New Mononuclear and Polynuclear Perfluoroarylmetalate Cocatalysts for Stereospecific Olefin Polymerization

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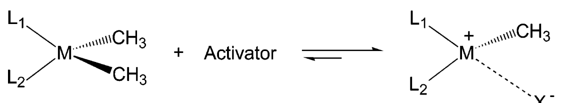
Summary: Mononuclear and polynuclear perfluoroarylborate, -aluminate, and -gallate cocatalysts for metallocene-mediated olefin polymerization have been synthesized as trityl fluoride adducts of known perfluoroarylmetalloid cocatalysts. Propylene polymerization experiments using these species as cocatalysts with the C_s-symmetric precatalyst [$Me_2C(Cp)(fluorenyl)]ZrMe_2$ reveal a marked counteranion dependence of polymerization activity, product polymer syndiotacticity, and relative [m] and [mm] stereoerror abundance, with the polynuclear perfluoroaryl cocatalysts uniformly giving enhanced product polymer stereoregularity vs the neutral analogues.

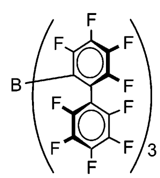
Metallocenium ion pair complexes (**A**; eq 1) produced in the reaction of metallocenes with various activators (cocatalysts) have been recognized as the active species in single-site olefin polymerization, and clear evidence shows that interionic structures and interactions have a profound influence on catalyst activity, lifetime, stability, chain-transfer characteristics, and stereoregulation.[1,2] Well-known cocatalysts include tris(perfluoro-



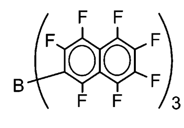
A (1)

phenyl)borane ($B(C_6F_5)_3$; **3**)[3] and related perfluoroarylboranes,[4] ammonium or trityl salts of $B(C_6F_5)_4^-$ (**5**),[5] and related perfluoroarylborates,[6] alanes (**6**),[7] and aluminates.[8]

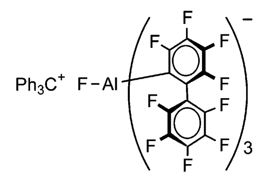
Recently, several sterically encumbered perfluoroaryl group 13 cocatalysts, tris(2,2′,2″-perfluorobiphenyl)borane (PBB; **4**),[4a] tris(*β*-perfluoronaphthyl)borane ($B(C_{10}F_7)_3$; PNB),[4b] and trityl tris(2,2′,2″-perfluorobiphenyl)fluoroaluminate ($Ph_3C^+PBA^-$; **8**)[8a] have been synthesized and their cocatalytic polymerization characteristics studied. Bulky PBB and PNB generate cationic



PBB; 4



PNB



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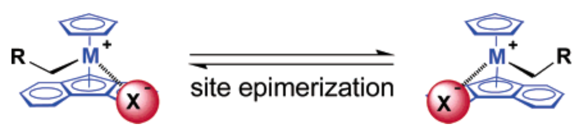
species with significantly higher activities for olefin polymerization and copolymerization than does $B(C_6F_5)_3$. Via M−F−Al coordination to the metal center, PBA^- affords more tightly bound and stereochemically immobile ion pairs which exhibit decreased enchainment and chain transfer rates, but more importantly, depressed syndiospecificity-degrading, *rrmr* stereoerror-inducing site epimerization rates in ion pairs generated from C_s-symmetric [$Me_2C(Cp)(fluorenyl)]ZrMe_2$ (**1**; eq 2).[9] These observations suggest that it would be of great



(2)

interest to synthesize new cocatalysts with substantially modified steric and charge-dispersing properties and to assess their influence on the polymerization process. Here we report the synthesis, molecular structures,

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(1) For recent reviews, see: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*(1), 283−315. (b) Pédeutour, J.-N.; Radhakrishnan, K.; Cramail, H.; Deffieux, A. *Macromol. Rapid Commun.* **2001**, *22*, 1095−1123. (c) Chen, Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*(4), 1391−1434. (d) *Chem. Rev.* **2000**, *100*, 1167−1682. (e) *Top. Catal.* **1999**, *7*, 1−208. (f) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

