In contrast, the $[Al\{OC(CF_3)_3\}_4]^-$ anion in **7** is much more stable and gives rise to a highly active and longer lived catalyst. The overall productivity and selectivity of the catalyst is dependent upon both cocatalyst stability and the nature of the anion present, and a reason for this effect has been suggested. Selectivity control by the cocatalyst has been ascribed to interaction of the anion with the active Cr center.

1. Introduction

The commercial oligomerization of ethylene is predominately carried out using transition-metal catalysts that produce a broad distribution of linear α-olefins (LAOs). Such distributions do not closely match present and future market demand, and as such the development of more selective routes to desired LAOs is currently of industrial and academic interest. In particular, 1-hexene and 1-octene are in high demand, due to their use as comonomers for polyethylene production (LLDPE). This has led to considerable interest in catalysts for the trimerization of ethylene to 1-hexene (Cr,[1−13] Ti,[14−16] Ta[17]), and more recently the tetramerization of ethylene to 1-octene with Cr complexes of PNP ligands **I**.[18−21] These routes largely avoid the production of undesirable olefins that conventional full-range oligomerization processes produce, and as such, the first commercial trimerization process has recently been started.[22]



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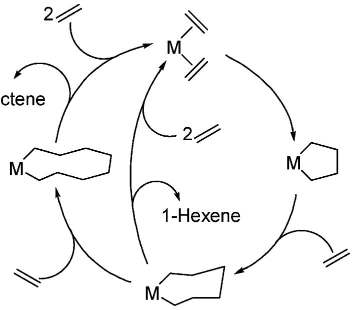
Scheme 1. Proposed Mechanism of Ethylene Trimerization and Tetramerization



The mechanism of ethylene trimerization and tetramerization is generally thought to follow a metallacyclic route, involving oxidative addition of two ethylene molecules to the metal followed by insertion of one (trimerization) or two (tetramerization) further ethylene units to yield higher metallacycles. Reductive β-hydride transfer can then release the α-olefin and regenerate the active metal species (Scheme 1). Support for this mechanism comes from a number of experimental[23−26] and theoretical[27−31] investigations. The key to the selectivity of these systems appears to be the energetically preferred tendency of these metallacycles to undergo 1-hexene or 1-octene eliminations rather than further ethylene insertions. This is clearly ligand dependent, and recent studies have shown that further ethylene insertion is possible and can lead to "runaway" metallacycle growth and concomitant unselective Schulz−Flory oligomerization.[32,33]

The importance of ancillary ligand influence in this mechanism has been demonstrated in a number of studies. For instance, the pendant arene group in Ti trimerization systems is thought to moderate its coordination strength throughout the catalytic cycle,[34] while the pyrrolyl ligand of the Phillips catalyst does likewise by undergoing haptotropic shifts between η^1 and η^5 coordination.[30] Ligand effects are perhaps most pronounced in trimerization and tetramerization catalysts based on Cr complexes of PNP ligands **I**. The activity and particularly selectivity of these systems show a strong dependency on the steric and coordinative properties of the ligand. The inclusion of *o*-OMe groups on arylphosphino derivatives of **I** leads to a catalyst that is highly selective to 1-hexene.[5] In the absence of ortho substitution on the aryl group, or with an alkylphosphino ligand structure, the selectivity shifts to predominately 1-octene.[18] It was subsequently shown that only a single *o*-OMe group is required to effect this selectivity shift,[19] and intermediate selectivity is obtained with the pendant alkoxy substitution on the nitrogen of **I**.[35] Hemilabile coordination of the ether group has been demonstrated[25] and seems to be responsible for the selectivity switch. A coordinating donor group is not essential, however, and it has been shown that the introduction of steric bulk (alkyl groups) in the ortho position leads to increased 1-hexene selectivity at the expense of 1-octene.[11] In this case, the relative ratio of 1-hexene to 1-octene was found to be dependent on the total amount of steric bulk, as measured by the number of ortho substituents and the nature of the N substituent. Furthermore, we have recently demonstrated that expansion of the chelate ring size in related P^P−Cr complexes also leads to a change in C_6/C_8 selectivity.[36] A major advantage of this catalyst class is thus apparent: a high degree of control over relative 1-hexene and 1-octene selectivities is available by careful ligand modification.

The available evidence to date is suggestive of formally cationic active species in Cr−**I**-catalyzed trimerization and tetramerization[24,37,38] and trimerization with other systems.[13,39,40] This is certainly consistent with the cocatalyst most often employed being methaluminoxane. The use of MAO as a cocatalyst in olefin oligomerization and polymerization is normally thought to implicate a cationic active metal center.[41] While MAO is relatively poorly defined, a great deal of work has been carried out on more well-defined polymerization systems based upon cation−anion pairs. The most common systems here incorporate the ubiquitous (perfluoroaryl)borate anions, which have allowed thorough characterization and isolation of active polymerization systems.[41] These studies have also highlighted the pronounced effects that the counterion in these systems can have on catalyst stability, activity, and stereoselectivity, and it is now realized that the nature of the metal−anion interaction is a decisive factor in catalyst performance.[42−51] To date, there have been very few investigations into such cocatalyst effects in selective ethylene oligomerization catalysts.[13,40]

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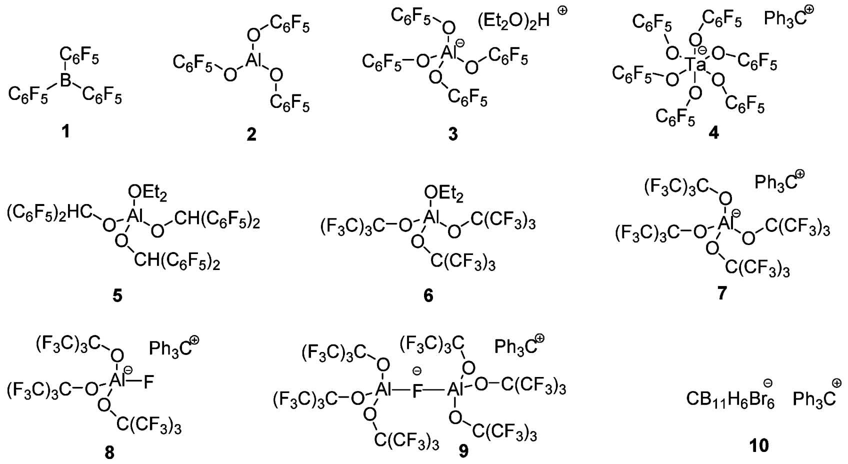
Chart 1. Cocatalysts Investigated for Ethylene Trimerization and Tetramerization



Given the dramatic selectivity changes that ligand modification can provide, a detailed investigation into alternative cocatalysts for ethylene trimerization and tetramerization seems justified. Such an investigation is not just of interest due to activity and selectivity effects that might arise. The use of excess MAO has economic implications when it comes to the large-scale use of such technology. The development of well-defined, stoichiometric cocatalysts for trimerization and tetramerization, in analogy to the work that has been done on polymerization catalysts, is therefore of interest.

