

SUPPORTING INFORMATION

Syntheses, Solution Multi-NMR Characterization, and Reactivities of $[\text{C}_6\text{F}_5\text{Xe}]^+$ Salts of Weakly Coordinating Borate Anions $[\text{BY}_4]^-$ ($\text{Y} = \text{CF}_3, \text{C}_6\text{F}_5, \text{CN}, \text{OTeF}_5$)

Karsten Koppe, Vural Bilir, Hermann-J. Frohn,* Hélène P. A. Mercier, Gary J. Schrobilgen*

Anorganische Chemie, Universität Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany;

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada.

Table S1. Solubilities (20 °C) of [C₆F₅Xe][BY₄] (Y = CN, CF₃, and C₆F₅) and [C₆F₅Xe][BF₄]

[C ₆ F ₅ Xe] ⁺ salt	solvent	solubility, mmol mL ⁻¹
[B(CF ₃) ₄] ⁻	CH ₃ CN	≥ 4.5
	PFB	≥ 1.2
	CH ₂ Cl ₂	~0.06
[B(C ₆ F ₅) ₄] ⁻ ^a	CH ₃ CN	~0.5
	DCE	~0.2
	CH ₂ Cl ₂	< 0.05
[B(CN) ₄] ⁻	CH ₃ CN	~4.3
	DCE, CH ₂ Cl ₂ , PFB	insoluble
	SO ₂ ClF	insoluble
[BF ₄] ⁻	CH ₃ CN	~4.8
	CH ₂ Cl ₂ , PFB, CCl ₄	insoluble
	SO ₂ ClF	insoluble

^a This salt contains the [C₆F₅Xe--NCCH₃]⁺ cation.

Table S2. Solution Decomposition Rates and Products (20 °C) for [C₆F₅Xe][BY₄] (Y = CF₃, C₆F₅, CN, OTeF₅) and [C₆F₅Xe][BF₄]

[C ₆ F ₅ Xe] ⁺ salts	solvent	time, days	% conversion ^a	C ₆ F ₅ -containing products, %		remarks
				C ₆ F ₅ H	C ₆ F ₅ X	
[B(CF ₃) ₄] [−]	CH ₃ CN	0.083(3)	0	—	—	
		2	5	100	—	
		11	14	100	—	HF (trace)
		30	57	100	—	HF
		43	100	100	—	HF
	CH ₂ Cl ₂	0.010(3)	0	—	—	
		3	4	—	C ₆ F ₅ Cl (100)	
		13	28	21	C ₆ F ₅ Cl (79)	
	PFB	22	50	20	C ₆ F ₅ Cl (80)	
		0.010(3)	0	—	C ₆ F ₅ Cl (100)	
[B(C ₆ F ₅) ₄] ^{−d}	CH ₃ CN	8	4	—	C ₆ F ₆ (6), C ₆ F ₅ X(31), ^b C ₆ F ₅ Y (63) ^c	
		2	11	100	—	
		6	44	80	(C ₆ F ₅) ₂ (20)	
		9	74	77	(C ₆ F ₅) ₂ (23)	
	CH ₂ Cl ₂	20	100	85	(C ₆ F ₅) ₂ (15)	
		0.031(3)	—	—	—	−40 °C
		0.083(3)	1	100	—	−40 °C
	DCE	0.667(6)	4	100	—	−40 °C
		0.010(3)	28	100	—	
		0.021(3)	57	100	—	
[B(CN) ₄] [−]	CH ₃ CN	0.042(3)	85	100	—	
		0.021(3)	0	—	—	
		2	2	100	—	
		8	6	100	—	} ^e
		28	21	100	—	
		58	94	100	—	
[B(OTeF ₅) ₄] [−]	CH ₃ CN	71	100	100	—	
		0.010(3)	11	100	—	
		2	29	100	—	
		10	39	100	—	
	CH ₂ Cl ₂	25	72	94	(6) ^f	
		0.021(3)	11	100	—	
[BF ₄] [−]	CH ₃ CN	2	66	89	C ₆ F ₅ Cl (6)	(5%) ^f
		9	69	90	C ₆ F ₅ Cl (7)	(5%) ^f
		24	81	81	C ₆ F ₅ Cl (14)	(5%) ^f
		0.083(3)	2	100	—	
		2	5	100	—	HF (trace)
	aHF	11	10	100	—	HF (trace)
		30	32	100	—	HF (trace)
		43	48	100	—	HF (trace)
		58	79	100	—	HF (trace)
		0.500(6)	0	—	C ₆ F ₆ (trace)	

