

Syntheses, Solution Multi-NMR Characterization, and Reactivities of $[\text{C}_6\text{F}_5\text{Xe}]^+$ Salts of Weakly Coordinating Borate Anions, $[\text{BY}_4]^-$ ($\text{Y} = \text{CF}_3$, C_6F_5 , CN , or OTeF_5)

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New examples of $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts of the weakly coordinating anions $[\text{B}(\text{CF}_3)_4]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{B}(\text{CN})_4]^-$, and $[\text{B}(\text{OTeF}_5)_4]^-$ have been synthesized by metathesis reactions of $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ with the corresponding $\text{M}[\text{BY}_4]$ salts ($\text{M}^I = \text{K}$ or Cs ; $\text{Y} = \text{CF}_3$, C_6F_5 , CN , or OTeF_5). The salts were characterized in solution by multi-NMR spectroscopy. Their stabilities in prototypic solvents (CH_3CN and CH_2Cl_2) and decomposition products are reported. The influence of the coordinating nature of $[\text{BY}_4]^-$ on the decomposition rate of $[\text{C}_6\text{F}_5\text{Xe}]^+$ as well as the presence of the weakly nucleophilic $[\text{BF}_4]^-$ ion has been studied. The electrophilic pentafluorophenylation of $\text{C}_6\text{H}_5\text{F}$ by $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ in solvents of different coordinating abilities (CH_3CN and CH_2Cl_2) and the effects of stronger nucleophiles (fluoride and water) on the pentafluorophenylation process have been investigated. Simulations of the ^{19}F and ^{129}Xe NMR spectra of $[\text{C}_6\text{F}_5\text{Xe}]^+$ have provided the complete set of aryl ^{19}F – ^{19}F and ^{129}Xe – ^{19}F coupling constants and their relative signs. The ^{19}F NMR parameters of the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation in the present series of salts are shown to reflect the relative degrees of cation–solvent interactions.

Introduction

The chemistry of xenon–carbon compounds was initiated in 1989 when two independent investigations of the reaction between XeF_2 and $\text{B}(\text{C}_6\text{F}_5)_3$ led to the syntheses and characterizations of $[\text{C}_6\text{F}_5\text{Xe}][(\text{C}_6\text{F}_5)_n\text{BF}_{4-n}]$ ($n = 1, 2$, and 3) and the first documented example of a C–Xe bond.^{1–3} The development of xenon–carbon chemistry has been previously reviewed.^{4,5} In the case of Xe^{II} –C compounds, two classes of compounds are known; (1) $[\text{RXe}][\text{A}]$, where $[\text{A}]^-$ is a weakly coordinating anion in which the C–Xe bond of the cation is a 2c–2e bond, and (2) R–Xe–L , where $[\text{L}]^-$

is a nucleophilic anion such as $[\text{C}_6\text{F}_5\text{CO}_2]^-$,⁶ Cl^- ,⁷ or F^- ,^{8,9} that forms a strong ion contact (donor–acceptor) interaction with $[\text{RXe}]^+$, leading to R–Xe–L molecules that possess asymmetric 3c–4e bonds.

Presently, three types of organo groups, R, have been shown to form organoxenonium salts, $[\text{RXe}][\text{A}]$ ($\text{R} = \text{aryl}$,^{1–5} alkenyl,^{10–13} and alkynyl^{14–16}). The majority of the presently known xenonium salts have an aryl group bonded to Xe^{II} .

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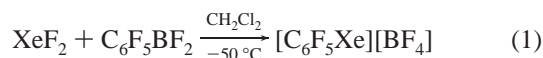
The syntheses of organoxenonium salts are generally carried out under acidic conditions, which entail acid-assisted fluorine/organo group substitution (xenodeborylation) starting from XeF_2 and an acidic borane, RBF_2 .

As a consequence of the electrophilic character of the xenonium cation, the organo group bonded to Xe^{II} and the counteranion must fulfill specific criteria: (1) the R group and the counteranion of the $[\text{RXe}]^+$ salt must be resistant to oxidation by Xe^{II} , which can be achieved by use of electron-withdrawing substituents such as F, Cl, CF_3 , or NO_2 , and (2) the R group must resist the inductive effect of Xe^{II} in the σ skeleton. The C_6F_5 group fulfills these criteria and yields the most stable $[\text{RXe}]^+$ salts. Moreover, the extended π system of the C_6F_5 group, in combination with the electron-poor nature of the carbon skeleton, results in sufficient polarization of the $[\text{C}_6\text{F}_5\text{Xe}]^+$ π system to develop a partial negative charge on the *ipso*-carbon atom, which leads to strengthening of the C–Xe bond by means of electrostatic contributions.¹⁷

In order to meet criteria (1) and (2) and to arrive at $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts having properties that approach those of the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation in the gas phase, a series of $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts of the weakly coordinating borate anions, $[\text{BY}_4]^-$ ($\text{Y} = \text{CF}_3$, C_6F_5 , CN, or OTeF_5), have been synthesized and their stabilities and reactivities have been investigated. The detailed structures and bonding of the $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ ($\text{Y} = \text{CF}_3$, C_6F_5 , or CN) salts will be described in a forthcoming paper.

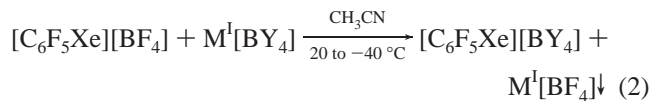
Results and Discussion

The most efficient way to form a $[\text{C}_6\text{F}_5\text{Xe}]^+$ salt, which can serve as the starting material for other $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts and is easy to handle at ambient temperature, is by means of the xenodeborylation reaction of XeF_2 with $\text{C}_6\text{F}_5\text{BF}_2$ (eq 1).¹⁸ The reaction of equivalent amounts of XeF_2 and



$\text{C}_6\text{F}_5\text{BF}_2$ in CH_2Cl_2 at -50°C yields pure $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ in 80–90% yield. The salt is a pale-yellow solid and is soluble in CH_3CN and anhydrous HF (aHF) but insoluble in the polar and weakly coordinating solvents CH_2Cl_2 , $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$ (PFB), $\text{C}_6\text{H}_5\text{F}$, $\text{ClCH}_2\text{CH}_2\text{Cl}$ (DCE), and SO_2ClF .

$[\text{C}_6\text{F}_5\text{Xe}]^+$ Salts with Weakly Coordinating $[\text{BY}_4]^-$ ($\text{Y} = \text{CF}_3$, C_6F_5 , CN, or OTeF_5) Anions. (a) Syntheses by Metathesis, Solid-State Stabilities, and Solubilities. Satisfactory solubilities of the starting material, $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$, and the products, $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$, in combination with the low solubility of $\text{M}^+[\text{BF}_4]^-$ ($\text{M}^+ = \text{K}$ or Cs) in CH_3CN (5 mmol L^{-1} at room temperature; negligible at -40°C) made CH_3CN the preferred solvent for the metathesis reactions described in eq 2 and allowed the preparation of the hitherto unknown $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ salts and their isolation in nearly quantitative yields (90–100%) and very high purities. The



salts, $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ ($\text{Y} = \text{CF}_3$ or CN) and $[\text{C}_6\text{F}_5\text{XeNCCCH}_3][\text{BY}_4]$ ($\text{Y} = \text{C}_6\text{F}_5$), were obtained as pale-yellow solids, but attempts to isolate solid $[\text{C}_6\text{F}_5\text{Xe}][\text{B}(\text{OTeF}_5)_4]$ from $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$, CH_2Cl_2 , $\text{CH}_3\text{CN}/\text{PFB}$, or PFB solutions failed because the product separated as a yellow oil when the solutions were cooled.

Thermoanalytical studies showed that the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $[\text{B}(\text{CF}_3)_4]^-$ salts have significantly lower thermal stabilities in the solid state than the $[\text{B}(\text{CN})_4]^-$, $[\text{BF}_4]^-$, and $[\text{AsF}_6]^-$ salts (Table 1). Both $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ and $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$ melt without decomposition, whereas the $[\text{B}(\text{CN})_4]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, and $[\text{B}(\text{CF}_3)_4]^-$ salts decompose without melting.

The solubilities of $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ and $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ in the weakly coordinating solvents, CH_2Cl_2 , DCE, and PFB as well as in CH_3CN were determined to provide the solubility database (Table S1) required for solution stability studies (see Solution Stabilities of $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$). Among the series of $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ salts discussed here, the solubility behavior of the $[\text{B}(\text{CN})_4]^-$ salt is most similar to that of the $[\text{BF}_4]^-$ salt. The solubility of $[\text{C}_6\text{F}_5\text{Xe}][\text{B}(\text{CN})_4]$ is ~ 4.3 mmol mL^{-1} in CH_3CN at 20°C compared with ~ 4.8 mmol mL^{-1} for the $[\text{BF}_4]^-$ salt, whereas both salts are insoluble in CH_2Cl_2 , DCE, PFB, $\text{C}_6\text{H}_5\text{F}$, and SO_2ClF . Salts having four fluoroorganic groups in the anion such as $[\text{C}_6\text{F}_5\text{Xe}][\text{B}(\text{CF}_3)_4]$ and $[\text{C}_6\text{F}_5\text{XeNCCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ have satisfactory solubilities in CH_3CN and low solubilities in halogenated hydrocarbons.