(2) For recent cocatalyst studies, see: (a) Busico, V.; Cipullo, R.; Cutillo, F.; Vacatello, M.; Castelli, V. V. *Macromolecules* **2003**, *36*, 4258−4261. (b) Mohammed, M.; Nele, M.; Al-Humydi, A.; Xin, S.; Stapleton, R. A.; Collins, S. *J. Am. Chem. Soc.* **2003**, *125*, 7930−7941. (c) Abramo, G. P.; Li, L.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 13966−13967. (d) Li, L.; Metz, M. V.; Li, H.; Chen, M.-C.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 12725−12741. (e) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Marks, T. J.; Nickias, P. N. *Organometallics* **2002**, *21*, 4159−4168. (f) Metz, M. V.; Sun, Y. M.; Stern, C. L.; Marks, T. J. *Organometallics* **2002**, *21*, 3691−3702. (g) Wilmes, G. M.; Polse, J. L.; Waymouth, R. M. *Macromolecules* **2002**, *35*, 6766−6772. (h) Lancaster, S. J.; Rodriguez, A.; Lara-Sanchez, A.; Hannant, M. D.; Walker, D. A.; Hughes, D. H.; Bochmann, M. *Organometallics* **2002**, *21*, 451−453. (i) Rodriguez, G.; Brant, P. *Organometallics* **2001**, *20*, 2417−2420. (j) Kaul, F. A. R.; Puchta, G. T.; Schneider, H.; Grosche, M.; Mihalios, D.; Herrmann, W. A. *J. Organomet. Chem.* **2001**, *621*, 177−183. (k) Chen, Y.-X.; Kruper, W. J.; Roof, G.; Wilson, D. R. *J. Am. Chem. Soc.* **2001**, *123*, 745−746. (l) Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223−237. (m) Kehr, G.; Roesmann, R.; Frohlich, R.; Holst, C.; Erker, G. *Eur. J. Inorg. Chem.* **2001**, 535−538. (n) Mager, M.; Becke, S.; Windisch, H.; Denninger, U. *Angew. Chem., Int. Ed.* **2001**, *40*, 1898−1902.

(3) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (b)Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625.

(4) (a) Li, L.; Stern, C. L.; Marks, T. J. *Organometallics* **2000**, *19*, 3332−3337. (b) Li, L.; Marks, T. J. *Organometallics* **1998**, *17*, 3996−4003. (c) Chen, Y.-X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451−12452. (d) Also see refs 2c−e. (e) For a recent chelating borane review, see: Piers, W. E.; Irvine, G. J.; Williams, V. C. *Eur. J. Inorg. Chem.* **2000**, 2131−2142.

(5) (a) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571. (b) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840−842. (c) Ewen, J. A.; Elder, M. J. Eur. Pat. Appl. 426637, 1991; *Chem. Abstr.* **1991**, *115*, 136987c, 136988d.

(6) For related fluorinated tetraarylborates, see: (a) References 2h−j,l. (b) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842−857. (c) Jia, L.; Yang, X.; Ishihara, A.; Marks, T. J. *Organometallics* **1995**, *14*, 3135−3137.

(7) (a) Reference 2f. (b) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908−5912. (c) Biagini, P.; Lugli, G.; Abis, L.; Andreussi, P. U. S. Patent 5,602,269, 1997.

