Protected (Fluoroarvl)borates as Effective Counteranions for Cationic Metallocene Polymerization Catalysts

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Summary: The functionalized (fluoroaryl)borate salts $Ph_{3}C^{+}B(C_{6}F_{4}TBS)_{4}^{-}$ and $Ph_{3}C^{+}B(C_{6}F_{4}TIPS)_{4}^{-}$ (TBS = ${}^{t}BuMe_{2}Si$; TIPS = ${}^{i}Pr_{3}Si$) are prepared in three steps from 1,4-HC₆F₄Br. Reaction with zirconocene dimethyls yields crystalline, thermally stable, soluble $L_2ZrCH_3^+B$ - $(C_6F_4SiR_3)_4^-$ and $L'_2ZrH^+B(C_6F_4SiR_3)_4^-$ salts $(L = \eta^5 - \eta^5 C_5H_5$; η^5 -1,2-Me₂ C_5H_3 ; $L' = \eta^5$ -Me₅ C_5) which function as highly active ethylene polymerization catalysts.

Recent observations suggest that many of the properties of highly active cationic metallocene olefin polymerization catalysts^{1,2} are closely connected with the nature of the cation-anion tight ion pairing (I).^{3,4}



L = cyclopentadienyl ligand

Despite numerous efforts to "engineer" the cationic portion of such catalysts, far less attention has been devoted to the charge-compensating anion (X^-) . Of the existing anions, $B(C_6F_5)_4^-$ -derived base-free catalysts exhibit some of the highest reported catalytic activities^{3a,4h,5} but have proven difficult to characterize in the pure state.⁶ In our hands, they exhibit poor thermal

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stability (as judged by exceedingly complex, timedependent 25 °C NMR spectra) and poor crystallizability (insoluble, hard to purify oils are frequently obtained).⁷ We report here on the interesting properties of "protected" fluoroarylborates designed to address some of these issues and to enforce greater cation-anion separations as a potential means to modulate cation reactivitv.8,9

Low-temperature halogen-metal interchange using 1-bromo-2.3.5.6-tetrafluorobenzene and "BuLi¹⁰ followed

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observations.