(b) Solution Stabilities of $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$; Solvent and Counteranion Dependencies. The thermal stabilities of $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ solutions were compared for different borate salts in different solvent media at 20°C . The $[\text{C}_6\text{F}_5\text{XeNCCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ salt is highly unstable in CH_2Cl_2 at 20°C ; consequently, this system was studied at -40°C . When possible, the stabilities of the $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ salts were compared with that of $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ in the same solvent. The extent of $[\text{C}_6\text{F}_5\text{Xe}]^+$ conversion, expressed in mole percent, was determined from the integrated ^{19}F NMR spectral intensities of $[\text{C}_6\text{F}_5\text{Xe}]^+$ and the C_6F_5 -containing products. The reaction products are expressed in mole percent of C_6F_5 products. These quantities and their corresponding reaction times are provided in Table 2, with specific entries from this table indicated in the ensuing discussion.

(i) $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$. The higher stabilities of $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts in acidic media relative to basic media have been generally recognized;¹⁸ however, rigorous comparisons of their relative stabilities were not available. In the case of $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$, the cation does not undergo significant solvolysis in aHF at -40°C .

Among the $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts examined in aprotic solvents during this comparative study, $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ solutions in CH_3CN are the most stable and solutions of $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ in aHF were found to be even more stable. After 54 days, only 15% of $[\text{C}_6\text{F}_5\text{Xe}]^+$ had decomposed to C_6F_6 in aHF (entry 5b), whereas a comparable conversion was only

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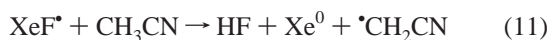
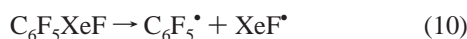
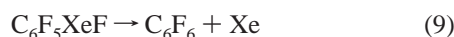
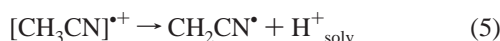
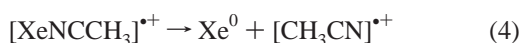
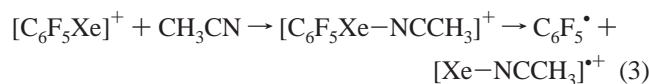
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Table 1. Melting Points and Decomposition Temperatures of [C₆F₅Xe][BY₄] (Y = CF₃, C₆F₅, or CN), [C₆F₅Xe][BF₄], and [C₆F₅Xe][AsF₆]

[C ₆ F ₅ Xe] ⁺ salt	mp, °C		decomp temp, °C	
	T _{onset}	T _{max}	T _{onset}	T _{max}
[B(CF ₃) ₄] ⁻			121.2	125.0
[B(C ₆ F ₅) ₄] ^{-a}			85.2	85.5
[B(CN) ₄] ⁻			152.2	154.8
[BF ₄] ⁻	79.5	85.8	156.6	180.5
[AsF ₆] ⁻	109.8	112.2	159.2	182.7

^a This salt contains the [C₆F₅XeNCCH₃]⁺ cation.

achieved in CH₃CN after 18 days and resulted in exclusive formation of C₆F₅H (entry 5c). Although the HF molecule can coordinate to the Xe^{II} center through fluorine, this interaction is expected to be weaker than CH₃CN coordination and leads to C₆F₆, Xe⁰, and [H(HF)_n][BF₄]. Thus, the exclusive formation of C₆F₅H in CH₃CN is consistent with the initial coordination of CH₃CN to the positively charged xenon center and rapid homolytic cleavage of the Xe–C bond (eqs 3–7). The absence of HF and C₆F₆ shows that the main decomposition channel arose from CH₃CN coordination and not from [BF₄]⁻ coordination (eqs 8–11).

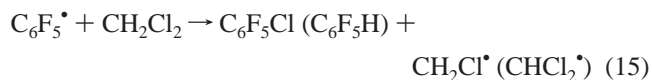
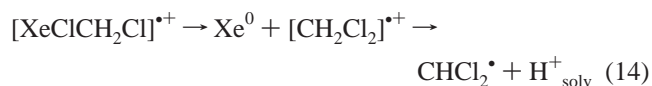
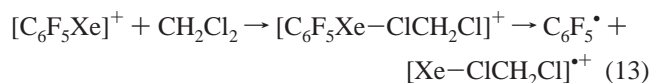


(ii) [C₆F₅Xe][B(CF₃)₄]. The decomposition of [C₆F₅Xe][B(CF₃)₄] was complete in CH₃CN after 43 days, and C₆F₅H, the only C₆F₅-containing product, and HF (56 mol % relative to C₆F₅H) were the sole products (entry 1a), whereas in CH₂Cl₂, 50% of the cation decomposed within 22 days, forming C₆F₅Cl (80%) and C₆F₅H (20%) (entry 1b). Decomposition in CH₃CN is likely initiated by coordination of CH₃CN, as previously described (eqs 3–6). The formation of HF is indicative of anion decomposition according to eq 12.



The weakly coordinating solvent, CH₂Cl₂, is capable of coordinating to strong Lewis acid centers.¹⁹ Thus, the decomposition sequence may be initiated by solvent coordination to [C₆F₅Xe]⁺, subsequent homolytic cleavage of the

Xe–C bond (eq 13), and electron transfer (eq 14) to give the observed products (eq 15). Abstraction of [CF₃]⁻



or F⁻ from [B(CF₃)₄]⁻ by “[C₆F₅]⁺” or [C₆F₅Xe]⁺ is ruled out in CH₃CN or CH₂Cl₂ solvents because neither C₆F₅CF₃ nor C₆F₆ was detected. Clearly, [C₆F₅Xe][B(CF₃)₄] is significantly more stable in PFB (entry 1c) than in CH₂Cl₂, with a decomposition rate that is approximately one-fourth of that in CH₂Cl₂. Two unidentified C₆F₅-containing products were formed in PFB (total, ~4 mol %) in addition to C₆F₆.

(iii) [C₆F₅XeNCCH₃][B(C₆F₅)₄]. The stabilities and reaction pathways are markedly different in the case of [C₆F₅XeNCCH₃][B(C₆F₅)₄]. Acetonitrile solutions of [C₆F₅XeNCCH₃][B(C₆F₅)₄] were completely decomposed after 20 days with the formation of C₆F₅H (85%) and (C₆F₅)₂ (15%) (entry 2a). The stability of [C₆F₅XeNCCH₃][B(C₆F₅)₄] in CH₂Cl₂ was strongly dependent on the temperature. At 20 °C, the salt completely decomposed in less than 20 min, forming C₆F₅H (46%) and (C₆F₅)₂ (9%), and the balance (45%) was comprised of a mixture of [(C₆F₅)₃BF]⁻, B(C₆F₅)₃, and [C₆F₅BF₃]⁻ (superimposed spectra prevented integration), resulting from anion decomposition, whereas at –40 °C, only 4% of the cation was converted to C₆F₅H after 16 h (entry 2b). The stability of [C₆F₅XeNCCH₃][B(C₆F₅)₄] in DCE at 20 °C was significantly greater than that in CH₂Cl₂, with only 85% of the cation consumed after 1 h, forming only C₆F₅H (entry 2c). The solvent, CH₂ClCH₂Cl molecule [ε = 10.7 (20 °C); IP = 11.1 eV], is more polar than CH₂Cl₂ [ε = 8.9 (25 °C); IP = 11.4 eV], and both solvents have comparable ionization potentials (IPs).

The higher polarity and coordinating ability of DCE apparently hinders the interaction of [C₆F₅Xe]⁺, after elimination of CH₃CN (eq 16), with nucleophilic sites of the [B(C₆F₅)₄]⁻ anion and accounts for the absence of (C₆F₅)₂ at 20 °C.

The formation of (C₆F₅)₂ is clearly associated with the [B(C₆F₅)₄]⁻ anion because none of the other [C₆F₅Xe][BY₄] salts considered in this study give rise to this product, which most likely results from attack of [C₆F₅Xe]⁺ on the anion (eq 17), with (C₆F₅)₂ resulting from decomposition of the intermediate, Xe(C₆F₅)₂ (eq 18). In contrast with the reversible step of Lewis acid elimination in eq 8, an irreversible elimination of B(C₆F₅)₃ is probable according to eq 17. The dominant product deriving from intrinsically unstable Xe(C₆F₅)₂ is, however, C₆F₅H (eqs 19 and 20). The relative

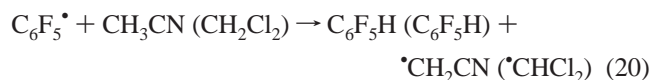
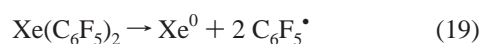
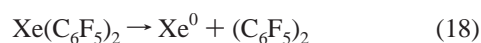
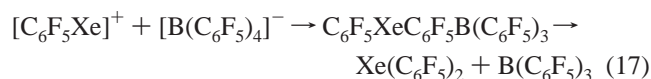
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Table 2. Solution Stabilities of [C₆F₅Xe][BY₄] (Y = CF₃, C₆F₅, CN, or OTeF₅) and [C₆F₅Xe][BF₄] at 20 °C and Their C₆F₅-Containing Decomposition Products

entry	[C ₆ F ₅ Xe] ⁺ salt	solvent	time, ^a days	% conversion ^b	C ₆ F ₅ products (mol %) ^c derived from [C ₆ F ₅ Xe] ⁺
1a	[B(CF ₃) ₄] ⁻	CH ₃ CN	43	100	C ₆ F ₅ H (100) ^d
1b		CH ₂ Cl ₂	22	50	C ₆ F ₅ H (20), C ₆ F ₅ Cl (80)
1c		PFB	8	4	C ₆ F ₆ (6), C ₆ F ₅ X (31), ^e C ₆ F ₅ Y (63) ^f
2a	[B(C ₆ F ₅) ₄] ^{-g}	CH ₃ CN	20	100	C ₆ F ₅ H (85), (C ₆ F ₅) ₂ (15)
2b		CH ₂ Cl ₂	0.010(3)	100	C ₆ F ₅ H (46), (C ₆ F ₅) ₂ (9), C ₆ F ₅ -B species (45)
		CH ₂ Cl ₂	0.667(6) (-40 °C)	4	C ₆ F ₅ H (100)
2c		DCE	0.042(3)	85	C ₆ F ₅ H (100)
3a	[B(CN) ₄] ⁻	CH ₃ CN	71	100	C ₆ F ₅ H (100) ^h
4a	[B(OTeF ₅) ₄] ⁻	CH ₃ CN	25	72	C ₆ F ₅ H (94), C ₆ F ₅ Z (6) ⁱ and OTeF ₅ compds
4b		CH ₂ Cl ₂	24	81	C ₆ F ₅ H (81), C ₆ F ₅ Cl (14), C ₆ F ₅ Z (5) ^j and OTeF ₅ compds
5a	[BF ₄] ⁻	CH ₃ CN	58	79	C ₆ F ₅ H (100)
5b		aHF	54	15	C ₆ F ₆ (100)
5c		CH ₃ CN	18	15	C ₆ F ₅ H (100)
6a	[B(CF ₃) ₄] ⁻ + [N(C ₄ H ₉) ₄][BF ₄] ^k	CD ₃ CN	2	100	C ₆ F ₅ H (~100), C ₆ F ₅ D (traces)
6b		CD ₂ Cl ₂	18	100	C ₆ F ₅ H (64), C ₆ F ₅ D (18), C ₆ F ₅ Cl (18)