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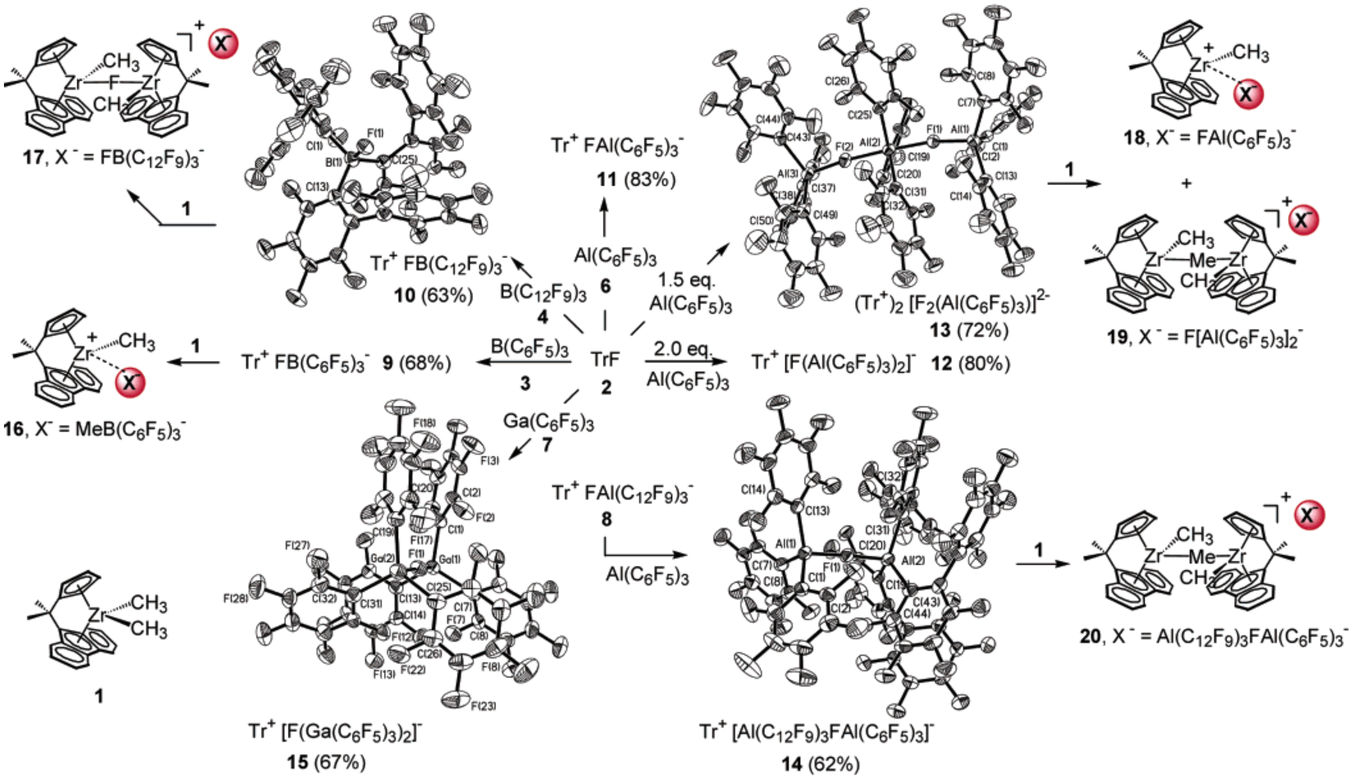
Scheme 1



reactivity, and single-site polymerization catalytic characteristics of a new series of mononuclear and polynuclear perfluoroarylborates, -aluminates, and -gallates. It will be seen that most are excellent cocatalysts, affording high catalytic activity and improved enchainment stereocontrol for syndiotactic propylene polymerization.

