

Very Large Counteranion Modulation of Cationic Metallocene Polymerization Activity and Stereoregulation by a Sterically Congested (Perfluoroaryl)fluoroaluminate

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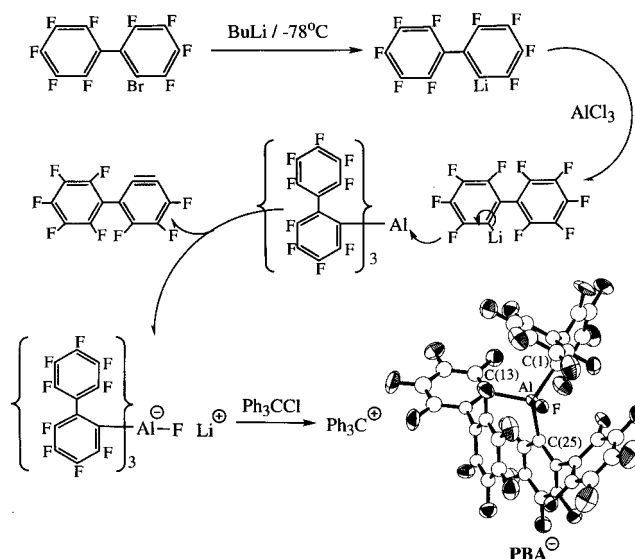
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Perfluoroaryl boranes¹ and borates² are currently of great scientific and technological interest as efficient abstractors/cocatalysts for generating highly active, cationic early transition metal olefin polymerization catalysts.³ Recent studies suggest that many of the properties of such catalysts are intimately connected with the nature of the relatively strong cation–anion ion pairing⁴ and that it would be of great interest to investigate the properties of other main group fluoroarylmets differing in size, shape, and latent ligational characteristics. We communicate here the unusual structural and cocatalytic features of a new, stable (perfluoroaryl)aluminate anion, tris(2,2',2''-nonafluorobiphenyl)fluoroaluminate (PBA⁻).⁵ Noteworthy features include very large ion pairing/metallocenium ancillary ligand structural effects on olefin polymerization activity and stereoselectivity.

Under a variety of conditions, reaction of (2-nonafluorobiphenyl)lithium⁶ with AlCl₃ leads to a compound having the composition Li⁺(C₁₂F₉)₃AlF⁻, which presumably results from aryl fluoride activation by strongly Lewis acidic, transient “tris-(perfluorobiphenyl)aluminum” (Scheme 1). Ion exchange metathesis with Ph₃CCl yields the corresponding trityl (perfluorobiphenyl)fluoroaluminate, Ph₃C⁺PBA⁻, which was characterized

Scheme 1



by standard spectroscopic and analytical techniques,⁷ as well as by single-crystal X-ray diffraction,⁸ revealing unassociated trityl cations and sterically congested chiral (C₃-symmetric) (fluoroaryl)aluminate anions (Scheme 1).

Reaction of Ph₃C⁺PBA⁻ with metallocene dialkyls in toluene cleanly generates the corresponding cationic complexes (eq 1),



- | | |
|----------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|
| Cp = η ⁵ -C ₅ H ₅ | 1a , Cp ₂ ZrCH ₂ Ph ⁺ PBA ⁻ |
| Cp'' = η ⁵ -1,2-Me ₂ C ₅ H ₃ | 2 , Cp'' ₂ ZrCH ₃ ⁺ PBA ⁻ |
| Cp ^{TMS} ₂ = η ⁵ -1,3-(SiMe ₃) ₂ C ₅ H ₃ | 3 , [Cp ^{TMS}] ₂ ZrCH ₃ ⁺ PBA ⁻ |
| Cp' = η ⁵ -C ₅ Me ₅ | 4 , Cp' ₂ ZrCH ₃ ⁺ PBA ⁻ |
| Me ₂ Si(η ⁵ -Me ₄ C ₅)(tBuN) = CGC | 5 , CGCZrCH ₃ ⁺ PBA ⁻ |
| Ind = η ⁵ -C ₉ H ₆ | 6 , CGCTiCH ₃ ⁺ PBA ⁻ |
| M = Ti, Zr; R = PhCH ₂ , CH ₃ | 7 , <i>rac</i> -Me ₂ Si(Ind) ₂ ZrCH ₃ ⁺ PBA ⁻ |

which were characterized by standard ¹H/¹³C/¹⁹F NMR and analytical techniques.^{7,9} Interestingly, the ¹⁹F–Al NMR data⁷ suggest some degree of M⁺–F–Al⁻ interaction, which is confirmed by the molecular structure of **5** (see below) and which qualitatively appears to diminish with increasing ancillary ligand steric bulk.¹⁰ The crystal structure of complex **5** (Scheme 2)¹¹ reveals cation–anion pairing via a nearly linear Zr–F–Al bridge (∠Zr–F–Al = 175.4(4)°) with Zr–F and Al–F distances of 2.123(6) and 1.780(6) Å, respectively. These can be compared to terminal and bridging Zr–F distances of 1.93(1) and 2.11(1) Å, respectively, in [Cp''₂ZrF]₂(μ-F)⁺B(C₆F₄-TBS)₄⁻¹² and Al–F = 1.682(5) Å in PBA⁻. The CGCZrCH₃⁺

(7) Experimental and characterization details are given in the Supporting Information.