^a The precision is ±0.5 days for all entries except 2b and 2c, where the error on the last digit is indicated in parentheses. ^b Conversion of the [C₆F₅Xe]⁺ cation and relative molar amounts of C₆F₅-containing products are in mole percent. ^c The integrated intensities given in parentheses are relative to the total C₆F₅-containing species in the sample. ^d HF (56). ^e Unknown product: δ(¹⁹F) = -143.0 (o), -154.7 (p), -163.1 (m) ppm. ^f Unknown product: δ(¹⁹F) = -143.1 (o), -155.2 (p), -162.5 (m) ppm. ^g This salt contains the [C₆F₅XeNCCH₃]⁺ cation. ^h Unassigned singlets also occurred at -144.9 (0.10) and -181.3 (0.42) ppm. ⁱ Unknown C₆F₅ species: δ(¹⁹F) = -138.1 (o), -151.0 (p), -161.3 (m) ppm; unassigned resonances also occurred at -130.6 and -136.7 ppm. ^j Unknown C₆F₅ species: δ(¹⁹F) = -137.5 (o), -150.4 (p), -160.8 (m) ppm; unassigned resonances also occurred at -126.9 and -134.9 ppm. ^k Equimolar amounts of [C₆F₅Xe][B(CF₃)₄]⁻ and [N(C₄H₉)₄][BF₄]⁻ were used.

ratios of C₆F₅H to (C₆F₅)₂ in CH₃CN and CH₂Cl₂ at 20 °C are very similar, whereas C₆F₅H is formed exclusively in DCE.



The reaction pathway leading to (C₆F₅)₂ is supported by prior studies that have shown that, while the [B(C₆F₅)₄]⁻ anion is generally classified as a weakly coordinating anion, this anion, with relatively open tetrahedral geometry and rigid C₆F₅ groups,¹ highly electron-withdrawing substituents, and decreased negative charge on the *ipso*-carbon atom, is still susceptible to [C₆F₅]⁻ abstraction by metal cation centers.^{20,21}

The proposed intermediate, Xe(C₆F₅)₂, is supported by its independent synthesis and characterization.^{8,9} Acetonitrile solutions of Xe(C₆F₅)₂ have been shown to decompose within 24 h at -40 °C to mainly (C₆F₅)₂ and trace amounts of C₆F₅H.⁹ Under these conditions, the C₆F₅• radical does not readily abstract an acidic hydrogen from a basic solvent such as CH₃CN, indicating that radical solvation as well as resonance stabilization of the C₆F₅• radical must be taken

into account. In a weakly basic solvent such as CH₂Cl₂, the radical lifetime is very short at low temperatures, and solvent attack occurs with the exclusive formation of C₆F₅H.

(iv) [C₆F₅Xe][B(CN)₄]. The decomposition rate of [C₆F₅Xe][B(CN)₄] in CH₃CN at 20 °C (entry 3a) was among the slowest encountered in this study and is similar to that of the [BF₄]⁻ salt in CH₃CN (entry 5a). After 71 days, the cation had been consumed, with C₆F₅H being the only C₆F₅-containing product. In addition, two unassigned singlets were observed [δ(¹⁹F) = -144.9 and -181.3 ppm].

(v) [C₆F₅Xe][B(OTeF₅)₄]. The stability of [C₆F₅Xe][B(OTeF₅)₄] (entries 4a and 4b) was significantly greater than that of [C₆F₅XeNCCH₃][B(C₆F₅)₄] (entries 2a and 2b), especially in CH₂Cl₂. The conversion of [C₆F₅Xe][B(OTeF₅)₄] was 72% (81%) in CH₃CN (CH₂Cl₂) after 25 (24) days, with 94% (81%) C₆F₅H as the major product and 6% (5%) of an unknown C₆F₅- compound as the minor product. In addition, a significant amount of C₆F₅Cl (14%) was formed as a decomposition product in a CH₂Cl₂ (eqs 13–15). The decomposition pathway that led to C₆F₅H in CH₃CN is similar to that represented by eqs 3–6. The formation of C₆F₅Cl can be explained by analogy with the decomposition of [C₆F₅Xe][B(CF₃)₄] (eqs 13–15) in CH₂Cl₂. Low-intensity overlapping AB₄ patterns corresponding to different OTeF₅-containing species were also obtained in CH₃CN and CH₂Cl₂.

(c) Reactions of [C₆F₅Xe][BY₄] Salts with the π Nucleophile, C₆H₅F. The reactions of [C₆F₅Xe][AsF₆] with monosubstituted benzenes, C₆H₅X (X = CH₃, F, CN, CF₃, or NO₂; 1.0–1.7 equiv), in CH₃CN at 20 °C have been previously reported.²² In addition to isomeric mixtures of the polyfluorobiphenyls, C₆F₅-C₆H₄X, traces or minor amounts of C₆F₅H were obtained as products. Reaction rates

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Table 3. Reactivities of [C₆F₅Xe][BY₄] (Y = CF₃, C₆F₅, and CN), [C₆F₅Xe][BF₄], and [C₆F₅Xe][AsF₆] with C₆H₅F at 20 °C and Their C₆F₅-Containing Reaction Products

entry	[C ₆ F ₅ Xe] ⁺ salt	time, ^a days	solvent	equiv of C ₆ H ₅ F ^b	% conversion	C ₆ F ₅ -C ₆ H ₄ F ^c	C ₆ F ₅ H	C ₆ F ₅ X
1a	[B(CF ₃) ₄] ⁻	5	CH ₃ CN	20	100	31/29/38	≤2	
1b	[B(CF ₃) ₄] ⁻	0.010(3)	CH ₂ Cl ₂		100	33/30/37		
2	[B(C ₆ F ₅) ₄] ^{-d}	6	CH ₃ CN		89	32/30/37		
3	[B(CN) ₄] ⁻	6	CH ₃ CN		100	33/30/37		
4a	[BF ₄] ⁻	15	CH ₃ CN	20	100	33/30/37		
4b	[BF ₄] ⁻	18	CH ₃ CN		100	32/30/38		
5a	[AsF ₆] ⁻	4	CH ₃ CN	1.2	100	32/30/38	41	
5b	[B(CF ₃) ₄] ⁻	1.62(2)	CH ₂ Cl ₂		82	18/19/22		
6a	[B(CF ₃) ₄] ⁻	0.069(3)	C ₆ H ₅ F	64	100	33/30/37	31	X = C ₆ F ₅ (39)
6b	[B(C ₆ F ₅) ₄] ^{-d}	<0.010(3)	C ₆ H ₅ F	100	100	10/8/12		
7a	[BF ₄] ⁻ + H ₂ O ^e	0.250(6)	CH ₃ CN	20	100	32/30/38		
7b	[BF ₄] ⁻ + 20 H ₂ O ^e	<0.017(3)	CH ₃ CN		100	32/30/38		
8a	[AsF ₆] ⁻ + H ₂ O ^e	0.792(6)	CH ₃ CN		96	32/30/38		
8b	[AsF ₆] ⁻ + 20 H ₂ O ^e	0.017(3)	CH ₃ CN		88	32/30/38		
9a	C ₆ F ₅ XeF	0.021(3)	CH ₂ Cl ₂ , -40 °C	11	46	9/9/13	33	X = Cl (36)
9b	[B(C ₆ F ₅) ₄] ^{-d} + [N(CH ₃) ₄] ^f	<0.010(3)	CH ₂ Cl ₂ , -55 °C ^g	20	100	22/32/26	15	X = C ₆ F ₅ (5)

^a The precision is ±0.5 days for all entries except 1b and 5b–9b, where the error on the last digit is indicated in parentheses. ^b Prepared from freshly distilled C₆H₅F that had been dried over P₄O₁₀. ^c The ratio of 2/3/4 isomers is given in mole percent. ^d This salt contains the [C₆F₅XeNCCCH₃]⁺ cation. ^e The relative molar amounts of the [C₆F₅Xe]⁺ salt and H₂O are indicated. ^f Equimolar amounts of [C₆F₅Xe][B(C₆F₅)₄] and [N(CH₃)₄]F were used. ^g Both starting materials were combined at -55 °C and allowed to warm to 20 °C.

were shown to decrease with an increase in the electron-withdrawing character of X and varied from 1.25 to 42 h for complete conversion of [C₆F₅Xe][AsF₆].