We recently communicated first results in this regard, whereby a number of Cr−**I** catalysts were tested under conditions of activation with $B(C_6F_5)_3/AlR_3$ and $[Ph_3C][B(C_6F_5)_4]/AlR_3$.[52] This work showed that while liquid fraction selectivities were similar to MAO activation, the catalyst rapidly deactivated and a variable, generally high, amount of polyethylene formation was observed. The rate of deactivation in these systems was found to increase with the amount of $AlEt_3$ alkylating agent employed. This led us to suggest degradation of the borane/borate through alkyl exchange with $AlEt_3$ as the source of catalyst deactivation. Such a deactivation process has been established for metallocene/$[Ph_3C][B(C_6F_5)_4]/AlR_3$-based polymerization systems,[53] and ligand exchange between $AlMe_3$ and $B(C_6F_5)_3$ has also been demonstrated.[54] If indeed this form of deactivation is occurring for trimerization and tetramerization catalyst systems, it implies that a more robust cocatalyst anion is required in order that highly productive alternatives to MAO activation might be devised. Confirmation of such a deactivation process and the development of more stable cocatalysts are therefore of interest. Herein we report detailed studies into the effect of varying the cocatalyst stability and anion coordination strength and the dramatic influence this has on catalyst activity and selectivity. As a result of these studies, we have developed highly active tetramerization catalysts without the requirement for MAO activation and have shown for the first time that the relative 1-hexene and 1-octene selectivities can be controlled by cocatalyst modification.[55]

2. Results and Discussion

2.1. Cocatalysts. In searching for alternative cocatalyst anions to MAO and perfluoroborates, we became interested in fluorinated alkoxymetalate- and aryloxymetalate-based weakly coordinating anions.[56,57] Marks has reported activation of metallocene polymerization catalysts with $[Ph_3C][Al(OC_6F_5)_4]$ and $[Ph_3C][Ta(OC_6F_5)_6]$ and investigated the effect of the anion upon catalysis.[58,59] In particular, we were drawn by reports of Krossing that bulky fluorinated alkoxy groups on aluminum give rise to very weakly coordinating and chemically robust anions.[60] For instance, the $[Al\{OC(CF_3)_3\}_4]^-$ anion is estimated to be one of the most weakly coordinating anions known and contains a strong Al−O bond that is resistant to alkoxide ion abstraction. This anion is even reported to be stable in aqueous HNO_3.[61] The halogenated carborane anion $[CB_{11}H_6Br_6]^-$ was also investigated, due to the reported robustness of this class of anions.[62] In particular, their stability toward alkylaluminum reagents[63] made them of interest in the context of this study.

The cocatalysts employed in this study are shown in Chart 1. These cocatalysts, which are based predominately upon fluorinated aluminates, were chosen to contain a range of anion coordinating strengths, steric protection, and, as will be shown, cocatalyst stability. Both neutral Lewis acidic species (in situ anion formation) and also preformed anions incorporating an alkyl abstracting agent (Ph_3C^+, H^+) are represented. The anions $[Al(OC_6F_5)_4]^-$ and $[Ta(OC_6F_5)_6]^-$,[58] $[Al\{OC(CF_3)_3\}_4]^-$,[60] $[AlF\{OC(CF_3)_3\}_3]^-$ and $[\{(CF_3)_3CO\}_3Al{-}F{-}Al\{OC(CF_3)_3\}_3]^-$,[64] and $[CB_{11}H_6Br_6]^-$ [65] have been reported previously.

The preparation of $Al(OC_6F_5)_3$ (**2**) proceeded smoothly through addition of an excess of perfluorophenol to $AlEt_3$ in toluene. A single-crystal X-ray analysis reveals a dimeric structure in the solid state, in which each Al center is tetrahedral (Figure 1). In $CDCl_3$ solution compound **2** is only sparingly soluble and the ^{19}F NMR spectrum reveals many broad and overlapping signals, possibly due to the dynamic formation of higher oligomers. The compound is more soluble in DMSO-d_6 and displays sharp signals (see Experimental Section), probably due to formation of a monomeric adduct, $(D_3C)_2SO{-}Al$-

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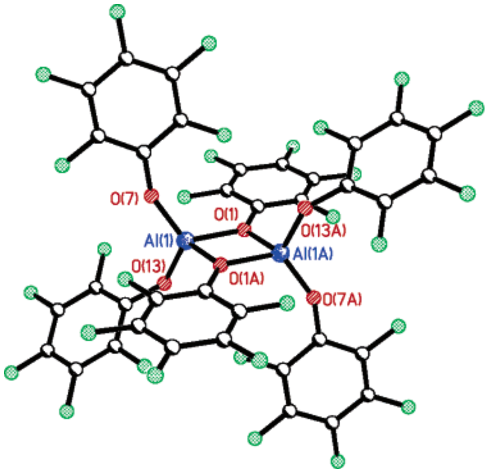


Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Al(1)−O(7), 1.6691(14); Al(1)−O(13), 1.6855(13); Al(1)−O(1), 1.8424(14); Al(1)-O(1A), 1.8543(14); O(7)−Al(1)−O(13), 118.68(7); O(7)−Al(1)−O(1), 118.85(7); O(1)−Al(1)−O(1A), 78.43(7).

$(OC_6F_5)_3$. In contrast, the boron analogue, $B(OC_6F_5)_3$, is monomeric both in the solid state and in solution.[66] Compound **2** is designated by its empirical formula throughout this paper, such that 1 equiv of **2** corresponds to 1 equiv of Al in the catalytic experiments. The solid-state bimetallic system has an $Al\cdots Al$ distance of 2.86 Å. The Al_2O_2 core is planar, as a consequence of crystallographic symmetry, while the bridging OC_6F_5 groups are essentially coplanar with this ring. The terminal O−Al−O angles (118.68(7) and 118.85(7)°) are almost trigonal, while the internal O−Al−O angle is very acute (78.43(7)°) in the four-membered ring. The terminal Al−O bonds (1.6691(14) and 1.6855(13) Å) are somewhat shorter than in anionic aluminates containing fluorinated alkoxide ligands (1.70−1.76 Å),[60,61] while the bridging Al−O bonds are longer at 1.8424(14) and 1.8543(14) Å. The same reaction, when carried out in ether, afforded $[(Et_2O)_2H][Al(OC_6F_5)_4]$ (**3**) and as such represents a convenient route to an aluminate analogue of Brookhart's acid $[(Et_2O)_2H][B\{C_6H_3(CF_3)_2\}_4]$.[67] Unfortunately, this reaction does not seem to be general, and when the more bulky alcohols $HOC(CF_3)_3$ and $HOC(H)(C_6F_5)_2$ were employed, the neutral etherate complexes $Al(OR^F)_3(OEt_2)$ (**5** and **6**) resulted. Slow crystallization of **5** from petroleum spirits led to two sets of crystals. Analysis of the minor product showed it to be the ether-free dimer $Al_2\{OCH(C_6F_5)_2\}_6$, which is comparable in structure to **2** (see the Supporting Information). Evidently, some loss of coordinated ether occurs during crystallization, resulting in formation of the dimer. The major set of crystals corresponds to the tetrahedral ether adduct, as shown in Figure 2. The Al−alkoxide bonds range in length from 1.681(5) to 1.730(4) Å, while the $Al-O_{ether}$ bond is 1.849(4) Å in length. Compound **6** proved extremely sensitive, and it was not possible to obtain a meaningful or reproducible elemental analysis. After a number of attempts, a crystal structure could be obtained, which is shown in Figure 3. The tetrahedral Al center of **6** is comparable to that of **5**, with Al−alkoxide lengths of 1.719(9)−1.731(8) Å and an $Al-O_{ether}$ length of 1.856(9) Å.