(8) Space group P $\bar{1}$; *a* = 12.179(5) Å, *b* = 12.473(5) Å, *c* = 18.334(5) Å, α = 99.21(3)°, β = 94.88(3)°, γ = 108.82° at -120 °C; *V* = 2574(1) Å³; *Z* = 2; *R*(*F*), *R*_w(*F*) = 0.072, 0.053. Important bond distances (Å): Al–F = 1.682(5), Al–C(1) = 2.027(9), Al–C(13) = 2.019(10), Al–C(25) = 2.009(9).

(9) While too thermally unstable to isolate, complex **4** can be generated in situ and characterized spectroscopically.⁷

(10) δ ¹⁹F–Al: -138.11 (Cp₂ZrCH₃⁺PBA⁻), -138.69 (CGCZrMe⁺-PBA⁻), -143.38 (Cp''₂ZrCH₃⁺PBA⁻), -144.23 ((Cp^{TMS})₂ZrCH₃⁺PBA⁻), -155.78 (Cp'₂ZrCH₃⁺PBA⁻), -176.81 (Ph₃C⁺PBA⁻).

(11) Space group P2₁/c; *a* = 18.461(9) Å, *b* = 13.934(6) Å, *c* = 23.85-(1) Å, β = 108.34(4)° at -120 °C; *V* = 5822(4) Å³; *Z* = 4; *R*(*F*), *R*_w(*F*) = 0.071, 0.056. Important bond distances (Å) and angles (deg): Al–F = 1.780(6), Zr–F = 2.123(6), Zr–C(16) = 2.21(1), Zr–F–Al = 175.4(4).

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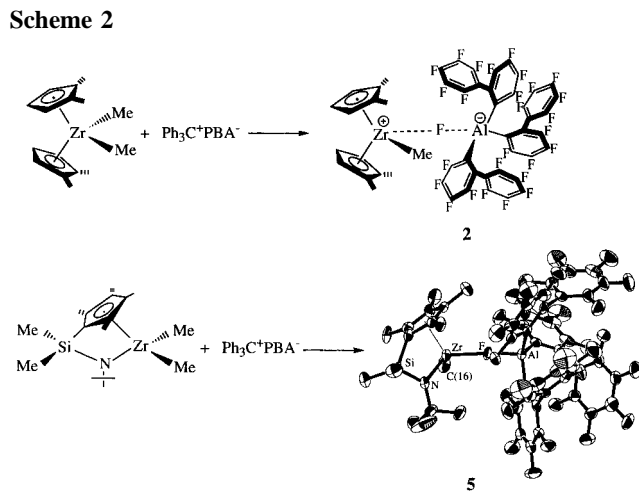
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Table 1. Ethylene Polymerization Activities with Metallocene/Ph₃C⁺PBA⁻ Catalysts and Polymer Properties^a

entry	catalyst	T _p (°C)	μmol of cat.	reaction time (min)	polymer yield (g)	activity ^b (g of polymer/ mol cat·atm·h)	M _w ^c	M _w /M _n	T _m ^d (°C)	ΔH _u (cal/g)
1	Cp ₂ ZrMe ₂ (1b)	25	20	20	0	0				
2	Cp ^{''} ₂ ZrMe ₂ (2)	25	20	30	0.18	1.80 × 10 ⁴	5.46 × 10 ⁵	6.0	139.4	40.5
3	(Cp ^{TMS}) ₂ ZrMe ₂ (3)	25	15	2.0	0.54	1.08 × 10 ⁶	1.26 × 10 ⁶	5.6	142.3	29.5
4	Cp ^{''} ₂ ZrMe ₂ (4)	25	15	0.67	1.15	6.90 × 10 ⁶	8.97 × 10 ⁴	4.6	138.0	53.9
5	CGCMMe ₂ (5 , 6)	25	15	10	0	0				
6	CGCTiMe ₂ (6)	60	30	30	0.20	1.33 × 10 ⁴	2.05 × 10 ⁶	3.9	139.2	19.5
7	CGCTiMe ₂ (6)	110	30	5.0	0.20	8.00 × 10 ⁴	2.05 × 10 ⁶	3.1	142.5	24.4

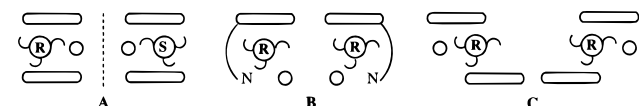
^a Carried out at 1.0 atm of ethylene in 50 mL of toluene on a high-vacuum line. See Supporting Information for polymerization procedures.