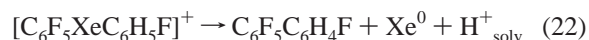
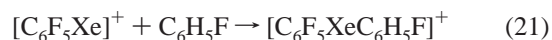
In the present study, the effects of the counteranion and the solvent (CH₃CN or CH₂Cl₂) on the reaction rates of [C₆F₅Xe]⁺ with C₆H₅F and on the product distributions as well as the influences of water and fluoride ion as nucleophiles were investigated (Table 3). The specific entries cited in the ensuing discussion appear in Table 3, unless otherwise noted.

(i) Influences of the Counteranion and Solvent on the Reactivity of [C₆F₅Xe]⁺ with C₆H₅F. The reaction of [C₆F₅Xe][BY₄] with rigorously dried C₆H₅F (20 equiv) in CH₃CN proceeded slowly. To exclude the possibility of large uncertainties, a series of four identical experiments were carried out for the slowest reaction of [C₆F₅Xe][BF₄] with C₆H₅F (20 equiv) in CH₃CN at room temperature. The result was comparable for all four experiments, ranging from 15 to 18 days for complete consumption of the [C₆F₅Xe]⁺ cation.

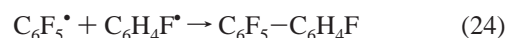
The conversion times are similar for [B(CF₃)₄]⁻ (ca. 5 days, entry 1a), [B(C₆F₅)₄]⁻ (89% consumed after 6 days, entry 2), and [B(CN)₄]⁻ (6 days, entry 3) but contrast with that of the less reactive [BF₄]⁻ salt (15–18 days, entries 4a,b) and the somewhat more reactive [AsF₆]⁻ salt (4 days, entry 5a) under the same conditions. In all cases, isomeric mixtures of polyfluorobiphenyls, C₆F₅-C₆H₄F, were obtained in nearly equimolar amounts of 2-, 3-, and 4-isomers, whereas C₆F₅H was only detected (≤2%) in the case of [C₆F₅XeNCCCH₃]-[B(CF₃)₄]. It is noteworthy that the single 4-position of C₆H₅F is arylated twice as often as the two 2- and 3-positions to give C₆F₅-C₆H₄F, which is likely a consequence of the higher negative charge on carbon in the 4-position.

The reaction rates with C₆H₅F are 4–8 times faster than the decomposition rates of [C₆F₅Xe][BY₄] salts in CH₃CN in the absence of C₆H₅F, where C₆F₅H was the only (Y = CF₃ or CN) or main (Y = C₆F₅) reaction product (Table 2). The experimental results are therefore consistent with

coordination of the π nucleophile, C₆H₅F, to the electrophilic Xe^{II} center (eq 21), competing with solvent (cf. eq 3) and/or counteranion coordination (cf. eqs 8 and 17), where all three types of coordination serve to destabilize the C–Xe bond. Following homolytic cleavage of the C–Xe bond, the C₆F₅• radical can combine, in a cage, with a C₆H₄F• radical, which results from a one-electron transfer, and is accompanied by the elimination of Xe⁰ and H⁺ from the intermediate radical cation, [XeC₆H₅F]^{•+} (eq 22). The ability of C₆H₅F to coordinate to [C₆F₅Xe]⁺ is enhanced when the coordinating abilities of the [BY₄]⁻ anion and solvent are weaker. From the reactivities of their [C₆F₅Xe]⁺ cations in CH₃CN, it may be concluded that the coordination abilities of the [BY₄]⁻ anions increase in the order [B(CF₃)₄]⁻ < [B(CN)₄]⁻ < [B(C₆F₅)₄]⁻ ≪ [BF₄]⁻.



The reactivity of the [C₆F₅Xe]⁺ cation toward C₆H₅F (20 equiv) was significantly enhanced when the strongly coordinating CH₃CN solvent was replaced by the weakly coordinating solvent, CH₂Cl₂. In CH₂Cl₂, [C₆F₅Xe][B(CF₃)₄] was consumed in only 15 min (entry 1b), compared to 5 days in CH₃CN (entry 1a), forming only C₆F₅-C₆H₄F. The reaction proceeded more slowly in CH₂Cl₂ when only 1.2 equiv of C₆H₅F was used (82% conversion of [C₆F₅Xe]-[B(CF₃)₄] after 1.62 days; entry 5b), showing that the reaction is not initiated by CH₂Cl₂ coordination to the cation because C₆F₅H (41%) is formed and C₆F₅Cl is absent (eqs 23 and 24).



In contrast, only 50% of [C₆F₅Xe][B(CF₃)₄] reacted after 22

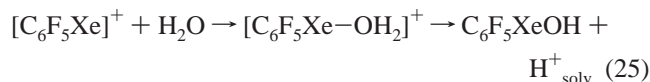
days in CH_2Cl_2 in the absence of $\text{C}_6\text{H}_5\text{F}$, yielding $\text{C}_6\text{F}_5\text{Cl}$ as the major product (80%) and $\text{C}_6\text{F}_5\text{H}$ (20%) (Table 2, entry 1b). The rapid reaction of $[\text{C}_6\text{F}_5\text{Xe}][\text{A}]$ with $\text{C}_6\text{H}_5\text{F}$ in CH_2Cl_2 and the dependence of the reaction rate on the $\text{C}_6\text{H}_5\text{F}$ concentration clearly demonstrate that the interaction of $[\text{C}_6\text{F}_5\text{Xe}]^+$ with the π nucleophile is favored in the presence of a weakly coordinating anion and solvent. The $[\text{C}_6\text{F}_5\text{Xe}][\text{B}(\text{CF}_3)_4]$ and $[\text{C}_6\text{F}_5\text{XeNCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ salts have solubilities comparable to those of CH_3CN in $\text{C}_6\text{H}_5\text{F}$ and react rapidly with neat $\text{C}_6\text{H}_5\text{F}$, whereas $[\text{C}_6\text{F}_5\text{Xe}][\text{B}(\text{CN})_4]$, $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$, and $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$ are insoluble in $\text{C}_6\text{H}_5\text{F}$. The $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation of $[\text{C}_6\text{F}_5\text{Xe}][\text{B}(\text{CF}_3)_4]$ is completely reacted within 100 min in $\text{C}_6\text{H}_5\text{F}$ (64 equiv), exclusively yielding an isomeric mixture of hexafluorobiphenyls (entry 6a), which supports the proposed reaction path (eqs 21 and 22). The reaction between $[\text{C}_6\text{F}_5\text{XeNCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ and $\text{C}_6\text{H}_5\text{F}$ (100 equiv) proceeded more than 4 times faster, but the product distribution differed. In addition to $\text{C}_6\text{F}_5\text{-C}_6\text{H}_4\text{F}$ (30%), $\text{C}_6\text{F}_5\text{H}$ (31%), and $(\text{C}_6\text{F}_5)_2$ (39%) were formed (entry 6b). The latter product again supports attack by the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation at the nucleophilic *ipso*-carbon of the anion (eqs 17 and 18) as a significant competing reaction pathway, with the formation of $\text{C}_6\text{F}_5\text{H}$ arising from C_6F_5^* radical attack on $\text{C}_6\text{H}_5\text{F}$ (eq 23) or coordinated CH_3CN (eqs 3–6).

(ii) Effects of H_2O and F^- on the Reactivity of $[\text{C}_6\text{F}_5\text{Xe}]^+$ with $\text{C}_6\text{H}_5\text{F}$. When the reactions of $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ salts in CH_3CN were initially carried out with freshly distilled, but not rigorously dried $\text{C}_6\text{H}_5\text{F}$ (1.2 equiv), the reaction rates accelerated for the $[\text{BF}_4]^-$, $[\text{B}(\text{CF}_3)_4]^-$, and $[\text{AsF}_6]^-$ salts but were less affected for the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salt. In all cases, minor amounts of $\text{C}_6\text{F}_5\text{H}$ were detected in addition to $\text{C}_6\text{F}_5\text{-C}_6\text{H}_4\text{F}$.

In order to evaluate the influence of water on this reaction in a controlled manner, the reactions of $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ and $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$ with rigorously dried $\text{C}_6\text{H}_5\text{F}$ (20 equiv) and H_2O (1 or 20 equiv) in CH_3CN were investigated at 20 °C (entries 7a–8b). A very pronounced effect of H_2O on the reaction rate was found, with the $[\text{BF}_4]^-$ salt reacting slightly faster than the $[\text{AsF}_6]^-$ salt. In the presence of 1 equiv of H_2O , the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation of the $[\text{AsF}_6]^-$ salt was consumed after only 19 h, and in the presence of 20 equiv of H_2O , it was consumed after only 25 min, or 60 and 950 times more rapidly, respectively, than in the absence of H_2O . The distributions of $\text{C}_6\text{F}_5\text{-C}_6\text{H}_4\text{F}$ isomers, the only C_6F_5 -containing products, were not noticeably influenced by the presence of H_2O . The absence of $\text{C}_6\text{F}_5\text{H}$ in experiments where H_2O was added confirms that $\text{C}_6\text{F}_5\text{H}$ formed during the decomposition of $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts in anhydrous CH_3CN solvent (Table 2) does not derive from fortuitous H_2O that had diffused through the walls of the FEP reaction vessels but by hydrogen abstraction from the only hydrogen source available, CH_3CN .

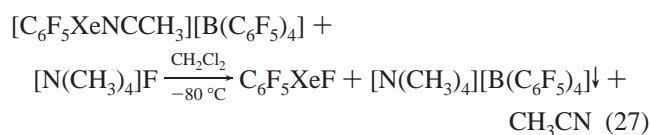
Coordination of H_2O to $[\text{C}_6\text{F}_5\text{Xe}]^+$ and subsequent solvent-assisted deprotonation to give the presently unknown $\text{C}_6\text{F}_5\text{XeOH}$ molecule (eq 25) as an unstable reaction intermediate may account for the products and enhanced

reactivities (cf. the reaction of $\text{C}_6\text{F}_5\text{XeF}$ with $\text{C}_6\text{H}_5\text{F}$ in $\text{CH}_2\text{-Cl}_2$ discussed below). The C_6F_5^* radical, resulting from the



decomposition of $\text{C}_6\text{F}_5\text{XeOH}$ (eq 26), may add preferentially to $\text{C}_6\text{H}_5\text{F}$ without attacking CH_3CN . The $\text{C}_6\text{F}_5\text{-C}_6\text{H}_4\text{F}$ products, in the absence of $\text{C}_6\text{F}_5\text{H}$, agree with this interpretation.