Reaction of trityl fluoride (Ph_3CF; **2**)[10] with $B(C_6F_5)_3$ (**3**) and $B(2\text{-}C_6F_5C_6F_4)_3$ (**4**)[4a] yields the corresponding trityl fluorometalate salts tris(perfluorophenyl)fluoroborate (**9**)[11] and trityl tris(2,2′,2′′-nonafluorobiphenyl)fluoroborate (**10**; Scheme 1).[12] ^{19}F NMR spectra of both fluoroborates exhibit characteristic broad, upfield B−F resonances at δ −186.99 (**9**) and −185.00 ppm (**10**).[13] The structure of anion **10** was confirmed by X-ray diffraction[14] and features an unassociated trityl cation and a sterically congested chiral, essentially C_3-symmetric borate anion (Scheme 1). Depending on the reagent molar ratio, either of three trityl tris(perfluorophenyl)fluoroaluminates $[(Ph_3C^+)_x\{F_x[Al(C_6F_5)_3]_y\}^{x-}$; $x = 1$, $y = 1$, **11**; $x = 1$, $y = 2$, **12**; $x = 2$, $y = 3$, **13**) can be isolated in good yield from reaction of **2** with $Al(C_6F_5)_3$ (**6**; Scheme 1). Trityl tris(2,2′,2′′-nonafluorobiphenyl)fluoroaluminate ($Ph_3C^+[FAl(2\text{-}C_6F_5C_6F_4)_3]^-$; **8**)[8a] also undergoes reaction with **6** to afford the trityl fluoro-bridged mixed aluminate ($Ph_3C^+[(C_6F_5)_3AlFAl(2\text{-}C_6F_5C_6F_4)_3]^-$; **14**). These fluoroaluminates were characterized by standard techniques[15] and also by single-crystal diffraction (**13**, **14**; Scheme 1). The structure of **13** features two unassociated trityl cations and a sterically congested pseudo-C_3-symmetric trinuclear anion,[16] where the three Al centers are connected by two μ-F atoms in a nearly linear Al−F−Al−F−Al configuration.[17] The crystal structure of **14** features an unassociated trityl cation and a sterically congested fluoro-bridged Al anion, with the two Al centers bridged by a single F atom, forming a nearly linear Al−F−Al configuration.[18] Trityl fluorobis[tris(perfluorophenyl)gallate] ($Ph_3C^+F[Ga(C_6F_5)_3]_2^-$; **15**) is derived from a "one pot" reaction of **2** with $Ga(C_6F_5)_3$ (**7**; Scheme 1), in turn generated in situ from reaction of $B(C_6F_5)_3 + Ga(CH_3)_3$ (eq 3).[19] The structure of **15** was confirmed by X-ray

$$GaMe_3 + \underset{\mathbf{3}}{B(C_6F_5)_3} \xrightarrow[\mathbf{2}]{Ph_3CF} \underset{\mathbf{15}\ (67\%)}{Ph_3C^+\{F[Ga(C_6F_5)_3]_2\}^-} \quad (3)$$

diffraction[20] as the first linear fluoro-bridged organogallium complex.[21]

The activation reactivities and olefin polymerization[22] cocatalytic characteristics (Table 1; Figure 1) of salts **9**−**15** were investigated with respect to the C_s-sym-

(8) (a) Chen, Y.-X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287−6305. (b) Chen, Y.-X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2582−2583. (c) Elder, M. J.; Ewen, J. A. Eur. Pat. Appl. EP 573,403, 1993; *Chem. Abstr.* **1994**, *121*, 0207d.

(9) (a) Chen, M.-C.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 11803−11804. (b) Chen, M.-C.; Roberts, J. A. S.; Marks, T. J. *J. Am. Chem. Soc.*, in press.

(10) Oishi, M.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*(8), 1445−1454.

(11) A similar fluoroborate ($Li^+[FB(C_6F_5)_3]^-$) has been claimed previously. See: Klemann, L. P.; Newman, G. H.; Stogryn, E. L. U. S. Patent 4,139,681, 1979.

(12) See the Supporting Information for full experimental details.

(13) Similarly, the F−Al resonance of $Ph_3C^+PBA^-$ (**8**) appears at δ −175.60 ppm.[8a]

(14) For **10** (50% probability thermal ellipsoids in Scheme 1), selected bond lengths (Å) and bond angles (deg) are as follows: B1−F1 = 1.437(6), B1−C1 = 1.649(7), B1−C13 = 1.659(6); F1−B1−C1 = 105.3(4), F1−B1−C13 = 106.8(3), C1−B1−C13 = 114.4(4), C1−B1−C25 = 112.2(3).

(15) The ^{19}F NMR spectra of complexes **11**−**14** exhibit broad singlets at δ −168.61, −167.30, −166.49, and −169.38 ppm, respectively, indicative of an Al−F bond.

Table 1. Comparison of Propylene Polymerization Results with 1 + the Indicated Cocatalysts at 25 °C under 1.0 atm of Propylene[a]