2.2. Ethylene Trimerization and Tetramerization. Throughout this study, we have employed an in situ formed catalyst

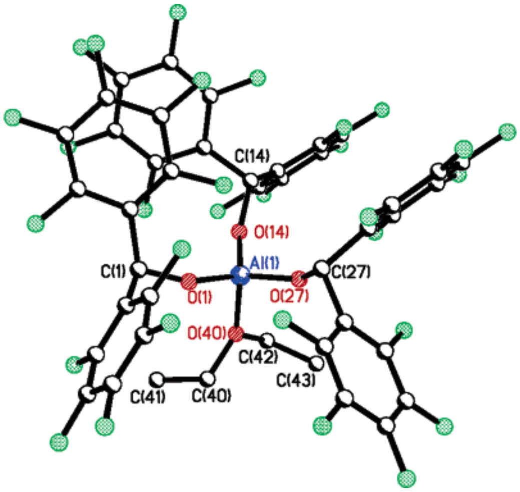


Figure 2. Molecular structure of **5**. Selected bond lengths (Å) and angles (deg): Al(1)−O(1), 1.681(5); Al(1)−O(14), 1.712(4); Al(1)−O(27), 1.699(4); Al(1)−O(40), 1.849(4); O(1)−Al(1)−O(14), 121.0(3); O(1)−Al(1)−O(27), 111.7(3); O(1)−Al(1)−O(40), 102.6(2).

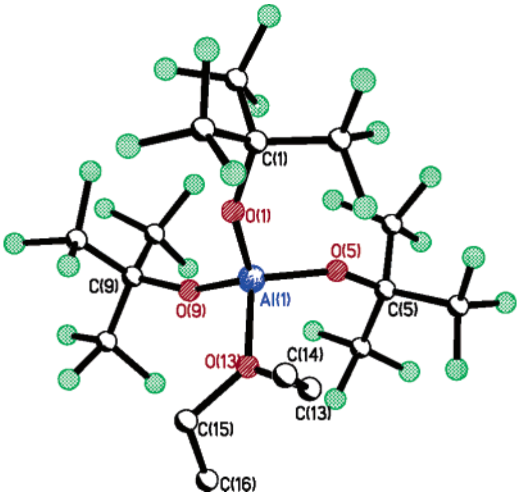
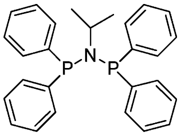


Figure 3. Molecular structure of **6**. Selected bond lengths (Å) and angles (deg): Al(1)−O(5), 1.728(10); Al(1)−O(1), 1.731(8); Al(1)−O(9), 1.719(9); Al(1)−O(13), 1.856(9); O(1)−Al(1)−O(9), 115.9(4); O(1)−Al(1)−O(5), 110.5(4); O(1)−Al(1)−O(13), 103.5(4).

system composed of $CrCl_3(thf)_3$ and PNP ligand **II** in a 1:1.2 ratio. In a typical experiment, a toluene solution of Cr−**II** was treated with $AlEt_3$ and stirred for 5 min before addition to the reactor. Immediately thereafter, a solution of the chosen cocatalyst, **1**−**10**, was injected and the reactor pressurized with ethylene. The majority of experiments were carried out at 45 °C. To compare relative C_6 and C_8 selectivities between catalysts, the value of the molar ratio of C_6/C_8 has been reported for each experiment. The results of these oligomerization runs are presented in Table 1.



II

For validation of this experimental setup, an ethylene tetramerization run was conducted with MMAO-3A as activator at 65 °C (entry 1), confirming that the expected selectivity to

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[66] Britovsek, G. J. P.; Ugolotti, J.; White, A. J. P. *Organometallics* **2005**, *24*, 1685.

[67] Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

Table 1. Ethylene Trimerization and Tetramerization with $CrCl_3(thf)_3$/II/$AlEt_3$/Cocatalyst[a]

entry	cocat. (amt (equiv))	amt of Cr (μmol)	AlR_3 (amt (equiv))	T (°C)	P (bar)	run time (min)	PE (%)	C_6 (1-C_6) (%)	C_8 (1-C_8) (%)	C_6/C_8 (molar)	prod[b]
1	MMAO-3A (800)	2.5		65	40	60	1.6	23.3 (81.2)	64.4 (99.2)	0.48	550 810
2[c]	MMAO-3A (300)	20		45	45	30	0.1	16.0 (66.4)	70.7 (97.9)	0.30	285 100
3	**1** (1.3)	10	$AlEt_3$ (50)	45	50	30	2.0	28.0 (73.0)	67.0 (99.0)	0.56	7 110
4	**1** (1.3)	10	$AlEt_3$ (100)	45	50	30	25.2	21.4 (73.3)	47.6 (96.9)	0.60	587
5	**2** (1.3)	30	$AlEt_3$ (300)	45	40	30	2.3	89.9 (95.6)	4.7 (74.4)	25	2 340
6	**2** (1.3)	30	$AlEt_3$ (30)	45	40	30	8.2	85.2 (98.5)	3.9 (94.6)	29	5 810
7	**2** (1.3)	30	$AlBu^i_3$ (100)	45	40	30	6.4	86.0 (97.8)	4.0 (96.8)	29	997
8	HOC_6F_5 (3.0)	30	$AlEt_3$ (30)	45	40	30	16.0	78.3 (97.9)	1.8 (84.4)	58	3 410
9	**3** (1.5)	10	$AlEt_3$ (100)	45	40	30	12.6	63.9 (95.0)	23.5 (97.6)	3.6	1 680
10	**4** (2.0)	10	$AlEt_3$ (100)	45	40	30	13.7	46.6 (89.7)	39.6 (98.5)	1.6	1 330
11	**5** (1.5)	10	$AlEt_3$ (100)	45	35	30	27.8	43.8 (86.7)	28.3 (98.2)	2.1	760
12	**6** (1.7)	20	$AlEt_3$ (100)	45	40	30	1.0	87.3 (97.0)	6.1 (88.5)	19	4 100
13	**7** (1.5)	10	$AlEt_3$ (100)	45	40	60	0.41	16.3 (68.9)	72.2 (99.0)	0.30	125 600
14	**7** (1.5)	10	$AlEt_3$ (100)	65	40	60	0.6	25.0 (82.5)	66.6 (99.2)	0.50	59 560
15	**7** (1.5)	10	$AlEt_3$ (300)	45	40	60	1.3	16.9 (66.3)	72.7 (98.0)	0.31	57 250
16	**7** (1.5)	10	$AlEt_3$ (600)	45	40	30	3.3	28.2 (66.3)	60.1 (96.7)	0.62	1 440
17	**8** (1.5)	10	$AlEt_3$ (100)	45	40	60	33.3	34.6 (80.8)	32.1 (87.7)	1.4	2 280
18	**9** (1.0)	10	$AlEt_3$ (100)	45	35	30	10.0	57.8 (94.7)	30.3 (95.4)	2.5	6 925
19	**9** (1.5)	10	$AlEt_3$ (100)	45	40	30	21.6	44.0 (95.9)	25.5 (98.2)	2.3	12 810
20	**9** (2.0)	10	$AlEt_3$ (100)	45	40	30	7.9	27.9 (85.9)	56.0 (99.2)	0.66	13 730
21	**9** (3.0)	10	$AlEt_3$ (100)	45	35	60	6.5	18.6 (76.3)	68.2 (99.4)	0.36	53 120
22	**10** (1.5)	10	$AlEt_3$ (100)	45	40	30	45.9	22.1 (84.8)	32.0 (97.2)	0.92	1 090

[a] Conditions: $CrCl_3(thf)_3$/**II** (1:1.2), toluene (100 mL). [b] Productivity: g of product/g of Cr. [c] From ref 18.