In order to compare the relative influences of water and fluoride ion, the reactivities of $[\text{C}_6\text{F}_5\text{XeNCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_2Cl_2 in the presence of both $\text{C}_6\text{H}_5\text{F}$ and a “naked” fluoride ion, $[\text{N}(\text{CH}_3)_4]\text{F}$, which yields $\text{C}_6\text{F}_5\text{XeF}$,^{8,23} were also studied. As a result of the strong interaction between $[\text{C}_6\text{F}_5\text{Xe}]^+$ and F^- , which leads to the 3c–4e-bonded $\text{C}_6\text{F}_5\text{XeF}$ molecule, $\text{C}_6\text{H}_5\text{F}$ coordination to xenon is expected to be inhibited, so that the rate of $\text{C}_6\text{F}_5\text{-C}_6\text{H}_4\text{F}$ formation decreases. In order to test this hypothesis, $\text{C}_6\text{F}_5\text{XeF}$ was synthesized according to eq 27 using an alternative method described in the Experimental Section that is based on that originally developed by Frohn and Theissen.⁸



At –40 °C, 46% of $\text{C}_6\text{F}_5\text{XeF}$ reacted in CH_2Cl_2 in the presence of $\text{C}_6\text{H}_5\text{F}$ (11 equiv) within 30 min, forming $\text{C}_6\text{F}_5\text{Cl}$ (36%), $\text{C}_6\text{F}_5\text{H}$ (33%), and $\text{C}_6\text{F}_5\text{-C}_6\text{H}_4\text{F}$ (31%) (entry 9a). The products, $\text{C}_6\text{F}_5\text{Cl}$ and $\text{C}_6\text{F}_5\text{H}$, likely result from C_6F_5^* radical attack on CH_2Cl_2 (eqs 13–15). A reaction mixture consisting of $[\text{C}_6\text{F}_5\text{XeNCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, $\text{C}_6\text{H}_5\text{F}$ (20 equiv), and $[\text{N}(\text{CH}_3)_4]\text{F}$ (1 equiv) was combined in CH_2Cl_2 at –55 °C, and the mixture was warmed to 20 °C. The reaction was complete within 15 min, yielding $\text{C}_6\text{F}_5\text{-C}_6\text{H}_4\text{F}$ (80%), $(\text{C}_6\text{F}_5)_2$ (5%), and $\text{C}_6\text{F}_5\text{H}$ (15%) (see Table 3, entry 9b).

Characterization of $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ ($\text{Y} = \text{CF}_3$, C_6F_5 , CN , or OTeF_5) and $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ by Multi-NMR Spectroscopy. Since the discovery of the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation, NMR data for $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts having different counteranions such as $[\text{AsF}_6]^-$,^{17,24,25} $[\text{PF}_6]^-$,²⁴ $[\text{SiF}_5]^-$,²⁶ $[\text{BF}_4]^-$,¹⁸ $[(\text{C}_6\text{F}_5)_n\text{BF}_{4-n}]^-$,^{1,2,25,27,28} $[\text{E}(\text{SO}_2\text{CF}_3)_{n-1}]^-$ ($\text{E} = \text{O}, \text{N}$, and C),²⁴ and $[\text{HF}_2]^-$ ²⁹ have been reported.^{4,5} However, only two of the six possible ^{19}F – ^{19}F couplings in the aryl group have

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been extracted from the ¹⁹F spectra in the course of these studies, namely, ³J(¹⁹F_o–¹⁹F_p) (*J*₂₄) and ⁴J(¹⁹F_m–¹⁹F_p) (*J*₃₄), but all three possible ¹²⁹Xe–¹⁹F couplings, ³J(¹⁹F_o–¹²⁹Xe), ⁴J(¹⁹F_m–¹²⁹Xe), and ⁵J(¹⁹F_p–¹²⁹Xe), have been reported.^{1,2} Moreover, the relative signs of the reported couplings have not been assigned. The availability of new [C₆F₅Xe][BY₄] (Y = CF₃, C₆F₅, CN, or OTeF₅) salts that are soluble in neutral polar solvents provided an opportunity to characterize these salts by ¹⁹F, ¹¹B, ¹³C, and ¹²⁹Xe NMR spectroscopy (Table 4) with the view to provide, for the first time, a complete determination of the ¹⁹F and ¹²⁹Xe NMR parameters of the [C₆F₅Xe]⁺ cation and to correlate the nature of the [C₆F₅Xe]⁺ cation–solvent interaction with its NMR parameters.

(a) Simulation of [C₆F₅Xe]⁺ ¹⁹F and ¹²⁹Xe NMR Spectra. The ¹⁹F NMR spectra of [C₆F₅Xe][BY₄] are well-resolved at 7.0463 T, exhibiting complex multiplet structures for the *o*- and *m*-C₆F₅ fluorine resonances and a triplet (*J*₃₄) of triplets (*J*₂₄) for the *p*-C₆F₅ fluorine resonance (Figure 1). All C₆F₅ resonances are accompanied by ¹²⁹Xe satellites (*I* = 1/2, 26.44%) arising from ³J(¹⁹F_o–¹²⁹Xe), ⁴J(¹⁹F_m–¹²⁹Xe), and ⁵J(¹⁹F_p–¹²⁹Xe) spin–spin couplings. The improved resolution afforded in the present circumstances provided the first fully resolved ¹²⁹Xe NMR spectra of [C₆F₅Xe]⁺ (Figure 2), showing all of the expected ¹⁹F–¹²⁹Xe spin–spin couplings as a triplet (o) of triplets (m) of doublets (p). The ³J(¹⁹F_o–¹²⁹Xe) and ⁵J(¹⁹F_p–¹²⁹Xe) spin–spin coupling constants were found to be identical, within experimental error, to those obtained in previous studies, whereas the ⁴J(¹⁹F_m–¹²⁹Xe) coupling was found to be significantly smaller (8.8 Hz) than that published earlier from ¹⁹F NMR spectra (18.7–19.5 Hz).^{1–3}

The present ¹⁹F and ¹²⁹Xe NMR spectral simulations for [C₆F₅Xe][B(CN)₄] have yielded the first complete set of ^J(¹⁹F–¹⁹F) couplings and assignments of their relative signs for [C₆F₅Xe]⁺. The ¹⁹F and ¹²⁹Xe NMR spectra of the [B(CN)₄][–] salt in CH₃CN solution were better resolved and therefore were used for spectral simulations. The spectrum of isoelectronic C₆F₅I was also compared and, in this case, chemical shifts and *J* couplings were remeasured in CD₃CN at 24 °C and used for simulation of the ¹⁹F NMR spectrum. The ¹⁹F ([C₆F₅Xe]⁺ and C₆F₅I) and ¹²⁹Xe ([C₆F₅Xe]⁺) NMR spectra were assigned and simulated using the multinuclear NMR simulation program *ISOTOPOMER*.³⁰ Spectra were simulated using the natural abundances of the spin-1/2 nuclei ¹⁹F (100%) and ¹²⁹Xe (26.44%). In the case of C₆F₅I, complete quadrupolar collapse of the ¹²⁷I–¹⁹F couplings was assumed. Full spectral simulations were achieved under *C*_{2v} symmetry for both [C₆F₅Xe]⁺ and C₆F₅I. In the case of [C₆F₅Xe]⁺, only the values of *J*₂₄ and *J*₃₄ were readily available from the ¹⁹F_p multiplet, while ³J(¹²⁹Xe–¹⁹F_o) (67.7 Hz), ⁴J(¹²⁹Xe–¹⁹F_m) (8.8 Hz), and ⁵J(¹²⁹Xe–¹⁹F_p) (3.7 Hz) were obtained from the ¹²⁹Xe NMR spectrum. Preliminary values for *J*₂₄, *J*₂₆, *J*₃₅, and *J*₂₅ were calculated from empirical relationships between δ(¹⁹F_p) = –140.9 ppm and the

fluorine–fluorine coupling constants of the C₆F₅ group (eqs 28–31)^{31,32} and were then manually iterated to give the best spectral fits.

$$J_{24} = 0.471\delta(^{19}\text{F}_p) + 74.6 = 8.24 \quad (28)$$

$$J_{26} = -0.396\delta(^{19}\text{F}_p) - 65.7 = -9.9 \quad (29)$$

$$J_{35} = 0.164\delta(^{19}\text{F}_p) + 23.94 = 0.83 \quad (30)$$

$$J_{25} = 0.091\delta(^{19}\text{F}_p) + 19.30 = 6.5 \quad (31)$$

The signs of the coupling constants used for the simulations are relative and have not been experimentally determined; however, extensive studies made on C₆F₅ derivatives^{31,32} indicate that these signs are also the correct absolute signs. The simulated spectra are in excellent agreement with the experimental spectra, accounting for all of the observed spectral features including asymmetries in the F_o and F_m multiplets arising from second-order effects. All trends (i.e., relative magnitudes and relative signs of the *J* values) are in agreement with those observed for C₆F₅I as well as for most other C₆F₅ derivatives:^{31,32} (1) *J*₂₃ (–20.2 Hz), *J*₂₆ (–12.8 Hz), and *J*₃₄ (–20.0 Hz) are of opposite sign to *J*₂₄ (5.6 Hz) and *J*₂₅ (1.2 Hz), which is also observed for C₆F₅I (–22.7, –4.9, –19.5, 2.1, and 7.2 Hz, respectively), (2) the *J*₃₅ (0.4 Hz) coupling is also very small but slightly positive (–1.2 Hz in C₆F₅I), and (3) the *J*₃₄ and *J*₂₃ couplings are negative and similar in magnitude for both [C₆F₅Xe]⁺ and C₆F₅I.