expt no.	cocat. ($R = C_6F_5$; $R' = C_{12}F_9$)	amt (μmol)	time (min)	amt of PP (g)	ΔT[c] (°C)	activity[d] ($\times 10^6$)	T_m[e] (°C)	*rmmr*[f] (%)	*mmrr* (%)	*rrmr* (%)	*rrrr* (%)	M_w[g] ($\times 10^3$)	M_w/M_n
1[b]	BR_3 (**3**)	20	40	5.9	1.0	0.44	101.4	1.5	3.1	10.6	69.5	79	1.81
2	$Tr^+FBR_3^-$ (**9**)	10	60	0.87	1.0	0.087	104.5	1.6	3.1	10.3	70.2	81	1.99
3[b]	BR'_3 (**4**)	10	5	2.92	3.0	3.5	130.3	1.5	3.1	4.2	83.5	101	1.85
4	$Tr^+FBR'_3{}^-$ (**10**)	20	12	1.39	1.0	0.35	137.6	1.7	3.2	2.8	86.3	94	2.11
5[b]	$Tr^+BR'_4{}^-$ (**5**)	4.8	1.25	0.89	3.0	8.9	130.7	1.4	3.0	4.2	84.0	112	1.95
6	AlR_3 (**6**)	20	45	0.84	1.0	0.056	139.5	1.7	2.8	3.4	85.5	74	2.2
7	Tr^+ $FAlR_3^-$ (**11**)	10	4	1.32	2.0	2.0	142.1	1.6	2.6	2.4	88.7	138	1.95
8	$Tr^+F(AlR_3)_2^-$ (**12**)	1.6	2	0.79	2.0	14	143.7	1.5	2.5	2.3	88.9	147	2.08
9	$Tr^+F_2(AlR_3)_3{}^{2-}$ (**13**)	2.5	3	0.99	1.0	7.9	143.5	1.4	2.5	2.2	89.3	144	1.98
10[b]	$Tr^+FAlR'_3{}^-$ (**8**)	20	75	5.0	0.5	0.20	145.7	1.3	2.6	1.3	91.0	147	1.85
11	$Tr^+(AlR_3FAlR'_3)^-$ (**14**)	2.6	5	0.94	1.0	4.4	145.8	1.5	2.4	1.4	90.8	121	1.91
12	GaR_3 (**7**)	20	40	1.30	0.5	0.098	138.0	1.6	2.7	3.4	86.2	77	2.85
13	$Tr^+F(GaR_3)_2^-$ (**15**)	10	3	1.17	3.0	2.33	140.5	1.5	2.5	2.5	88.6	129	1.93

[a] In 50 mL of toluene with precise polymerization temperature control (exotherm <3 °C). [b] See ref 11b. [c] Internal temperature variation (±). [d] In units of g of polymer/((mol of cat.) atm h). [e] Second scan by DSC. [f] Pentad analysis by ^{13}C NMR (±0.3%). [g] GPC relative to polystyrene standards.

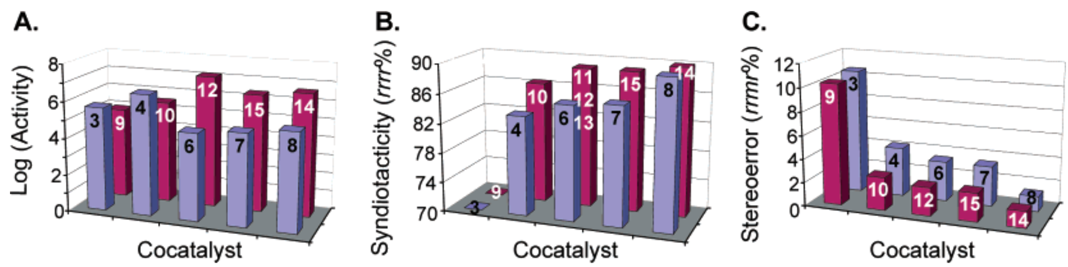


Figure 1. Activity (A), syndiotacticity (*rrrr*%) (B), and stereoerror (*rrmr*%) data (C) for polypropylenes produced by metallocene **1** + the indicated cocatalysts at 25 °C under 1.0 atm of propylene.