^b Reproducibility between runs = 10–15%. ^c GPC relative to polystyrene standards. ^d DSC from the second scan.

Scheme 2

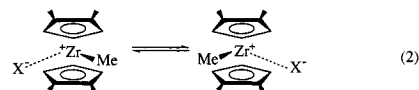
metrical parameters are similar to those in CGCZr-CH₃⁺CH₃B(C₆F₅)₃⁻.¹³

The ion pairing interplay of PBA⁻ chirality and cation stereochemistry is evident in the NMR spectra as is the strength of the Zr–F–Al interaction. In contrast to the seven ¹⁹F signals observed in Ph₃C⁺PBA⁻, all of the cationic complexes exhibit nine, indicative of restricted internal C₆F₅ rotation but free anion rotation (at 25 °C) about the M–F–Al axes. In the C_{2v}-symmetric metallocenium cations of **1** and **2** (enantiomers **A**), anion dissymmetry renders the Cp ligands diaste-



reotopic. Broadening and coalescence of the signals at higher temperatures (ΔG[‡] = 16.4(2) kcal/mol in **1b**) can be associated with anion stereomutation. With diastereotopic 1,2-Me₂ Cp substitution, **2** exhibits four Cp Me signals at 25 °C, indicating dissymmetry with respect to the Cp centroid–Zr–Cp centroid plane and that perpendicular (cf. **A**). On raising the temperature, broadening and collapse of this pattern to two Me signals is observed, with ΔG[‡] = 16.9(2) kcal/mol. A barrier comparable to that in **1b** (suggesting anion racemization) and the lack of significant additional symmetrization (ΔG[‡] > 19.9(3) kcal/mol at 87 °C) argues that anion dissociation (eq 2) has a higher barrier in these systems than in analogous metallocenium (fluoroaryl)borates.^{1d,4a,c,12} Indeed, **5–7** each exist as pairs of unequally populated diastereomers (**B** and **C**; enantiomers not shown) which undergo spectroscopic exchange (ΔG[‡] = 15.8-

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(2) kcal/mol for **5**) without permutation of diastereotopic Cp^{''} Me groups in **5** and **6** (ΔG[‡] > 20.5(4) kcal/mol for **5**) or indenyl fragments in **7** (ΔG[‡] > 20.8(4) kcal/mol).

Perhaps the most interesting aspect of **1–7** chemistry is the remarkable sensitivity of olefin polymerization characteristics (Table 1) to ion pairing as inferred from ancillary ligand bulk, structural data, and δ¹⁹F–Al.¹⁰ Thus, while Cp₂ZrCH₃⁺PBA⁻ and CGCZrCH₃⁺PBA⁻ exhibit negligible ethylene polymerization activity at 25 °C and 1.0 atm, increasing ancillary ligand bulk effects dramatic, and to our knowledge unprecedented,^{1–4} increases in polymerization activity which roughly parallel trends in δ¹⁹F–Al. Furthermore, CGCMMCH₃⁺ polymerization characteristics are markedly temperature-dependent, with **6**-mediated polymerization at 60 and 110 °C affording ultrahigh molecular weight polyethylene. In regard to anion effects on chiral cation stereoregulation, propylene polymerization (1.0 atm of C₃H₆, 15 μmol of catalyst, 50 mL of toluene, 60 °C) mediated by *rac*-Me₂Si(Ind)₂ZrMe⁺B(C₆F₅)₄⁻ (B(C₆F₅)₄⁻ is known to be weakly coordinating^{2b,12}) yields products of low isotacticity ([*mmi*] = 47%, [*mr*] = 33%, and [*rrr*] = 20%),^{14a} while under the same conditions, the strongly ion-paired PBA⁻ analogue produces highly isotactic polypropylene ([*mmmm*] = 98%).^{14b} The present findings complement and support recent observations of Eisch and co-workers¹⁵ that weakening of ion pairing enhances propylene polymerization activity at the expense of syndiospecificity and of Herfert and Fink^{4h} that syndiospecificity is sensitive to solvent polarity.

These results considerably expand what is known about the consequences of strong cation–anion interactions for group 4-mediated olefin polymerization. For anions that coordinatively “intrude” into the cation coordination sphere, the effects can be dramatic.

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Supporting Information Available: Details of Ph₃C⁺PBA⁻ and catalyst synthesis, characterization and X-ray experimental details, and tables of positional and thermal parameters, bond lengths and angles, and labeled drawings (64 pages). See any current masthead page for ordering and Internet access instructions.

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(14) (a) 2.97 × 10⁶ g of polymer/(mol·cat·atm·h), M_w = 2.34 × 10⁴, M_w/M_n = 3.59, amorphous. (b) 1.63 × 10⁴ g of polymer/(mol·cat·atm·h), M_w = 6.97 × 10⁴, M_w/M_n = 2.40, T_m = 145 °C.

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