When [C₆F₅Xe]⁺ and isoelectronic C₆F₅I are compared, it is noteworthy that, other than *J*₂₃, the greatest differences are observed for *J* couplings involving F_o, suggesting that they are related to the proximity of the positively charged xenon atom. The *J*₂₆ coupling is significantly more negative than that in C₆F₅I, but comparable negative values have been observed for C₆F₅SO₂Cl^{33,34} and C₆F₅NO₂.^{31,32,35} The only value that is markedly different is that of *J*₂₅, which appears to be among the smallest measured *J*₂₅ couplings.

(b) Chemical Shift and Coupling Constant Trends. To systematize the interpretation of chemical shift trends, a model has been used in which the weakly coordinating anion and the solvent compete for coordination to the positively charged electrophilic Xe^{II} center of [C₆F₅Xe]⁺. Two sets of conditions may be distinguished: (1) the anions are weakly coordinating when compared with CH₃CN and (2) both the anion and the solvent are weakly coordinating.

In the first case, very similar ¹⁹F NMR chemical shifts are obtained for [C₆F₅Xe][BY₄], [C₆F₅Xe][BF₄], and [C₆F₅Xe][AsF₆] when dissolved in CH₃CN (Table 4). This is consistent with [C₆F₅XeNCCH₃]⁺ formation and counter-

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Table 4. ^{19}F , ^{13}C , ^{11}B , and ^{129}Xe NMR Parameters for $[\text{C}_6\text{F}_5\text{Xe}]^+ \text{a}$ in $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]^-$ ($\text{Y} = \text{CF}_3$, C_6F_5 , CN , or OTeF_5), $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]^-$, $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]^-$, $[\text{C}_6\text{F}_5\text{Xe}][\text{SiF}_5]^-$, and $[\text{C}_6\text{F}_5\text{Xe}][\text{HF}_2]^-$

$[\text{C}_6\text{F}_5\text{Xe}]^+$ salt	^{19}F NMR spectra										solvent	T ($^\circ\text{C}$)
	δ (ppm)	$^1J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)	$^2J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)	$^3J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)	$^4J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)	$^5J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)	$^6J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)	$^7J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)	$^8J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)	$^9J(^{19}\text{F}-^{129}\text{Xe})$ (Hz)		
$[\text{BF}_4]^-$	-124.8	66.6	-141.9	20.0	5.6	4.2	-154.7	8.6	-148.4			
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	-124.9	67.6	-141.1	19.9	5.5	3.8	-154.0	9.1	{ -132.1 (o) -162.4 (p) -166.8 (m) }			
$[\text{B}(\text{CN})_4]^-$	-124.5	67.7	-140.9	20.0	5.6	3.7	-153.8	8.8	-61.3		CH_3CN	24
$[\text{B}(\text{CF}_3)_4]^-$	-124.8	67.5	-141.0	19.9	5.6	3.6	-154.0	8.8	{ -61.3 -38.8 (F_A) -45.4 (F_B) -64.1 ($[\text{AsF}_6]^-$) }			
$[\text{B}(\text{OTeF}_5)_4]^-$	-125.5	68	-141.8	20	6	4	-154.7	9	-63.9		CH_2Cl_2	24
$[\text{AsF}_6]^-$	-124.8	67.8	-141.3	20.0	5.6	n.r.	-154.2	8.6	{ -63.9 -148.7 }			
$[\text{SiF}_5]^-$	-126.8	n.r.	-143.0	n.r.	n.r.	n.r.	-154.9	n.r.	{ -132.9 (o) -162.2 (p) -166.7 (m) }		CH_3CN	-40
$[\text{HF}_2]^-$	-127.1	73	-144.6	n.r.	n.r.	n.r.	-156.1	n.r.	-61.9			
$[\text{B}(\text{CF}_3)_4]^-$	-123.4	66.5	-135.3	20.9	6.6	2.2	-149.6	8.8	-63.9		CH_2Cl_2	-80
$[\text{BF}_4]^-$	-125.5	68.1	-142.3	20.5	5.3	n.r.	-155.1	n.r.	{ -61.9 -61.8 }			
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	-125.5	68.9	-141.7	20.5	5.5	n.r.	-154.5	n.r.	-63.9		CH_3CN	-40
$[\text{B}(\text{CN})_4]^-$	-125.2	69.3	-141.4	20.5	5.4	n.r.	-154.2	n.r.	-60.1			
$[\text{B}(\text{CF}_3)_4]^-$	-125.5	68.9	-141.6	20.4	5.4	n.r.	-154.5	n.r.	-60.1		CH_2Cl_2	-80
$[\text{B}(\text{CF}_3)_4]^-$	-124.6	68.3	-137.1	21.9	5.5	n.r.	-150.8	n.r.	-60.1		PF_6	24
$[\text{B}(\text{CF}_3)_4]^-$	-124.3	62.9	-138.9	18.9	6.2	n.r.	-152.3	n.r.	-148.6		aHF	-40
$[\text{BF}_4]^-$	-123.6	58.1	-138.2	18.8	6.4	n.r.	-151.8	n.r.	{ -148.6 -148.6 }			

$[\text{C}_6\text{F}_5\text{Xe}]^+$ cation	^{13}C NMR spectra										solvent	T ($^\circ\text{C}$)		
	δ (ppm)	$^1J(^{13}\text{C}-^{19}\text{F})$ (Hz)	$^2J(^{13}\text{C}-^{19}\text{F})$ (Hz)	$^3J(^{13}\text{C}-^{19}\text{F})$ (Hz)	$^4J(^{13}\text{C}-^{19}\text{F})$ (Hz)	$^5J(^{13}\text{C}-^{19}\text{F})$ (Hz)	$^6J(^{13}\text{C}-^{19}\text{F})$ (Hz)	$^7J(^{13}\text{C}-^{19}\text{F})$ (Hz)	$^8J(^{13}\text{C}-^{19}\text{F})$ (Hz)	$^9J(^{13}\text{C}-^{19}\text{F})$ (Hz)				
$[\text{BF}_4]^-$	139.7	260.1	15.3	146.9	260.2	13.4	4.5	145.4	257.8	14.9	84.3	113.0		
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	140.1	259.1	14.6	147.2	262.4	13.3	4.5	145.5	258.2	14.9	84.7	114.4		
$[\text{B}(\text{CN})_4]^-$	140.0	259.1	15.0	147.1	262.4	13.3	4.5	145.4	257.0	14.9	84.6	114.2		
$[\text{B}(\text{CF}_3)_4]^-$	140.0	258.2	15.2	147.1	262.4	13.3	4.5	145.4	259.1	15.2	84.4	114.4		
$[\text{AsF}_6]^-$	140.0	257.0	15.3	147.0	261.8	13.3	4.5	145.4	259.2	13.1	83.9	n.r.		
$[\text{BF}_4]^-$	139.0	-	-	146.0	-	-	-	144.6	-	-	83.8	117.2		
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	139.2	-	-	146.2	-	-	-	144.6	-	-	84.0	118.7		
$[\text{B}(\text{CN})_4]^-$	139.2	-	-	146.3	-	-	-	144.6	-	-	84.0	118.1		
$[\text{B}(\text{CF}_3)_4]^-$	139.1	-	-	146.2	-	-	-	144.5	-	-	83.7	119.1		
$[\text{AsF}_6]^-$	139.1	-	-	146.2	-	-	-	144.6	-	-	83.7	118.6		

[C ₆ F ₅ Xe] ⁺ salt	¹¹ B NMR spectra			¹²⁹ Xe NMR spectra					solvent	T (°C)
	δ(¹¹ B) (ppm)	J(¹¹ B– ¹⁹ F) (Hz)	¹ J(¹¹ B– ¹³ C) (Hz)	δ(¹²⁹ Xe) (ppm)	³ J(¹⁹ F– ¹²⁹ Xe) (Hz)	⁴ J(¹⁹ F– ¹²⁹ Xe) (Hz)	⁵ J(¹⁹ F– ¹²⁹ Xe) (Hz)			
[BF ₄] [−]	−1.5	n.r.	n.r.	−3802.8	66.6	8.6	4.2	CH ₃ CN	24	
[B(C ₆ F ₅) ₄] [−]	−16.8	n.r.	n.r.	−3798.1	67.6	9.1	3.8			
[B(CN) ₄] [−]	−38.8	—	71.7	−3792.6	67.7	8.8	3.7	PFB	24	
[B(CF ₃) ₄] [−]	−19.1	25.9	73.4	−3802.0	67.5	8.8	3.6			
[AsF ₆] [−]	—	—	—	−3802.3	67.8	8.6	n.r.	aHF	−40	
[B(CF ₃) ₄] [−]	−19.1	25.9	73.2	−3821.1	62.9	8.7	n.r.			
[BF ₄] [−]	−1.3	11.5	—	−3831.5	58.1	n.r.	n.r.	CH ₃ CN	−40	
[BF ₄] [−]	—	—	—	−3783.0	68.1	n.r.	n.r.			
[B(C ₆ F ₅) ₄] [−]	—	—	—	−3772.2	68.9	n.r.	n.r.	CH ₃ CN	−40	
[B(CN) ₄] [−]	—	—	—	−3776.7	69.3	n.r.	n.r.			
[B(CF ₃) ₄] [−]	—	—	—	−3779.6	68.9	n.r.	n.r.	CH ₃ CN	−40	
[AsF ₆] [−]	—	—	—	−3781.4	68.6	n.r.	n.r.			