metric precatalyst $[Me_2C(Cp)(fluorenyl)]ZrMe_2$ (**1**). As monitored by in situ ^1H and ^{19}F NMR, reaction of **1** (methide abstraction) with **9**–**15** is rapid,[12] and spectroscopically identified products are shown in Scheme 1. For reaction of **1** with cocatalyst **9**, $[Me_2C(Flu)(Cp)ZrMe]^+[MeB(C_6F_5)_3]^-$ (**16**) is observed as the major product (~30% yield),[23] suggesting B–F/Zr–Me metathesis. Not unexpectedly, lower polymerization activity (~20%) but with similar polypropylene syndiotacticity (~70.2(3) *rrrr*%) results from propylene polymerization catalyzed by the **9**-derived ion-pair complex, compared to **1**/$B(C_6F_5)_3$ (**3**; Table 1, entries 1 and 2). For reaction of **1** with cocatalyst **10**, formation of a pair of dinuclear $\{[Me_2C(Flu)(Cp)ZrMe]_2(\mu\text{-}F)\}^+[FB(2\text{-}C_6F_5C_6F_4)_3]^-$ diastereomers (**17**) is observed in a 2:1 ratio by NMR.[24] In comparison to **1**/PBB (**4**), lower polymerization activity but increased polypropylene syndiotacticity (86.3(3) vs 83.5(3) *rrrr*%) results from **1**+**10** (Table 1, entries 3 and 4).

For reaction of **1** with cocatalysts **11**–**13**, in situ NMR assigns a mixture of $[Me_2C(Flu)(Cp)ZrMe]^+[FAl(C_6F_5)_3]^-$ (**18**) and a pair of diastereomeric μ-methyl complexes $\{[Me_2C(Flu)(Cp)ZrMe]_2(\mu\text{-}Me)\}^+\{F[Al(C_6F_5)_3]_2\}^-$ (**19**) in differing ratios for all three cocatalysts (Scheme 1). Despite the complexity of these reactions, it is found that the active species generated by in situ reactions are effective agents for highly syndiospecific propylene polymerization (~89.0(3) *rrrr*%, Table 1).[25] In comparison to the borate-derived catalyst **1**+**5** (84.0(3) *rrrr*%) and alane-derived catalyst **1**+**6** (85.5(3) *rrrr*%), the new bridged fluoroaluminate cocatalyst **12** provides a system with the highest polymerization activity along with the highest product stereoregularity. In the reaction of **1** with cocatalyst **14**, a pair of diastereomeric μ-methyl complexes $\{[Me_2C(Flu)(Cp)ZrMe]_2(\mu\text{-}Me)\}^+[(C_6F_5)_3AlFAl(2\text{-}C_6F_5C_6F_4)_3]^-$ (**20**; 3:2 ratio) is obtained (Scheme 1). When cocatalysts **1**–**15** are compared in propylene

(16) For **13** (50% probability thermal ellipsoids in Scheme 1), selected bond lengths (Å) and bond angles (deg) are as follows: Al1–F1 = 1.740(2), Al1–C1 = 1.998(4), Al2–F1 = 1.964(2), Al2–F2 = 1.966(2), Al2–C19 = 1.997(4), Al3–F2 = 1.734(2), Al3–C37 = 1.999(4); Al1–F1–Al2 = 168.66(14), F1–Al2–F2 = 176.95(11), Al3–F2–Al2 = 173.53(15), F1–Al1–C1 = 106.39(14), C1–Al1–C7 = 110.36(16), F1–Al2–C19 = 89.63(13), F2–Al2–C19 = 91.18(13), C19–Al2–C25 = 116.97(16), F2–Al3–C37 = 104.84(14).

(17) (a) A similar M–F–M–F–M arrangement is seen in a Bi system. For a recent review of metal fluorides, see: Roesky, H. W.; Haiduc, I. *J. Chem. Soc., Dalton Trans.* **1999**, 2249–2264. (b) For the first structural study of a fluoro-bridged organoaluminum complex, $K^+[(Et)_3Al\text{–}F\text{–}Al(Et)_3]^-$, with F–Al = 1.80(6) Å, see: Natta, G.; Allegra, G.; Perego, G.; Zambelli, A. *J. Am. Chem. Soc.* **1961**, *83*, 5033–5033.

(18) For **14** (50% probability thermal ellipsoids in Scheme 1), selected bond lengths (Å) and bond angles (deg) are as follows: Al1–F1 = 1.771(2), Al2–F1 = 1.795(2), Al1–C1 = 1.979(4), Al2–C31 = 1.999(4); Al1–F1–Al2 = 176.93(15), F1–Al1–C1 = 102.07(15), C1–Al1–C7 = 113.62(17), F1–Al2–C19 = 100.24(14), C19–Al2–C31 = 116.62(17).