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⁽¹⁰⁾ Tamborski, C.; Soloski, E. J. J. Org. Chem. 1966, 31, 743-745. (11) TBS triflate (Aldrich, 17.0 g, 64.6 mmol) was injected into a suspension of LiC_6HF_4 (prepared from C_6HBrF_4 (14.8 g, 64.6 mmol) and "BuLi (40 mL, 1.6 M in hexanes) with stirring at -78 °C. The mixture was slowly warmed to 25 °C over a period of 8 h and the resulting suspension filtered. After the solvent was removed at 25 °C under reduced pressure, the nonvolatile residue was distilled (45 °C/ 0.8 mm) and a colorless liquid was collected. Yield of 1a: 80%. ¹H NMR (CD₂Cl₂): δ 0.40 ("t", 6H), 0.93 (s, 9H), 7.10 (m, 1H). ¹⁹F NMR (CCl₂D₂): δ -128.2 (b), -132.4 (b). ¹³C NMR (CD₂Cl₂): δ -3.7, 18.1, 26.5, 108.0, 144.8, 148.1, 151.4. Compound 1a (5.4 g, 20.4 mmol) was dissolved in Et₂O, and ⁿBuLi (13 mL, 1.6 M in hexanes) was then added dropwise with stirring at -78 °C. After 2 h, BCl₃ (4.2 mL, 1.0 M in hexanes) was injected. The mixture was warmed to room temperature over a period of 16 h, and the resulting suspension was filtered. The product was recrystallized from Et₂O/pentane and collected as large colorless crystals. Yield of **2a**: 74%. ¹H NMR (C₆D₆): δ 0.20 (s, 24H), 0.80 (m, 12H), 0.82 (s, 36H), 3.05 (q, J = 7.1 Hz, 8H). ¹⁹F NMR $(C_6D_6): \delta - 129.4$ (b), -133.8 (b). Compound **2a** (3.8 g, 3.1 mmol) and $(C_6H_5)_3CCl (0.88 \text{ g}, 3.1 \text{ mmol})$ were suspended in pentane and stirred for 6 h at 25 °C, and the orange product was collected by filtration. The crude product was then dissolved in CH₂Cl₂ and filtered to remove LiCl, followed by pentane addition to precipitate the orange solid. Yield of **3a**: 86%. ¹H NMR (CCl₂D₂): δ 0.31 (s, 24H), 0.88 (s, 36H), 7.64 (d, J = 6.9 Hz, 6H), 7.85 (t, J = 6.9 Hz, 6H), 8.25 (⁴t", J = 6.9 Hz, 3H). ¹⁹F NMR (CCl₂D₂): δ -133.0 (b), -144.5 (b). ¹³C NMR (CCl₂D₂): δ -3.8, 17.8, 26.4, 108.4, 131.0, 140.2, 143.0, 144.0, 147.4 ($J_{C-F} = 262$ Hz), 149.6 ($J_{C-F} = 262$ Hz), 211.3 Anal. Calcd for C₆₇H₇₈BF₁₆Si₄: C, 61.55; H, 5.78. Found: C, 61.83; H, 5.61. The same procedures were used in the syntheses of **1b**, **2b**, and **3b**. **1b**: ¹H NMR (CCl₂D₂) δ 0.98 (d, J = 7.5 Hz, 72H), 1.50 (⁺p", J = 7.5 Hz, 12H), 7.10 (m, 1H); ¹⁹F NMR (CCCl₃) δ -128.2 (b), -132.4 (b). **2b**: ¹H NMR (CCCl₃) δ 0.80 (t, J = 7.1 Hz, 12H), 1.08 (d, J = 7.5 Hz, 72H), 1.52 (⁺p", J = 7.5 Hz, 12H), 3.05 (q, J = 7.1 Hz, 8H); ¹⁹F NMR (CDCl₃) δ -131.3 (b), -132.1 (b); ¹³C NMR (CDCl₃) δ 1.28, 18.8, 108.6, 130.6, 139.2, 142.4, 144.0, 146.8 ($J_{C-F} = 261$ Hz), 148.9 ($J_{C-F} = 259$ Hz), 211.3 Anal. Calcd for C₇₉H₉₉BF₁₆-Si₄: C, 64.30; H, 6.76. Found: C, 64.57; H, 6.89. The crude product was then dissolved in CH₂Cl₂ and filtered to remove



by quenching with a trialkylsilyl triflate (Scheme 1) yields silyl-substituted tetrafluoroarenes.¹¹ Subsequent ⁿBuLi metalation, reaction with BCl₃, and cation metathesis affords the corresponding tetraarylborates¹¹ as crystalline trityl salts (B(C₆F₄TBS)₄⁻, **3a**; B(C₆F₄TIPS)₄⁻, **3b**). Zirconocenium salts **4** are then cleanly and rapidly obtained using these methide abstraction reagents^{5a} and the corresponding zirconocene dimethyls (eq 1).¹² The

$$\begin{split} L_{2}ZrMe_{2} + 3 &\xrightarrow{\text{toluene}} \\ L_{2}ZrMe^{+}B(C_{6}F_{4}SiR_{3})_{4}^{-} + Ph_{3}CMe \ \ (1) \\ & 4a-d \end{split} (1) \\ & 4a-d \\ & 4a, Cp_{2}ZrMe^{+}B(C_{6}F_{4}TBS)_{4}^{-}; \\ & 4b, Cp_{2}ZrMe^{+}B(C_{6}F_{4}TIPS)_{4}^{-}; \\ & 4c, (1,2-Me_{2}Cp)_{2}ZrMe^{+}B(C_{6}F_{4}TIPS)_{4}^{-}; \\ & 4d, (1,2-Me_{2}Cp)_{2}ZrMe^{+}B(C_{6}F_{4}TIPS)_{4}^{-} \end{split}$$