^a The abbreviations n.r. and n.o. denote not resolved and not observed, respectively, and the symbol “—” denotes not measured or not applicable for the given species. ^b From ref. 26. ^c From ref. 29. ^d ¹J(¹³C(2,6)–¹⁹F) = 241.1 Hz; ²J(¹³C(2,6)–¹⁹F) was not resolved. ^e ¹J(¹³C(3,5)–¹⁹F) = 243.8 Hz; ²J(¹³C(3,5)–¹⁹F) = 13.9 Hz. ^f ¹J(¹³C(4)–¹⁹F) = 244.7 Hz; ²J(¹³C(4)–¹⁹F) = 14.0 Hz. ^g ¹J(¹³C(1)–¹¹B) = 73.4 Hz; ³J(¹³C(1)–¹⁹F) = 3.8 Hz; ¹J(¹³C–¹⁹F) = 304.3 Hz.

anions that are less basic than CH₃CN. Strong coordination of the anion to the positively charged xenon center yields asymmetric 3c–4e C–Xe–L bonds and results in more shielded fluorine environments and larger coupling constants.

In the second case, only [C₆F₅Xe][B(CF₃)₄] has sufficient stability and solubility in the weakly coordinating solvents CH₂Cl₂ and PFB (stable at 20 °C for more than 3 and 5 days, respectively, contrasting with CH₂Cl₂ solutions of [C₆F₅XeNCCH₃][B(C₆F₅)₄] and [C₆F₅Xe][B(OTeF₅)₄], which must be maintained below −40 °C to avoid rapid decomposition) to allow NMR studies in these media. A comparison of the ¹⁹F NMR chemical shifts of [C₆F₅Xe]–[B(CF₃)₄] in CH₂Cl₂, PFB, and CH₃CN at 24 °C (Table 4) shows that the fluorine resonances of the C₆F₅ group are shifted to higher frequencies (deshielded) in CH₂Cl₂ (~5 ppm for F_m and F_p and ~1.5 ppm for F_o) and PFB (~2 ppm for F_m and F_p and ~0.5 ppm for F_o) relative to those in CH₃CN, consistent with a more weakly coordinated [C₆F₅Xe]⁺ cation and significant polarization of the C₆F₅ group by Xe^{II}.

A more weakly coordinated [C₆F₅Xe]⁺ cation was also achieved by dissolution of [C₆F₅Xe][BF₄] in aHF. The ¹⁹F NMR chemical shifts at −40 °C are similar to those obtained for [C₆F₅Xe][B(CF₃)₄] in PFB at 24 °C (Table 4). Hydrogen fluoride presumably solvates the anion, resulting in a much larger [BF₄·(HF)_n][−] anion, which disperses the negative charge over more than four fluorine atoms, rendering it less basic. The [BF₄·(HF)_n][−] anion exhibits a broadened 1:1:1:1 quartet in the ¹⁹F NMR spectrum at −148.6 ppm and a quintet splitting in the ¹¹B NMR spectrum at −1.3 ppm that arises from ¹J(¹⁹F–¹¹B) = 11.5 Hz. The quartet in the ¹⁹F NMR spectrum arises because the electric field gradient at the quadrupolar ¹¹B nucleus is nearly zero, and quadrupolar relaxation is slow as a result of the highly symmetric ligand environment and rapid dynamics of the solvation shell. The overlapping equal-intensity septet arising from ¹J(¹⁹F–¹⁰B) was insufficiently resolved to provide a directly measured value for this coupling constant (calcd, 3.9 Hz).

The ¹²⁹Xe NMR chemical shifts of [C₆F₅Xe][BY₄] and [C₆F₅Xe][BF₄] in CH₃CN at 24 °C differ only slightly, ranging from −3792.6 ([B(CN)₄][−]) to −3802.8 ppm ([BF₄][−]), having spin–spin coupling constants of ³J(¹⁹F_o–¹²⁹Xe) = 66.6 ([BF₄][−]) to 67.6 Hz ([B(C₆F₅)₄][−]), ⁴J(¹⁹F_m–¹²⁹Xe) = 8.6 ([BF₄][−]) to 9.1 Hz ([B(C₆F₅)₄][−]), and ⁵J(¹⁹F_p–¹²⁹Xe) = 3.6 ([B(CF₃)₄][−]) to 4.2 Hz ([BF₄][−]) (Table 4). The temperature dependencies of the ¹²⁹Xe NMR chemical shifts of [C₆F₅Xe]⁺ salts are in good agreement with the previously published results for [C₆F₅Xe][AsF₆] in CD₃CN/C₂H₅CN (1:3, v/v) of −0.35 ppm K^{−1}.³⁶ The ¹²⁹Xe NMR chemical shifts of the [C₆F₅Xe][BY₄] salts in CH₃CN at −40 °C (−3772.2 to −3783.0 ppm) are only slightly shifted to higher frequency when compared with that of C₆F₅XeF (−3793.4 ppm) in CH₂Cl₂ at −40 °C. The chemical shifts

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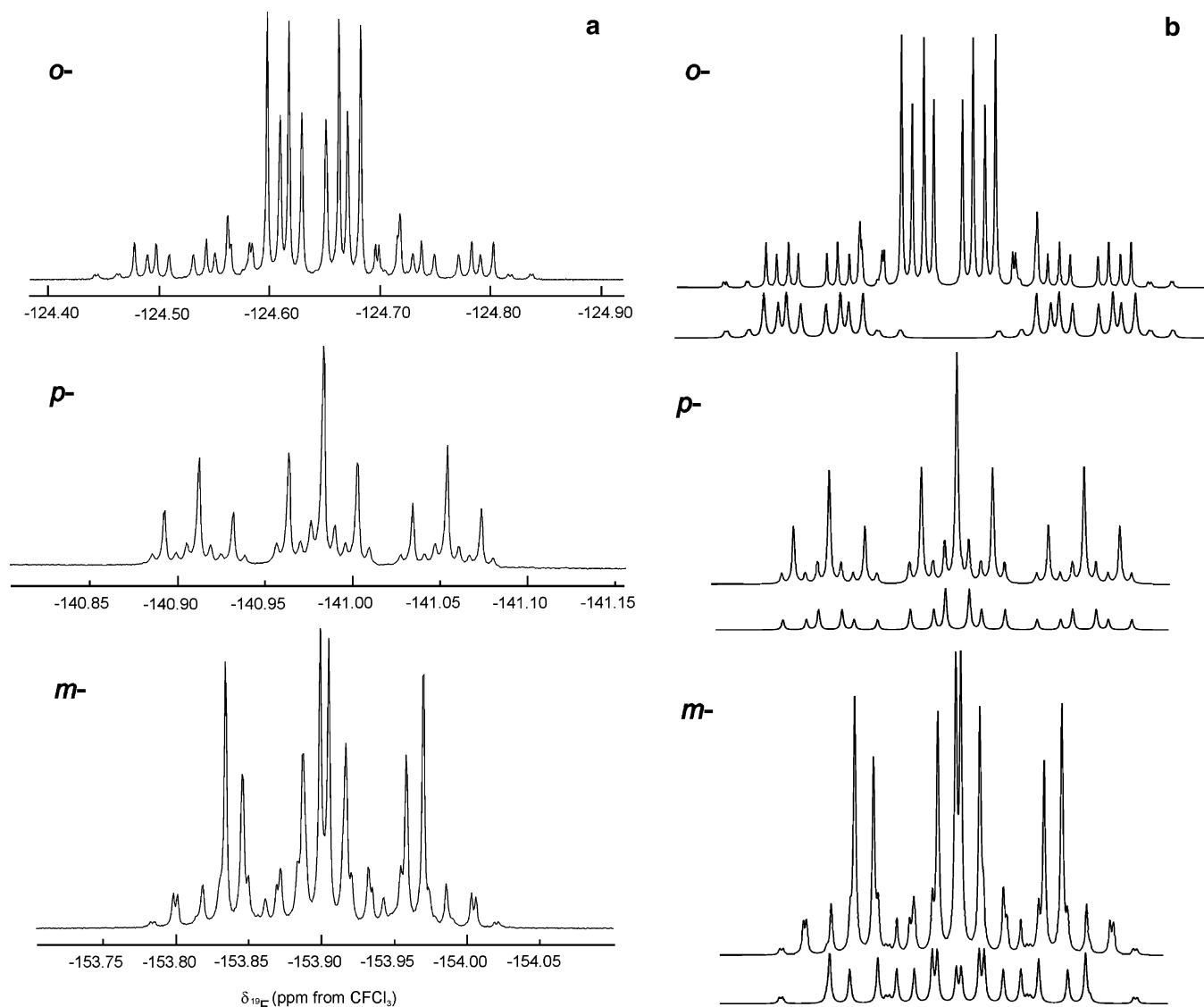


Figure 1. ^{19}F NMR spectra (282.40 MHz) of the *o*-, *p*- and *m*- C_6F_5 fluorine resonances of the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation in $[\text{C}_6\text{F}_5\text{Xe}][\text{B}(\text{CN})_4]$ recorded in CH_3CN at 24 °C. Spectra were resolution-enhanced by Gaussian multiplication (a traces). The simulated spectra (b traces) are provided for comparison with the lower traces depicting the subspectra, drawn to scale, that arise from ^{19}F coupling to natural abundance (26.44%) ^{129}Xe .

of the counteranions were not influenced by $[\text{C}_6\text{F}_5\text{XeNCCH}_3]^+$ formation and are very similar to those reported previously for $[\text{B}(\text{CF}_3)_4]^-$,³⁷ $[\text{B}(\text{CN})_4]^-$,³⁸ and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ³⁹ and are therefore not discussed.