(19) Several products are observed in this reaction; however, pure **15** can be isolated in good yield by fractional crystallization. The ^{19}F NMR spectrum of **15** exhibits a characteristic broad, upfield resonance at δ −210.11 ppm, indicative of Ga–F bond formation.

(20) For **15** (50% probability thermal ellipsoids in Scheme 1), selected bond lengths (Å) and bond angles (deg) are as follows: F1–Ga1 = 1.896(2), F1–Ga2 = 1.918(2), C1–Ga1 = 1.991(4), C19–Ga2 = 1.992(4); Ga1–F1–Ga2 = 173.37(12), F1–Ga1–C1 = 103.02(13), C1–Ga1–C7 = 113.98(16), F1–Ga2–C19 = 97.39(13), C19–Ga2–C25 = 119.52(16).

(21) For recent examples of organogallium–F complexes, see: (a) Werner, B.; Kräuter, T.; Neumüller, B. *Organometallics* **1996**, *15*, 3746–3751. (b) See ref 17a for examples of nonlinear fluoro-bridged Ga complexes. (c) Kräuter, T.; Neumuller, B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 597–606.

(22) Polymerizations were carried out under 1.0 atm of propylene pressure in toluene at 25 °C using conditions minimizing mass transfer and exotherm effects; product isolation and characterization utilized standard techniques.[2d,9,12]

(23) The other product is an unidentified precipitate which exhibits very broad peaks in the ^1H NMR (CD_2Cl_2), and structural identification is ambiguous.

(24) In the ^{19}F NMR, the Zr–F–Zr and F–B signals of ion pair **17** appear at δ −77.97 and −184.47 (br), respectively. In addition, free $B(C_{12}F_9)_3$ is also observed in ~50% yield.

polymerization, cocatalyst **14** achieves the highest syndioselectivity (90.8(3)%), comparable to $Ph_3C^+PBA^-$ (**8**) but with 20× greater catalytic activity (Table 1, entries 10 and 11; Figure 1). In the reaction of **1** with cocatalyst **15**, rapid methide abstraction and formation of a complex mixture, including unidentified dinuclear species, is observed. In propylene polymerization, the bridged fluoro-gallate **15** produces a polymer with high product syndiotacticity (88.6(3)%), comparable to the results for fluoroaluminates **11**−**13**. Substantially higher polymerization activity is exhibited by the fluoro-bridged gallate **15**, compared to $Ga(C_6F_5)_3$.

In summary, several new classes of mono- and polynuclear trityl fluorotris(perfluoroaryl)borates, -aluminates, and -gallates have been synthesized and characterized. These new cocatalysts demonstrate efficient and rapid activation of C_s-symmetric group 4 complexes to generate highly active single-site agents for propylene polymerization.[26] Polymerization activities (Figure 1A), product molecular weights (Table 1), product syndiotacticities (Figure 1B), and %*rrmr* stereoerrors (Figure 1C) are markedly sensitive to the cocatalyst. These new cocatalysts achieve higher stereoregulation by depressing %*rrmr* stereoerrors. In addition, bridged fluoro polynuclear cocatalysts effecting similar stereocontrol exhibit significantly higher polymerization activities than mononuclear cocatalysts.

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Supporting Information Available: Text giving detailed synthetic procedures and analytical data for **9**−**15** and complete X-ray experimental details, tables of bond lengths, angles, and positional parameters for **10** and **13**−**15**, and text giving a description of polymerization experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) The highest catalytic activity is exhibited with the highest **19**:**18** ratio (∼2:1) when cocatalyst **12** is used. The lowest polymerization activity is observed at the lowest **19**:**18** ratio (∼1:1) when **11** is used. Similar product syndiotacticities are observed for all three cocatalysts, arguing that the same (or very similar) species serve as the active catalyst(s) in all three polymerization systems. Since the activity increases as **19** content is increased, this argues that **19** is the precursor to the actual active species.

(26) Product polydispersities are consistent with well-defined single-site processes (Table 1).