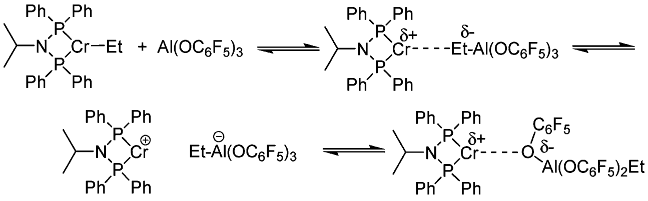
1-hexene and 1-octene is obtained ($C_6/C_8 = 0.48$). A high productivity was obtained over the 1 h run, although much higher catalyst activities are achievable with this system under optimized conditions.[36] Entry 2, from previous work,[18] shows that the selectivity obtained at 45 °C is somewhat different, with more C_8 formed at the expense of C_6 ($C_6/C_8 = 0.30$).

Full results of activation with perfluoroborane and borate cocatalysts have been reported;[52] herein two catalytic runs with $B(C_6F_5)_3$ (**1**) are included for reference (entries 3 and 4). These show that a much reduced productivity is observed that is dependent upon the amount of $AlEt_3$ alkylating agent employed. While the initial activity is quite high with this system, as judged by ethylene uptake, a rapid catalyst deactivation occurs early in the run. This appears to be accelerated by increased $AlEt_3$ loadings beyond 50 equiv. A somewhat higher C_6/C_8 value is observed compared to MAO activation (cf. 0.56 for **1** to 0.30 for MMAO-3A at 45 °C), although this was not recognized as significant previously. In light of the results presented below, it now seems probable that it is.

The first aluminate cocatalyst to be prepared and tested was $Al(OC_6F_5)_3$ (**2**). To our surprise, the use of this cocatalyst lead to a remarkable shift in selectivity toward 1-hexene, such that the C_8 content in each case was below 5% (entries 5−7). Within the C_6 fraction, the purity of 1-hexene is high (95.6−98.5%), and very little cyclic C_6 (methylcyclopentane, methylene cyclopentane) is formed, in contrast to a normal tetramerization run with this ligand.[26] Overall, the product selectivity is much like that obtained with a trimerization PNP ligand containing *o*-OMe substitution[5,19] or ortho steric bulk[11] and has not previously been observed with ligand **II**. In common with $B(C_6F_5)_3$ activation, a rather low productivity is obtained that seems to stem at least in part from rapid catalyst deactivation over 5−10 min, this again being dependent upon the amount of $AlEt_3$ employed. A relatively high amount of polyethylene is also formed in comparison to activation with MMAO-3A.

There are a number of possible reasons for this dramatic selectivity shift toward trimerization. A trimerization system based on aryloxyaluminum compounds together with a Cr source has been reported previously and probably operates via formation of an aryloxychromium active species.[6] On the basis of this, it occurred to us that the trimerization activity observed may be due to a $Cr-OC_6F_5$ species, formed via ligand exchange between Cr and **2**. To test for this, a catalytic run was conducted with $CrCl_3(thf)_3$ (30 μmol), HOC_6F_5 (90 μmol), and $AlEt_3$ (30 equiv), in the absence of ligand **II**. Although a productivity of 3710 g/g of Cr was obtained, the product was composed of 95% polyethylene with no selectivity in the liquid fraction. This clearly shows that the PNP ligand **II** is essential to trimerization activity. This is not the say that $[OC_6F_5]^-$ transfer to Cr cannot or does not occur (see below), but it does not appear to be responsible for trimerization selectivity. A more likely reason, it seems, is that activation with **2** gives rise to a more coordinating anion. The anion or anion-like species initially formed presumably is $[AlEt(OC_6F_5)_3]^-$. This could coordinate with the formally cationic Cr center, either via bridging alkyl coordination, as has been established for $[B(C_6F_5)_3R]^-$, or through a bridging oxygen donor. Such coordination may mimic the hemilabile coordination of *o*-OMe substitution in aryl PNP ligands, which is known to lead to increased trimerization selectivity (Scheme 2).

Scheme 2



The cocatalyst could also be prepared in situ, by addition of HOC_6F_5 to the reactor in place of **2** (entry 8). In this case, trisubstitution of the aluminum is unlikely, the initial product prior to reaction with Cr probably being $AlEt_2(OC_6F_5)$. This increased the C_6/C_8 value to 58, at the same time producing a higher amount of polyethylene (16%).

On the basis of the premise that anion coordination strength can control C_6/C_8 selectivity, the preformed anionic activator $[H(OEt_2)_2][Al(OC_6F_5)_4]$ (**3**) was expected to lead to increased tetramerization. This was found to be the case (entry 9), and 23.5% C_8 resulted from activation with this cocatalyst ($C_6/C_8 = 3.6$). The hexacoordinated Ta aryloxide **4** should be even less coordinating than **3**, and consistent with this, the selectivity to C_8 increased to 39.6% (entry 10; $C_6/C_8 = 1.6$). With both of these cocatalysts, however, the same catalyst deactivation as observed previously was found to occur, and polymer production was high. Nonetheless, these results confirm the pronounced selectivity influence that the cocatalyst can have on this system, which seems most likely to arise from the differing coordination strengths of the anions.

The performance of cocatalysts **5** and **6** is not easy to predict, due to coordination of ether to these compounds, which would buffer the Lewis acidity to an extent even in the presence of $AlEt_3$, which can act as a scavenger. The very bulky cocatalyst **5** does give rise to a poorly active catalyst (entry 11), with a C_6/C_8 ratio of 2.1, suggesting a Cr−anion interaction similar to that obtained with **4**. It is possible that the poor activity and high relative amount of polymer formed in this case is due to ineffectual catalyst activation (alkyl abstraction) with this compound. The etherate **6** gave somewhat better catalyst activation (entry 12), and in this case a low amount of polymer was formed. The C_6/C_8 selectivity (19.0) with this cocatalyst is again different from that obtained previously and lies somewhere between those of cocatalysts **2** and **3**.

The aluminate anion in cocatalyst **7**, $[Ph_3C][Al\{OC(CF_3)_3\}_4]$, is reported to be one of the most weakly coordinating and chemically robust anions known.[56] As shown in entry 13, these properties have a marked effect on catalyst activity, stability, and selectivity when this activator is employed. The catalyst formed displays a high activity, and this is maintained to an extent that ethylene uptake continues, albeit slowing, over a 1 h run time. This results in an overall productivity of 125 600 g/g of Cr, which is by far the highest we have seen for a non-alumoxane-activated tetramerization catalyst. The selectivity is shifted back toward tetramerization, and the C_6/C_8 ratio (0.30) is the same as that obtained with MMAO-3A under comparable conditions. Importantly, the amount of polymer formed is also much reduced compared to that for the other cocatalysts tested. Increasing the temperature to 65 °C with MMAO-3A activation leads to an increased C_6/C_8 value (entry 1); thus, a further run was conducted at 65 °C with cocatalyst **7** (entry 14). It can be seen that C_6/C_8 selectivity is almost the same in each run, although the higher temperature leads to a faster deactivation with the aluminate cocatalyst. Despite the high activity and stability at 45 °C and 100 equiv of $AlEt_3$, increasing the loading of $AlEt_3$ still leads to catalyst deactivation (entries 15 and 16). This becomes pronounced with 600 equiv of $AlEt_3$, and in this case the relative amount of trimerization is also increased ($C_6/C_8 = 0.62$). Evidently, the amount of $AlEt_3$ still has an effect on the stability of cocatalyst **7**, although this effect is much reduced, and an optimum productivity is achieved with 100−200 equiv of $AlEt_3$.