only exception is $(Me_5C_5)_2ZrMe_2$, for which the abstraction process is sluggish (presumably for steric reasons). However, the corresponding hydride^{4g} cations are readily obtained under H₂ (eq 2).¹¹ Complex classes 4 and 5 are crystalline solids and have been characterized by stan-

$$(\operatorname{Me}_{5}\operatorname{C}_{5})_{2}\operatorname{Zr}\operatorname{Me}_{2} + 3 \xrightarrow[H_{2}(1 \text{ atm}), 25 \circ C]{} (\operatorname{Me}_{5}\operatorname{C}_{5})_{2}\operatorname{Zr}\operatorname{H}^{+}\operatorname{B}(\operatorname{C}_{6}\operatorname{F}_{4}\operatorname{SiR}_{3})_{4}^{-} (2)$$
5a, (Me.C.). ZrH⁺B(C.F.TBS).⁻

5a,
$$(Me_5C_5)_2ZrH^{+}B(C_6F_4TBS)_4$$
;
5b, $(Me_5C_5)_2ZrH^{+}B(C_6F_4TIPS)_4^{-}$

dard spectroscopic and analytical techniques.¹¹ The methyl derivatives exhibit low-field $Zr^{-13}CH_3$ NMR resonances characteristic of zirconocene methyl cations.^{4a} In contrast to the aforementioned $B(C_6F_5)_4^-$ analogues, 4 and 5 exhibit high thermal stability, as evidenced by negligible ¹H NMR spectroscopic changes over the course of several hours at 100 °C in toluene- d_8 and half-lives on the order of 1 h at 130 °C in toluene- d_8 .

In regard to tight ion pair structure in solution, variable-temperature ¹H NMR studies of 4c,d in toluene d_8 reveal diastereotopic Cp-Me group permutation indicative of rapid reorganization/symmetrization of the evidently dissymmetric ground-state ion pairing (eq 3).



Derived ΔG^{\ddagger} values of 15.1(8) (4c) and 15.8(5) kcal/mol (4d) (60 °C) are significantly lower than in (1,2-Me₂-Cp)₂ZrMe⁺MeB(C₆F₅)₃⁻ ($\Delta G^{\ddagger} = 18.3(2)$ kcal/mol at 80 °C),^{4a} indicating substantially "looser" ion pairing in the case of the functionalized borates. At -90 °C in toluened₈, the ¹⁹F NMR spectrum of 4a reveals 12 signals (not all of equal intensity), indicating a low-symmetry instantaneous cation-anion structure. Significant displacements of the aryl ¹⁹F resonances from the δ -130 ppm region of 3, with signals at δ -167.6 and -162.0, suggest weak Zr⁺···F(aryl) interactions as identified crystallographically in (1,2-Me₂Cp)₂ZrH⁺MeB(C₆F₅)₃⁻ (II).^{4a,g} As the temperature is raised, spectral line



broadening and coalescence ultimately give rise to two aryl 19 F signals by 25 °C. Although all members of the 4, 5 series are crystalline, severe disordering and twinning have to date frustrated attempts at highquality diffraction analyses.

Ethylene polymerization experiments and polymer characterization were carried out using previously described procedures.^{4a,c} Polymerization activity assays are carried out under rigorously anhydrous/anaerobic high-vacuum-line conditions,^{4a,c} are designed to minimize mass transport effects (rapid mixing, short reaction times),¹³ and aim for constant polymer yields to allow catalyst activity comparisons. All polymeric products exhibit the characteristic ¹H/¹³C NMR spectroscopic