Table S2. (continued ...)

[B(CF ₃) ₄] [−] + [BF ₄] ^{−g}	CD ₃ CN	2	1	–	C ₆ F ₆ (100)	
		11	6	–	C ₆ F ₆ (100)	
		33	12	–	C ₆ F ₆ (100)	
		54	15	–	C ₆ F ₆ (100)	
		0.125(6)	24	100	–	
	CD ₂ Cl ₂	2	100	~100	C ₆ F ₅ D (traces)	
		0.125(6)	0	–	–	
		2	30	50	C ₆ F ₅ D (23)	C ₆ F ₅ Cl (27%)
		7	41	66	C ₆ F ₅ D (12)	C ₆ F ₅ Cl (22%)
		18	100	64	C ₆ F ₅ D (18)	C ₆ F ₅ Cl (18%)

^a Conversion of the [C₆F₅Xe]⁺ cation and relative molar amounts of C₆F₅-containing products in mole %. ^b Unassigned C₆F₅-species; δ(¹⁹F), ppm: *o*-F, −143.0; *p*-F, −154.7; *m*-F, −163.1. ^c Unassigned C₆F₅-species; δ(¹⁹F), ppm: *o*-F, −143.1; *p*-F, −155.2; *m*-F, −162.5. ^d This salt contains the [C₆F₅Xe--NCCH₃]⁺ cation. ^e Unassigned ¹⁹F NMR resonances (singlets) also occurred at −144.9 ppm and −181.3 ppm. ^f C₆F₅OTeF₅; δ(¹⁹F), ppm: *o*-F, −130.6; *p*-F, −141.4; *m*-F, −162.7. ^g Equimolar amounts of [C₆F₅Xe][B(CF₃)₄] and [N(C₄H₉)₄][BF₄] were used.