The $[FAl\{OC(CF_3)_3\}_3]^-$ anion[64] contained in cocatalyst **8** is reportedly very stable but somewhat more coordinating than $[Al\{OC(CF_3)_3\}_4]^-$.[68] As a result, activation with **8** did not lead to the high productivity achieved with **7**, and the product selectivity was shifted back toward trimerization ($C_6/C_8 = 1.4$, entry 17).

The fluoride-bridged anion of cocatalyst **9**, $[\{(F_3C)_3CO\}_3Al-F-Al\{OC(CF_3)_3\}_3]^-$, has been suggested as the least coordinating anion known.[57,69] We were therefore surprised to find that this cocatalyst gave a poor activity and more 1-hexene than 1-octene ($C_6/C_8 = 2.5$, entry 17). It was subsequently found, however, that both activity and selectivity with this cocatalyst are markedly influenced by the amount employed (entries 19−21). This is more clearly illustrated in Figure 4, which shows the C_6/C_8 selectivity and productivity as a function of concentration of **9** (equivalents relative to Cr). As the amount of **9** is increased, an increase in catalyst productivity and selectivity to C_8 results. With 3 equiv of **9** the C_6/C_8 value approaches that observed with MAO and **7**, and a high productivity is obtained. These observations seem to suggest an anion coordination strength that is dependent upon the concentration of the cocatalyst. A possible explanation for this lies in the ability of $[\{(F_3C)_3CO\}_3Al-F-Al\{OC(CF_3)_3\}_3]^-$ to dissociate, as shown in reaction 1. This anion is known to break down to constituent monomers in the presence of donor solvents ($(FAl(OR^F)_3^- + D \rightarrow Al(OR^F)_3$),[68] and as such this proposal seems reasonable. A higher concentration of **9** would increase the relative concentration of the less coordinating dinuclear anion, and as such the concentration effects observed are consistent with such a process. Additionally, there is some precedent for this, whereby Cp_2TaMe_3 reacts with 1 equiv of $M(C_6F_5)_3$ (M = B, Al) to yield a mixture of $[Cp_2TaMe_2][CH_3M(C_6F_5)_3]$ and $[Cp_2TaMe_2][(C_6F_5)_3M-CH_3-M(C_6F_5)_3]$ in dynamic equilibrium.[70] Addition of excess $M(C_6F_5)_3$ drives the equilibrium toward the bridged anion, and in the case of $Al(C_6F_5)_3$ it was possible to isolate pure $[Cp_2TaMe_2][(C_6F_5)_3Al-Me-Al(C_6F_5)_3]$. Such a process has also been invoked to explain the increased polymerization activity observed when excess $M(C_6F_5)_3$ is used to activate metallocene and constrained-geometry catalysts.[44,51]

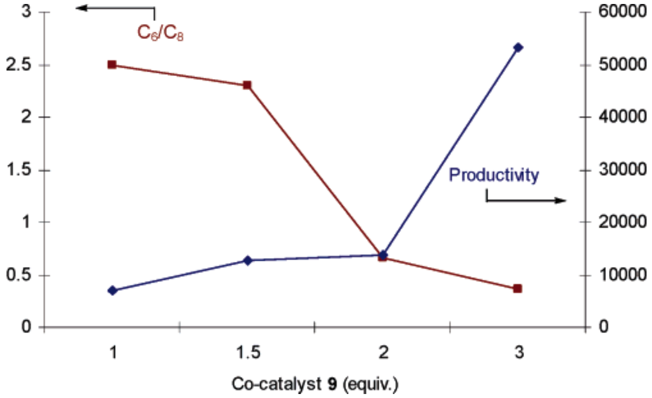
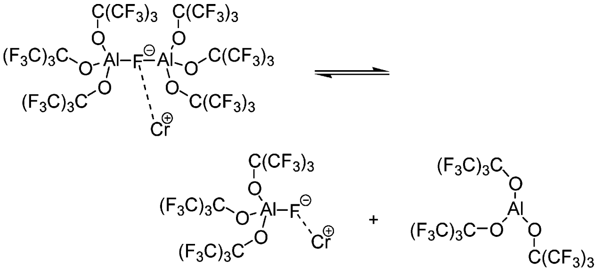


Figure 4. Molar C_6/C_8 ratio and productivity (g/g of Cr) as a function of amount of cocatalyst **9** (equivalents relative to Cr). Conditions: 10 μmol of $CrCl_3(thf)_3$, 12 μmol of **II**, 100 $AlEt_3$, 45 °C, 30−60 min.



(1)

The final cocatalyst tested was $[Ph_3C][CB_{11}H_6Br_6]$ (**10**). The results obtained with this were disappointing (entry 22), with a low activity and high polymer content resulting. Overall, the results were similar to those for activation with **8**. It seems unlikely that this result is due to degradation of the carborane, given the high stability of this class of anion, especially toward alkylaluminum.[63] In comparison to weakly coordinating anions

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(68) Krossing, I. Personal communication, 2005.

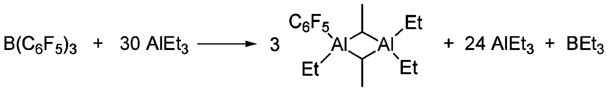
(69) Bihlmeier, A.; Gonsior, M.; Raabe, I.; Trapp, N.; Krossing, I. *Chem. Eur. J.* **2004**, *10*, 5041.

(70) Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 5541.

such as $[Al\{OC(CF_3)_3\}_4]^-$, most carboranes are thought to be more strongly coordinating to electrophilic cations.[56] This is reflected here in the C_6/C_8 ratio (0.92) that is obtained with this cocatalyst. Less coordinating carborane anions, such as $[1\text{-Me-}CB_{11}F_{11}]^-$,[71] may be more successful here but have not been studied as part of this work.

2.3. Cocatalyst Degradation Studies. As outlined in the Introduction, one of the aims of this study was to investigate cocatalyst (anion) stability and to evaluate what effect this has on overall catalyst stability. In previous trimerization and tetramerization studies with $B(C_6F_5)_3$ (**1**),[13,52] and in this work, the amount of AlR_3 employed has repeatedly been found to affect the rate of catalyst deactivation. We have therefore studied the interaction of selected cocatalysts with excess $AlEt_3$ by NMR spectroscopy.