⁽¹²⁾ $[(C_6H_5)_3C]^+[B(C_6F_4TBS)_4]^-$ (390 mg, 0.30 mmol) and Cp_2ZrMe_2 (82 mg, 0.32 mmol) were stirred in toluene for 8 h. Then, pentane was added to precipitate the product, which was collected after filtration and washed with pentane. Yield of **4a**: 310 mg, 75%. **4a**: ¹H NMR (C_6D_6) δ 0.23 (s, 24H), 0.56 (s, 3H), 0.85 (s, 36H), 5.75 (s, 10H); ¹⁹F NMR (C_6D_6): δ -128.2 (b), -130.6 (b); ¹³C NMR ($C_6D_4Cl_2$) δ -4.4, 17.2, 25.8, 49.6, 111.6, 114.8, 119.8, 147.0, 149.8. Anal. Calcd for $C_{59}H_{73}BFS_{14}Zr$: C, 54.49; H, 5.66. Found: C, 54.30; H, 5.35. The same procedures were used to synthesize **4b**-**d**. Similar procedures were used to synthesize **5a**,**b**, except that the reactions were carried out under 1 atm of H₂. **4b**: ¹H NMR (C_6D_6) δ 0.54 (s, 3H), 1.01 (d, J = 7.5 Hz, 72H), 1.43 ("p", J = 7.5 Hz, 12H), 5.75 (s, 10H); ¹⁹F NMR (C_6D_6) δ -130.1 (b), -131.4 (b); ¹³C NMR ($C_6D_4Cl_2$) δ 12.0, 19.2, 111.6, 114.8, 120, 146.6, 150. Anal. Calcd for $C_{71}H_{97}BF_{16}Si_4Zr$: C, 58.06; H, 6.66. Found: C, 58.32; H, 6.79. **4c**: ¹H NMR (C_6D_6) δ 0.21 (s, 24H), 0.34 (s, 3H), 0.83 (s, 36H), 1.37 (s, 6H), 1.61 (s, 6H), 5.00 (b, 2H), 5.69 (b, 2H), 5.97 (t, 2H); ¹³C NMR (C_6D_6) δ -3.9, 12.5, 17.7, 26.4, 45.9, 108.1, 110.1, 111.8, 119.8, 133.5, 147.7, 150.9. Anal. Calcd for $C_{63}H_{81}$ -BF₁₆Si₄Zr: C, 55.78; H, 6.02. Found: C, 55.56; H, 6.01. **4d**: ¹H NMR (toluene-*d₈*): δ 0.37 (s, 3H), 1.08 (d, J = 7.5 Hz, 72H), 1.43 (s, 6H), 1.51 ("t", J = 7.5 Hz, 12H), 1.73 (s, 6H), 5.08 (b, 4H), 5.75 (b, 4H), 6.01, 1.51 ("t", J = 7.5 Hz, 12H), 1.73 (s, 6H), 7.90 (b, 1H); ¹³C NMR (C_6D_6) δ -3.9, 11.2, 17.7, 26.5, 110.1, 122.5, 147.7, 151.0. Anal. Calcd for $C_{68}H_{91}BF_{16}Si_4Zr$: C, 57.24; H, 6.43. Found: C, 56.87; H, 6.46. 5b: ¹H NMR (C_6D_6) δ 1.12 (d, J = 7.5 Hz, 72H), 1.50 ("p", J = 7.5 Hz, 12H), 1.72 (es, 30H), 7.96 (b, 1H); ¹³C NMR (che_6B_6) δ -3.9, 11.2, 17.7, 26.5, 110.1, 122.5, 147.7, 151.0. Anal. Calcd for $C_{68}H_{91}BF_{16}Si$

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Table 1. Ethylene Polymerization Characteristics of Metallocene Cations Having Various Anions^a