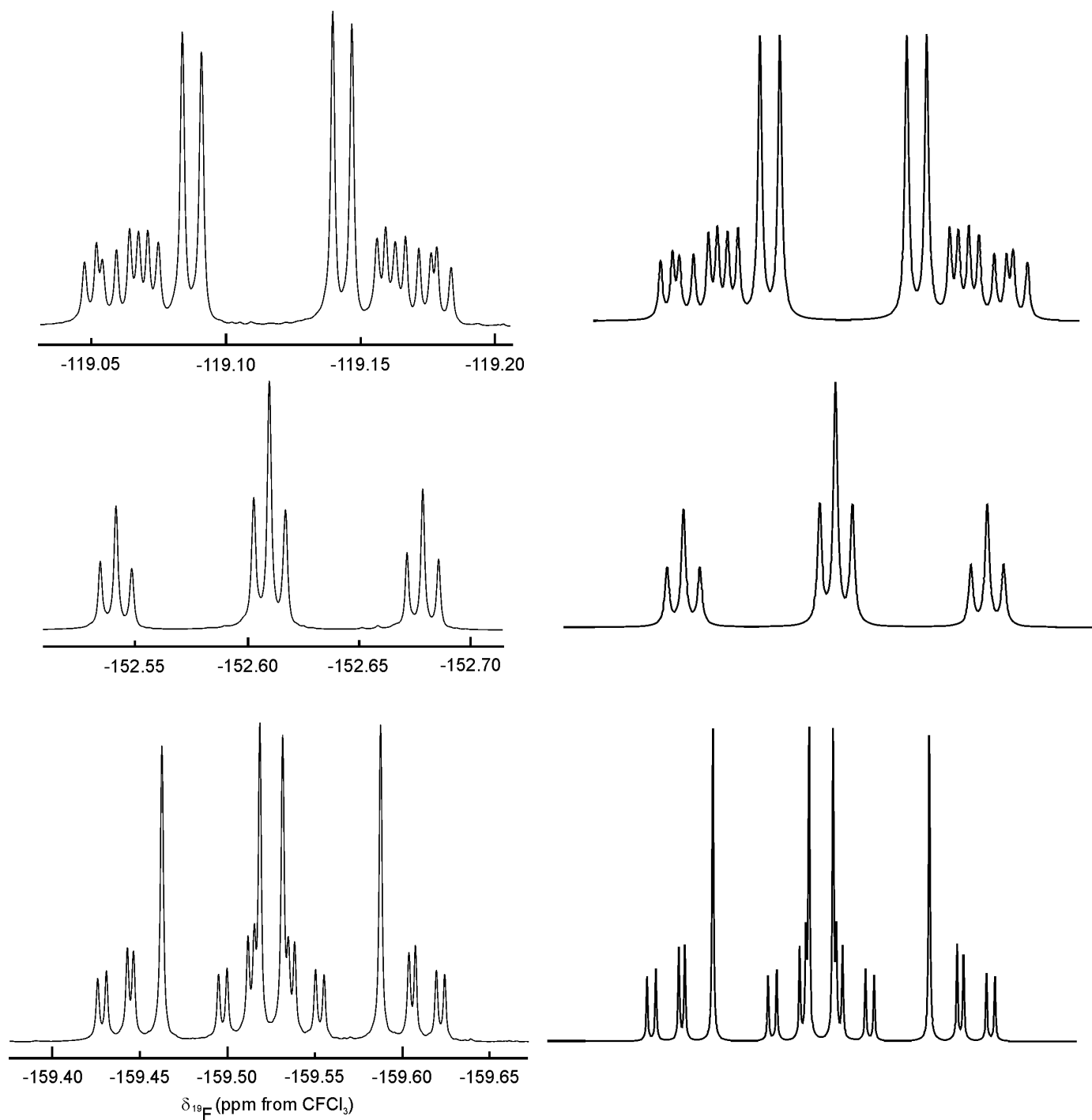


Figure S1. The ^{19}F NMR spectra (282.40 MHz) of the *o*-, *m*- and *p*- C_6F_5 fluorine resonances of $\text{C}_6\text{F}_5\text{I}$ recorded in CD_3CN at 24 $^\circ\text{C}$; spectra were resolution enhanced by Gaussian multiplication (left-hand traces). The simulated spectra (right-hand traces) are provided for comparison.