Treatment of **1** with 30 equiv of $AlEt_3$ at room temperature in CD_2Cl_2 results in complete loss of the ^{19}F signals for **1** by the time the spectrum is run. In their place, three sets of signals are observed, the major species (88% abundance) having peaks at −122.0 (*o*-F), −154.1 (*p*-F), and −162.4 ppm (*m*-F). The ^1H NMR spectrum cannot be fully interpreted due to overlapping peaks, but previous[72,73] low-temperature studies on $AlEt_3$ (the Al_2Et_6 dimer) and mixed Al−alkyl dimers aid in assigning those new signals which are resolved. The spectrum is consistent with reaction 2, whereby the terminal methylene protons adjacent to the C_6F_5 group appear at 0.99 ppm (2H) and the other terminal methylenes appear at 0.75 ppm (4H). The bridging methylene signals likely overlap with the CH_3 resonances, as found previously with Al_2Et_6. The other two sets of ^{19}F signals occur in 5% and 7% abundance and are very similar in chemical shift to the corresponding signals for **1**. On the basis of this, it seems likely these species are mixed ethyl−aryl boranes, $B(C_6F_5)_xEt_{3-x}$ ($x = 1, 2$). These results are in line with previous studies on the rapid exchange between stoichiometric $AlMe_3$ amd **1**.[54] They confirm that rapid alkyl−aryl group exchange between **1** and $AlEt_3$ is occurring, and it seems likely that this process leads to catalyst deactivation in ethylene tetramerization. This could be due either to the formation of more coordinating counterions, such as $[(C_6F_5)AlEt_3]^-$, or Al-mediated exchange of the C_6F_5 group onto the active Cr center, as Bochmann has shown for zirconocene polymerization catalysts.[53]



(2)

The same experiment conducted with $Al(OC_6F_5)_3$ (**2**) and 30 equiv of $AlEt_3$ showed that all of **2** is likewise consumed after ca. 10 min, giving a 77:23 mixture of two species by ^{19}F NMR. The relative abundance of these changes to 91:9 after 2 h. The terminal methylene and methyl group signals for the major species are resolved and indicate that the dimer $Et_2Al(\mu\text{-}OC_6F_5)(\mu\text{-}Et)AlEt_2$ has formed. The minor species observed in the ^{19}F spectrum is presumably derived from the $Al(OC_6F_5)_2Et$ unit and would also be a dimer, $Al_2(OC_6F_5)_2Et_4$, although the structure of this cannot be determined from the NMR data. Again, this result illustrates that this cocatalyst is susceptible to degradation in the presence of $AlEt_3$, and this is reflected in the catalytic results observed.

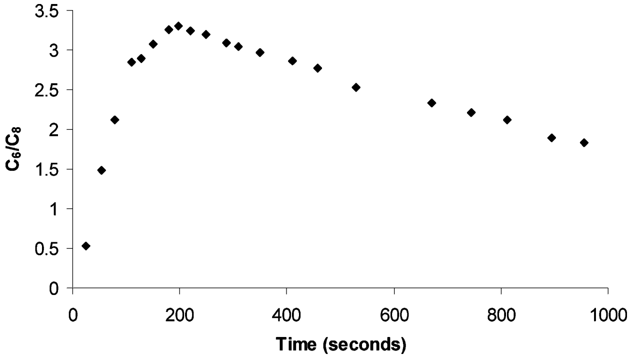


Figure 5. Molar C_6/C_8 ratio as a function of time for catalysis with 3 equiv of $Al(OC_6F_5)_3$ (**2**). Conditions: 10 μmol of $CrCl_3(thf)_3$, 12 μmol of **II**, 30 $AlEt_3$, 45 °C, 40 bar.

The stability toward $AlEt_3$ of the two best cocatalysts, **7** and **9**, was also investigated by treating metal salts of the anions with 30 equiv of $AlEt_3$. $Li[Al\{OC(CF_3)_3\}_4]$ did not react with $AlEt_3$, either at the time of addition or after sitting overnight. Thus, the longer catalyst lifetime with this activator can be rationalized. $Ag[\{(CF_3)_3CO\}_3Al{-}F{-}Al\{OC(CF_3)_3\}_3]$ is not quite as robust, and some reaction does take place, as shown by the appearance of five minor new signals in the ^{19}F NMR spectrum. The major species, however, remains the starting compound. It is not possible to say from the NMR data whether these changes are due to scrambling of the $OC(CF_3)_3$ and ethyl groups or whether they result from an equilibrium involving the dimer, similar to that suggested in section 2.2.

Degradation of the cocatalyst by this exchange process would significantly reduce the Lewis acidity of the cocatalyst or increase the coordinating ability of the anion that is formed. This could not only reduce catalyst activity but also, on the basis of the results of section 2.2, should affect the C_6/C_8 selectivity. Although the rate of degradation of **1** and **2** has not been quantified, this process appears to occur on a time scale approximately comparable with the early stages of a tri-/tetramerization run. For this reason, an ethylene oligomerization experiment was conducted in which the product was sampled at intervals over the run and the C_6/C_8 selectivity monitored. The tri-/tetramerization of ethylene was carried out at 45 °C with 30 equiv of $AlEt_3$ and 3 equiv of **1** relative to Cr. The results are presented in Figure 5, which shows that indeed the selectivity changes over time. At the start of the run, the catalyst is predominately a tetramerization system, but it rapidly converts to a trimerization catalyst. Shortly after activation (20 s), the C_6/C_8 ratio is 0.53, which is approaching that obtained with MAO and **7**.

The selectivity to C_6 reaches a maximum after 4 min, after which it slowly reduces. This subsequent slow reduction in C_6 selectivity is not expected, as it would seem to suggest formation of a less coordinating anion in the latter stages of the reaction. The explanation for this behavior is revealed in Figure 6, which plots C_6 and C_8 production over time. While the production of C_8 is reasonably constant (the active species responsible for tetramerization is stable once $AlEt_3$/**2** exchange approaches equilibrium), the production of C_6 starts to tail off after 4 min. The Cr−anion pair responsible for trimerization undergoes a more rapid deactivation.

These combined results provide strong evidence for a cocatalyst that is changing over time, and an anion coordination strength that quickly increases at the start of a run. A mechanism by which this occurs is suggested in Scheme 3. The reason for the more rapid deactivation of the trimerization active species may be linked to the greater interaction between Cr and the

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[71] Ivanov, S. V.; Rockwell, J. J.; Polyakov, O. G.; Gaudinski, C. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *J. Am. Chem. Soc.* **1998**, *120*, 4224.

[72] Ramey, K. C.; O'Brien, J. F.; Hasegawa, I.; Borchert, A. E. *J. Phys. Chem.* **1965**, *69*, 3418.

[73] Yamamoto, O.; Hayamizu, K. *J. Phys. Chem.* **1968**, *72*, 822.

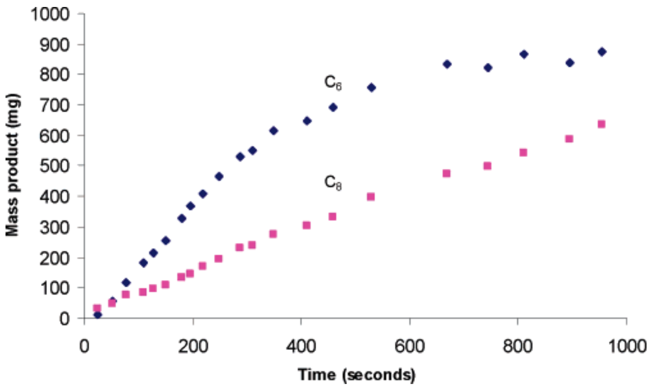
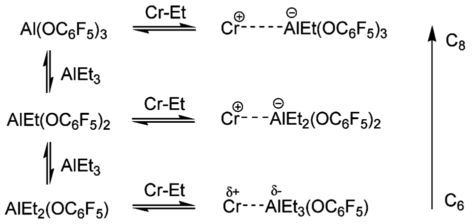


Figure 6. Mass of C_6 and C_8 formed as a function of time for catalysis with 3 equiv of $Al(OC_6F_5)_3$ (**2**). Conditions: 10 μmol of $CrCl_3(thf)_3$, 12 μmol of **II**, 30 $AlEt_3$, 45 °C, 40 bar.