entry no.	metallocene cation	anion	[cat.] (mM)	reacn time (s)	polymer yield ^b (g)	activity (×10 ⁶ g PE/ mol of Zr•atm•h)	$M_{ m w}^c$ (×10 ⁵)	$M_n^c \times 10^5)$
1	Cp_2ZrMe^{+d}	$MeB(C_6F_5)_3^-$	0.32	40	1.6	4.5(4)	1.24	0.61
2	$(1,2-Me_2Cp)_2ZrMe^+ d$	$MeB(C_6F_5)_3^-$	0.14	66	1.7	6.8(6)	5.21	3.67
3	$(Me_5C_5)_2ZrMe^{+d}$	$MeB(C_6F_5)_3^-$	0.14	62	0.9	3.8(5)	2.55	1.26
4	Cp_2ZrMe^+	$B(C_6F_4TBS)_4^-$	0.14	62	1.4	5.7(6)	8.78	5.12
5	Cp_2ZrMe^+	$B(C_6F_4TIPS)_4^-$	0.14	60	1.5	6.2(6)	5.65	4.29
6	$(1,2-Me_2Cp)_2ZrMe^+$	$B(C_6F_4TBS)_4$	0.14	10	1.9	50(20)	8.29	5.29
7	$(1,2-Me_2Cp)_2ZrMe^+$	$B(C_6F_4TIPS)_4^-$	0.14	10	1.6	42(20)	6.02	3.03
8	$(Me_5C_5)_2ZrH^+$	$B(C_6F_4TBS)_4^-$	0.14	20	0.9	11(2)	21.6	10.8
9	$(Me_5C_5)_2ZrH^+$	$B(C_6F_4TIPS)_4^-$	0.14	20	0.8	10(2)	12.8	4.5
10	Cp ₂ ZrMe ⁺ ^e	$B(C_6F_5)_4^-$	0.20	60	2.1	6.4(6)	9.87	7.13
11	(1,2-Me ₂ Cp) ₂ ZrMe ⁺ ^e	$B(C_6F_5)_4^{-1}$	0.20	22	3.2	28(6)	7.03	4.38
12	(Me ₅ C ₅) ₂ ZrMe ⁺ ^e	$B(C_6F_5)_4$	0.20	20	1.1	10(2)	5.32	3.20

^{*a*} Procedure of ref 4c; toluene solvent (100 mL). ^{*b*} Average yield of ≥ 3 runs. ^{*c*} By GPC relative to polystyrene. ^{*d*} Data of ref 4c. ^{*c*} Catalyst generated by in situ reaction of the corresponding zirconocene dimethyl with Ph₃C⁺B(C₆F₅)₄⁻ in toluene for 5 min. Longer reaction times gave lower catalytic activities. For example, the activity of the B(C₆F₅)₄⁻ catalyst in entry 11 declines by 90% on standing in toluene solution for 3 h at 25 °C.

signatures of highly linear polyethylene.¹⁴ Molecular weight characteristics (Table 1) are unexceptional for single-site metallocene catalysts operating under these conditions.¹⁻⁴ With regard to catalyst characteristics, the polymerization activity and polymer characterization data reveal several noteworthy trends (Table 1). In comparison to $CH_3B(C_6F_5)_3$ -derived zirconocene catalysts, the corresponding $B(C_6F_4TBS)_4$ - and $B(C_6F_4-TIPS)_4$ -derived catalysts exhibit significantly higher polymerization activity and yield polyethylenes of significantly higher molecular weight. Particularly striking are the results for the $(1,2-Me_2Cp)_2ZrCH_3^+$ systems, in which ethylene polymerization activities rival or exceed any values previously measured in this laboratory.^{3c,15} The cation and anion structure-reactivity

trends in Table 1 likely reflect subtle electronic effects and matching/mismatching of steric encumbrances about the cation olefin activation zone¹⁶ of the tight ion pair. The data in Table 1 also reveal that *freshly prepared* $B(C_6F_5)_4$ -based catalysts have polymerization activities roughly similar to those of the $B(C_6F_4TBS)_4$ - and $B(C_6F_4TIPS)_4$ - analogues; however, standing at room temperature significantly erodes the catalytic performance (Table 1, footnoted), in accord with the aforementioned thermal stability observations.

The present results indicate that the properties of metallocene cation—anion ion pairs can be substantially modified by functionalization of the weakly coordinating anion. Trialkylsilyl substitution of the (fluoroaryl)borate framework can be effectively employed to enhance catalyst stability, polymerization activity, and solubility.

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