Synthesis of $B(C_6F_5)_3$. Pentafluorophenyl magnesium bromide was prepared in a three-neck round bottom flask (250 mL) equipped with a reflux condenser and a dropping funnel. Bromopentafluorobenzene (25.46 g; 103.1 mmol) was diluted with Et_2O (40 mL) and added dropwise within 20 min to magnesium turnings (3.40 g; 140 mmol) in dry Et_2O (60 mL) at the reflux temperature ($-35\text{ }^{\circ}C$) and stirred for 70 min. The completion of the reaction was confirmed by ^{19}F NMR spectroscopy. In a second round bottom flask, freshly distilled $BF_3 \cdot Et_2O$ (4.8 g; 31 mmol) was diluted in Et_2O (10 mL), cooled to $-78\text{ }^{\circ}C$ and transferred to the cold ($-78\text{ }^{\circ}C$) Grignard suspension within 5–10 min by means of a 1.5 mm o.d. PTFE tube. The suspension was initially stirred for 15 min at $-60\text{ }^{\circ}C$ and for 45 min at $0\text{ }^{\circ}C$, and then allowed to warm to room temperature and stirred for a further 3.5 h until all C_6F_5MgBr had reacted, yielding $B(C_6F_5)_3$. The completion of the reaction was confirmed by NMR spectroscopy and the solvent was subsequently removed under dynamic vacuum. The crude, brown and sticky solid was extracted three times with boiling ($69\text{ }^{\circ}C$) *n*-hexane (75 mL portions). The hexane solutions were combined and stored at room temperature. Over time, clear, colorless crystals (2–4 mm) of $B(C_6F_5)_3$ grew. The $B(C_6F_5)_3$ crystals (9.78 g; 19.10 mmol; 61.9%) were isolated, dried, and sublimed under dynamic vacuum at $100\text{--}110\text{ }^{\circ}C$ onto a water-cooled cold-finger. The cold-finger was dried and transferred into a drybox where $B(C_6F_5)_3$ (6.73; 13.14 mmol; 42.6%) was recovered.

Synthesis of $Cs[B(C_6F_5)_4]$. Bromopentafluorobenzene (1.783 g; 7.22 mmol) was dissolved in Et_2O (25 mL) and cooled to $-80\text{ }^{\circ}C$. A butyllithium/*n*-pentane solution (2.5 M; 5 mL; 12.50 mmol) was added dropwise at $-80\text{ }^{\circ}C$ and stirred for 2 h. The reaction was monitored until complete by ^{19}F NMR spectroscopy. A sample was solvolyzed with CH_3OH (250 mL) at $-40\text{ }^{\circ}C$ and the amount of C_6F_5H determined by integration of the ^{19}F NMR spectrum against the internal standard, benzotrifluoride, (10.0 μL ; 0.082 mmol). Lithium pentafluorobenzene is unstable in Et_2O at temperatures higher than $-20\text{ }^{\circ}C$ and must be handled at low temperatures.

In a second round bottom flask, $B(C_6F_5)_3$ (2.896 g; 5.66 mmol) was suspended in *n*-pentane (50 mL) and cooled to $-80\text{ }^{\circ}C$. The $C_6F_5Li/Et_2O/n$ -pentane solution was transferred to the $B(C_6F_5)_3/n$ -pentane suspension through a 1.5-mm o.d. Teflon tube and the mixture stirred for 15 min at $-60\text{ }^{\circ}C$, 60 min at $-40\text{ }^{\circ}C$ and 30 min at room temperature whereupon a white solid precipitated. The mother liquor was separated and the solid washed three times (20 mL each) with *n*-pentane. All solutions were combined and checked by ^{19}F NMR spectroscopy and showed no signals. The white solid, $[Li(Et_2O)_x][B(C_6F_5)_4]$, was dried under vacuum for 8 h at room temperature. The solid was dissolved in H_2O (30 mL) and the H_2O was subsequently removed under vacuum. This treatment was repeated twice to remove coordinated Et_2O . A vacuum dried (room temperature, 2 h) white solid corresponding to $[Li(H_2O)_x][B(C_6F_5)_4]$ (3.42 g, 5 mmol; yield 88%, calculated for one molecule of H_2O) was isolated.

$[Li(H_2O)_x][B(C_6F_5)_4]$ (3.02 g; 4.30 mmol) was dissolved in water (50 mL) and combined with a saturated solution of $CsOH \cdot H_2O$ (1.854 g; 11.00 mmol) in H_2O (40 mL), whereupon a white precipitate immediately formed. The suspension was stirred for 2 h at room temperature and the mother liquor was separated. The solid was washed with H_2O until the pH was neutral. The white solid was dried under vacuum for 6 h at room temperature, yielding 2.777 g; 3.42 mmol of $Cs[B(C_6F_5)_4]$ (80% yield).