Scheme 3



anion in this case. Marks has shown that Zr and Ti polymerization catalysts activated with $[Ta(OC_6F_5)_6]^-$ undergo catalyst degradation that arises from transfer of the OC_6F_5 group to the Zr or Ti center.[59] An increased interaction between the Cr center and the aluminate can reasonably be expected to favor this process. At this stage we have not attempted to characterize such a $Cr-OC_6F_5$ species.

Given these observations, the results in Table 1 must be reinterpreted to an extent. In the experiments where rapid catalyst deactivation is observed (with cocatalysts **1**−**6** and **8**), the C_6/C_8 ratio reported more likely represents an average over the run, corresponding to the "average" anion coordination strength during catalysis.

3. Summary and Conclusion

A variety of new and existing cocatalysts have been evaluated for the trimerization and tetramerization of ethylene with a Cr−PNP catalyst system. The stability of selected cocatalysts has been studied, and the less effective ones have been found to undergo degradation upon treatment with $AlEt_3$. In contrast, the use of a stable and noncoordinating anion leads to a high productivity in the absence of alumoxanes. These studies have led us to the easily prepared cocatalyst $[Ph_3C][Al\{OC(CF_3)_3\}_4]$ (**7**), which due to its high stability and weakly coordinating nature gives a highly productive tetramerization catalyst.

Herein it has been shown for the first time the remarkable influence that the cocatalyst can have on relative C_6/C_8 selectivity, which provides strong evidence for a formally cationic (or cation-like) active species, in which the coordinating strength of the anion effects the selectivity. It is a combination of both coordinating ability and anion stability that controls activity and selectivity, however, as the two are related in that poor stability can lead to a more coordinating anion over the lifetime of a catalytic run. We have previously shown the effect that ligand modification has on selectivity with this class of ligand. Herein we have shown that further control over this versatile catalyst system is available through careful cocatalyst modification.[55]

In terms of the mechanism by which coordination of the anion would suppress C_8 formation, it can be speculated that it does so by hindering ethylene uptake at the $Cr-C_6$ metallacyclic stage. A number of studies on metallocene polymerization catalysts have shown that ethylene must first displace the anion from the coordination sphere prior to insertion,[45,48] and the same condition could apply here. It is interesting that MAO and **7** lead to the same selectivity. It is likely that the anion present when these activators are employed is near the limit of complete dissociation, and as such the anion has less effect on ethylene coordination. Under these conditions solvent coordination could become the dominant factor.

4. Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox, using solvents purified and dried by standard procedures. $[Ph_3C][Ta(OC_6F_5)_6]$ (**4**),[59] $[Ph_3C][Al\{OC(CF_3)_3\}_4]$ (**7**),[60] and $[Ph_3C][CB_{11}H_6Br_6]$[65] were prepared via literature procedures. $[Ph_3C][FAl\{OC(CF_3)_3\}_3]$ (**8**) and $[Ph_3C][\{(F_3C)_3CO\}_3Al-F-Al\{OC(CF_3)_3\}_3]$ (**9**) were supplied by Prof. Ingo Krossing, while their preparation has been described.[64]

X-ray Crystallography. Data were collected on Rigaku MM007/CCD diffractometers (Mo Kα radiation, confocal optics, λ = 0.710 73 Å) and were corrected for absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 values of all data.[74]

(a) $Al_2(OC_6F_5)_6$·(toluene) (2). Crystal data: $C_{36}Al_2F_{30}O_6.C_7H_8$. M_r = 1244.45, colorless prism, crystal size 0.15 × 0.15 × 0.15 mm, triclinic, $P\bar{1}$, a = 10.247(3) Å, b = 10.451(3) Å, c = 11.196(3) Å, α = 99.367(6)°, β = 107.070(4)°, γ = 104.356(5)°, V = 1073.9(5) Å^3, Z = 1, D_{calcd} = 1.924 Mg m^{-3}, μ = 0.251 mm^{-1}, T = 93(2) K, 6752 data (3714 unique, R_{int} = 0.0254, 3.28 < θ < 25.34°), $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.0990, conventional R = 0.0383 for F values of reflections with $F_o^2 > 2\sigma(F_o^2)$ (2981 observed reflections), S = 0.703 for 381 parameters. Residual electron density extremes were 0.364 and −0.253 e Å^{-3}.

(b) $(Et_2O)Al\{OCH(C_6F_5)_2\}_3$ (5). Crystal data: $C_{43}H_{13}AlF_{30}O_4$. M_r = 1190.51, colorless platelet, crystal size 0.10 × 0.10 × 0.02 mm, monoclinic, $P2_1/n$, a = 10.7382(6) Å, b = 46.564(3) Å, c = 17.1024(9) Å, β = 92.971(3)°, V = 8540.0(8) Å^3, Z = 8 (two independent molecules), D_{calcd} = 1.852 Mg m^{-3}, μ = 0.225 mm^{-1}, T = 93(2) K, 55 419 data (13 975 unique, R_{int} = 0.0577, 2.23 < θ < 25.35°), $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1856, conventional R = 0.1081 for F values of reflections with $F_o^2 > 2\sigma(F_o^2)$ (11 680 observed reflections), S = 1.174 for 1406 parameters. Residual electron density extremes were 0.623 and −0.478 e Å^{-3}.

(c) $Al_2\{OCH(C_6F_5)_2\}_6$ (5′). Crystal data: $C_{78}H_6Al_2F_{60}O_6$. M_r = 2232.79, colorless prism, crystal size 0.13 × 0.13 × 0.10 mm, monoclinic, $P2_1/n$, a = 14.526(3) Å, b = 13.990(3) Å, c = 18.153(4) Å, β = 92.314(10)°, V = 3685.9(14) Å^3, Z = 2, D_{calcd} = 2.012 Mg m^{-3}, μ = 0.252 mm^{-1}, T = 93(2) K, 19 844 data (6412 unique, R_{int} = 0.1291, 2.29 < θ < 25.35°), $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.2985, conventional R = 0.1127 for F values of reflections with $F_o^2 > 2\sigma(F_o^2)$ (3730 observed reflections), S = 1.061 for 381 parameters. Residual electron density extremes were 0.916 and −0.514 e Å^{-3}. The molecular structure of this compound is shown in the Supporting Information.

(d) $(Et_2O)Al\{OC(CF_3)_3\}_3$ (6). Crystal data: $C_{16}H_{10}AlF_{27}O_4$. M_r = 806.22, colorless prism, crystal size 0.03 × 0.03 × 0.03 mm, monoclinic, $P2_1/n$, a = 9.910(5) Å, b = 16.630(7) Å, c = 16.280(7) Å, β = 91.16(2)°, V = 2682(2) Å^3 , Z = 4, D_{calcd} = 1.996 Mg

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(74) Sheldrick, G. M. SHELXTL, version 6.1; Bruker AXS, Madison, WI, 2001.

m^{-3}, $\mu = 0.289$ mm^{-1}, $T = 93(2)$ K, 16 045 data (4750 unique, $R_{int} = 0.2077$, $1.75 < \theta < 25.22°$), $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.3827$, conventional $R = 0.1457$ for F values of reflections with $F_o^2 > 2\sigma(F_o^2)$ (2016 observed reflections), $S = 1.076$ for 434 parameters. Residual electron density extremes were 0.607 and −0.616 e Å^{-3}.

Ethylene Oligomerization. Ethylene oligomerization was carried out in a 300 mL stainless steel reactor with mechanical stirring. The oven-dried vessel was purged with N_2, followed by ethylene, and charged with 90 mL of toluene. After heating to 45 °C, a solution of Cr/**II**/$AlEt_3$ in 5 mL of toluene was injected, followed by a 5 mL toluene solution of the cocatalyst. The reactor was immediately charged with ethylene and maintained at the desired pressure over the duration of the reaction. At the end of a run, the reactor was cooled in an ice bath and excess ethylene bled before addition of an internal standard (nonane, 1000 μL). After quenching with MeOH followed by 10% HCl, the organic phase was analyzed by GC, while the solids were filtered, washed, dried, and weighed.

$Al(OC_6F_5)_3$ (2). A solution of 2 M perfluorophenol (7.0 mL, 14 mmol) in toluene was added to a flask, and a 1.9 M solution of triethylaluminum (2.0 mL, 3.8 mmol) was added dropwise. The solution was then heated to 60 °C for 4 h and cooled. The solvent toluene was reduced under vacuum and 10 mL of petroleum spirits added. The resulting powder that formed was washed four times with petroleum spirits (5 mL) and dried under vacuum to afford a white powder. Yield: 1.694 g (77%) Anal. Calcd (found) for $C_{18}F_{15}O_3Al$: C, 37.52 (37.34). ^{19}F NMR (282 MHz, DMSO-d_6; δ): −161.2, −162.1, −162.8 (2F, *o*-F); −169.9 (2F, *m*-F); 179.0 (1F, *p*-F). ^{13}C NMR (75 MHz, DMSO-d_6; δ): 143.0, 142.4, 139.2, 136.0, 132.8, 129.7 (*C*F). The molecular structure of the compound is shown in Figure 1.

$[(Et_2O)_2H][Al(OC_6F_5)_4]$ (3). At 0 °C a solution of perfluorophenol (7.5 mL, 15 mmol) in 20 mL of diethyl ether was treated dropwise with 1.9 M triethylaluminum solution (1.7 mL, 3.2 mmol). After 2 h at room temperature the solvent was removed under vacuum and the product washed twice with petroleum spirits to give a white powder. Yield: 1.641 g (56%). Anal. Calcd (found) for $C_{32}H_{21}O_6F_{20}Al$: C, 42.31 (42.28); H, 2.33 (2.47). ^1H NMR (300 MHz, $CDCl_3$; δ): 5.60 (br, 1H, $H(OEt_2)$); 4.39 (q, $J = 7$ Hz, 8H, OCH_2CH_3); 1.55 (t, $J = 7$ Hz, 12H, OCH_2CH_3). ^{19}F NMR (282 MHz, $CDCl_3$; δ): −163.7 (d, 2F, $J = 22$ Hz, *o*-F); −165.8 (t, 2F, $J = 22$ Hz, *m*-F); −171.1 (t, 1F, $J = 22$ Hz, *p*-F). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 142.0, 140.0, 138.8, 136.6 (*C*F); 71.9 (OCH_2); 13.9 (OCH_2C_3).

$(Et_2O)Al\{OCH(C_6F_5)_2\}_3$ (5). At 0 °C a solution of $(C_6F_5)_2C(H)OH$ (5.79 g, 15.9 mmol) in 15 mL of diethyl ether was treated dropwise with 1.9 M $AlEt_3$. The addition of $AlEt_3$ was continued portionwise until the starting alcohol was completely consumed by NMR analysis. The solvent was then removed under vacuum, the residue taken up in diethyl ether, and the solvent removed again to yield a white powder. Yield: 5.743 g (91%). Anal. Calcd (found) for $C_{43}H_{13}O_4F_{30}$: C, 43.38 (44.14); H, 1.10 (1.50). ^1H NMR (300 MHz, $CDCl_3$; δ): 6.65 (s, 3H, OCH); 4.18 (q, $J = 7$ Hz, 4H, OCH_2CH_3); 1.32 (t, $J = 7$ Hz, 6H, OCH_2CH_3). ^{19}F NMR (282 MHz, $CDCl_3$; δ): −144.5 (2F, *o*-F); −155.2 (2F, *m*-F); −162.6 (1F, *p*-F). ^{13}C NMR (75 MHz, $CDCl_3$; δ): 146.5, 143.2, 139.6, 136.2 (*C*F); 116.8 (*ipso*-*C*); 69.6 (OCH_2CH_3); 61.7 (OCH); 13.3 (OCH_2CH_3). The molecular structure of the compound is shown in Figure 2.

$(Et_2O)Al\{OC(CF_3)_3\}_3$ (6). A solution of 4 mL (29 mmol) of perfluoro-*tert*-butyl alcohol in 10 mL of diethyl ether was cooled to 0 °C and treated with a 1.9 M solution of triethylaluminum (3 mL, 5.7 mmol). After it was stirred overnight, the solution was heated to 65 °C for a further day. After this solution was cooled, the solvent was removed under vacuum to give fine needles of colorless product. Yield: 4.383 g (95%). ^1H NMR (300 MHz, $CDCl_3$; δ): 4.34 (q, $J = 7$ Hz, 4H, OCH_2CH_3); 1.43 (t, $J = 7$ Hz, 6H, OCH_2CH_3). ^{19}F NMR (282 MHz, $CDCl_3$; δ): −75.9 (CF_3). The molecular structure of this compound is shown in Figure 3.

NMR Spectra of 1 + 30 $AlEt_3$ in CD_2Cl_2. Major species: ^{19}F NMR (282 MHz; δ) −122.0 (dt, $J = 7$ Hz, 15 Hz, *o*-F), −154.1 (tt, $J = 3$ Hz, 14 Hz, *p*-F), −162.4 (m, *m*-F); ^1H NMR (300 MHz; δ) 0.75 ("t", $J = 7$ Hz, 4H, $AlCH_2$), 0.99 ("t", $J = 7$ Hz, 2H, $AlCH_2$). Minor species (7%): ^{19}F NMR (282 MHz; δ) −127.1, −152.8, −159.2. Minor species (5%): ^{19}F NMR (282 MHz; δ) −126.3, −152.6, −159.2.

NMR Spectra of 2 + 30 $AlEt_3$ in CD_2Cl_2. Major species: ^{19}F NMR (282 MHz; δ) −156.9 (d, $J = 22$ Hz, *o*-F), −162.3 (td, $J = 22$ Hz, 4 Hz, *m*-F), −164.4 (tt, $J = 22$ Hz, 4 Hz, *p*-F); ^1H NMR (300 MHz; δ) 0.83 (t, $J = 12$ Hz, 12H, $AlCH_2CH_3$), 0.0 (m, $AlCH_2CH_3$, 8H). Minor species: ^{19}F NMR (282 MHz; δ) −157.1 (d, $J = 21$ Hz, *o*-F), −163.3 (m, $J = 21$ Hz, *m*-F), −164.7 (tt, $J = 21$, 4 Hz, *p*-F).

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Supporting Information Available: CIF files giving crystallographic data for the structures reported and a figure giving the molecular structure diagram of $Al_2\{OCH(C_6F_5)_2\}_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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