Generally, the nature of the counteranion influences the $^3J(^{19}\text{F}_o-^{129}\text{Xe})$ coupling constant, which is 68 ± 1 Hz for $[\text{C}_6\text{F}_5\text{XeNCCH}_3]^+$ in the presence of weakly coordinating $[\text{BY}_4]^-$ anions and 70 and 73 Hz in the case of more nucleophilic anions such as $[\text{SiF}_5]^-$ ²⁶ and $[\text{HF}_2]^-$,²⁹ respectively. The more strongly coordinating the anion is, the greater the magnitude of the $^3J(^{19}\text{F}_o-^{129}\text{Xe})$ coupling, trending toward 80 Hz in $\text{C}_6\text{F}_5\text{XeF}$ (CH_2Cl_2 , -80 °C; see the Experimental Section) and 94.2 Hz in $\text{C}_6\text{F}_5\text{XeCl}$ (CH_2Cl_2 , -60 °C).⁷

Conclusions

The $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts of the weakly coordinating $[\text{BY}_4]^-$ ($\text{Y} = \text{CF}_3$, C_6F_5 , CN , or OTeF_5) anions, which were obtained

by the metatheses of $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$ and $\text{M}^+[\text{BY}_4]$ salts, showed no direct correlation between their decomposition temperatures (neat or in solution) and the nucleophilicity of the anion. The only salt in which CH_3CN is coordinated to the cation, $[\text{C}_6\text{F}_5\text{XeNCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, was the least stable among the $[\text{C}_6\text{F}_5\text{Xe}]^+$ salts considered in both the solid state and in weakly coordinating CH_2Cl_2 and strongly coordinating CH_3CN solvents.

In all cases except $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, the only decomposition product was $\text{C}_6\text{F}_5\text{H}$ in CH_3CN , whereas the decomposition of $[\text{C}_6\text{F}_5\text{XeNCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_2Cl_2 yielded significant amounts of $(\text{C}_6\text{F}_5)_2$, which resulted from cation attack at the nucleophilic *ipso*-carbon of the anion. The decompositions of $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ ($\text{Y} = \text{CF}_3$ or OTeF_5) in CH_2Cl_2 result in hydrogen and chlorine abstraction by the $\text{C}_6\text{F}_5^\bullet$ radical, whereas $[\text{C}_6\text{F}_5\text{XeNCCH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ also forms significant quantities of $(\text{C}_6\text{F}_5)_2$.

In general, $[\text{C}_6\text{F}_5\text{Xe}][\text{BY}_4]$ salts exhibited a range of stabilities, which were not leveled by coordination of the

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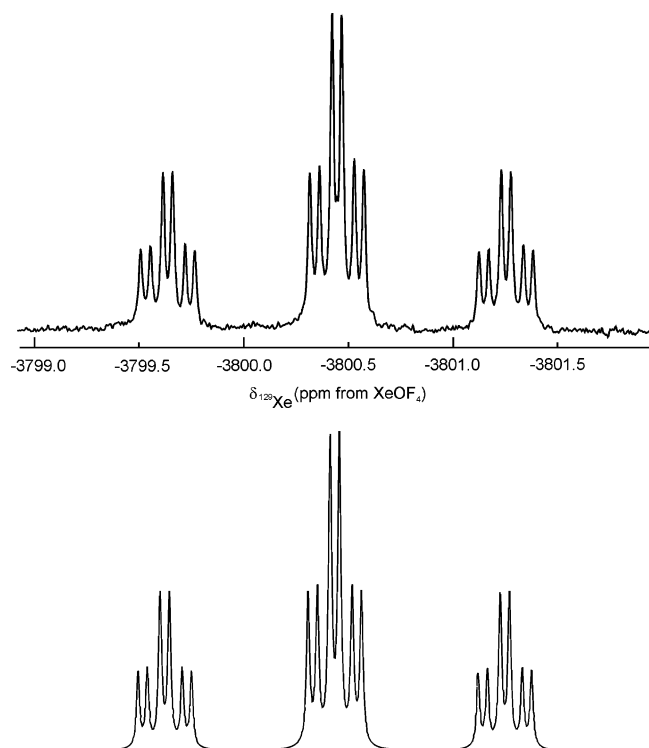


Figure 2. ¹²⁹Xe NMR spectrum (83.02 MHz) of the [C₆F₅Xe]⁺ cation in [C₆F₅Xe][B(CN)₄] recorded in CH₃CN at 24 °C. The spectrum was resolution-enhanced by Gaussian multiplication. The simulated spectrum is provided for comparison (bottom trace).

nucleophile, CH₃CN. Accordingly, the reactivities of [C₆F₅Xe][BY₄] with an excess of the π nucleophile, C₆H₅F, differed in CH₃CN. All reactions of [C₆F₅Xe][BY₄] with C₆H₅F proceeded significantly faster than their decompositions in the solvent alone. The reaction rates and product distributions were dependent upon Y, the solvent, and the presence of additional molecular (e.g., H₂O) or anionic (e.g., F⁻) nucleophiles. The major products in all of these reactions were isomeric mixtures of hexafluorobiphenyls, C₆F₅–C₆H₄F. Their formation proceeded faster in weakly coordinating CH₂Cl₂ than in strongly coordinating CH₃CN. The factors that influence the rates of pentafluorophenylation and the product distributions are in accordance with the intermediate coordination of C₆H₅F at [C₆F₅Xe]⁺ and the subsequent radical attack of C₆H₅F by C₆F₅•.

The ¹⁹F NMR parameters of the [C₆F₅Xe]⁺ cation in the present series of salts are shown to reflect the relative degrees of cation–solvent interactions. The high-frequency shifts of the ¹⁹F NMR resonances of [C₆F₅Xe]⁺ in CH₂Cl₂ and PFB are consistent with a more weakly coordinated [C₆F₅Xe]⁺ cation and significant polarization of the C₆F₅ group by Xe^{II} relative to the ¹⁹F NMR chemical shifts obtained for [C₆F₅Xe]⁺ in CH₃CN solutions of [C₆F₅Xe][BY₄] (Y = CF₃, C₆F₅, CN, or OTeF₅) and [C₆F₅Xe][BF₄]. In the latter case, the enhanced shielding and narrow chemical shift range are consistent with [C₆F₅XeNCCH₃]⁺ formation. The ¹⁹F NMR chemical shifts of [C₆F₅Xe][BF₄] in aHF are similar to those obtained for [C₆F₅Xe][B(CF₃)₄] in a PFB solution and are also indicative of a weakly coordinated [C₆F₅Xe]⁺ cation. Hydrogen fluoride presumably

solvates the anion, resulting in a much larger [BF₄•(HF)_n]⁻ anion, which disperses the negative charge over more than four fluorine atoms, rendering it less basic. Simulations of the ¹⁹F and ¹²⁹Xe NMR spectra of [C₆F₅Xe]⁺ have provided the complete set of aryl ¹⁹F–¹⁹F and ¹²⁹Xe–¹⁹F coupling constants and their relative signs, which are in accord with those of isoelectronic C₆F₅I.

Experimental Section

Apparatus and Materials. Manipulations of volatile materials were carried out on glass vacuum lines. Solid and moisture-sensitive materials were handled inside a drybox (Fa. Braun, MB 100G, Ar atmosphere; H₂O < 1 ppm). The reaction vessels, constructed from 4.1-mm o.d. FEP tubing, were dried under dynamic vacuum for several hours. Molecular sieves (Bayer AG, 3 Å) were washed with boiling water and predried at ~80 °C, followed by drying under vacuum (10⁻³ mbar) at 180 °C for 1 h and at 340 °C for a further 4 h. Organic solvents were purified and dried using standard literature methods.⁴⁰ Acetonitrile (KMF Laborchemie Handels GmbH; >99%) was refluxed with KMnO₄ (5 g L⁻¹ of CH₃CN), distilled, repeatedly refluxed with P₄O₁₀ and distilled until the P₄O₁₀ suspension was colorless. Finally, CH₃CN was distilled onto and stored over dry 3 Å molecular sieves. Dichloromethane (Fluka, >99.9%; KMF, >99.9%), 1,1,1,3,3-pentafluorobutane (Solvay, >99.5%), and 1,2-dichloroethane (Aldrich, 99%) were refluxed with P₄O₁₀, distilled, and stored over dry 3 Å molecular sieves. Two grades of C₆H₅F (Fluorochem Ltd.) were used in this study: (1) redistilled C₆H₅F that had been stored under argon and (2) C₆H₅F that had been freshly refluxed with P₄O₁₀, distilled, and stored over 3 Å molecular sieves. Benzotrifluoride, C₆H₅CF₃ (Aldrich; >99%, anhydrous), was stored over dry 3 Å molecular sieves.

Sulfuryl chloride fluoride, SO₂ClF (Allied Chemical), was purified using the standard literature method.⁴¹ Anhydrous hydrogen fluoride (Harshaw Chemical Co.) was purified by treatment with fluorine gas as previously described⁴² and was then vacuum-distilled into a dry Kel-F storage vessel equipped with a Kel-F valve and stored at room temperature until used. Alternatively, HF (Solvay) was dried electrochemically in a stainless steel cell using nickel electrodes as previously described,⁴³ transferred into a high-density polyethylene, FEP, or PTFE storage vessel, and stored at -21 °C until used.

Samples for reactivity studies were contained in FEP vessels and were stored at 20 °C (unless noted otherwise) inside a rigorously dry, argon-flushed glass vessel to minimize diffusion of moisture through their FEP walls and PTFE stoppers. Samples were shielded from light and were periodically agitated. The reaction progress was periodically monitored by ¹⁹F NMR spectroscopy at 24 °C.

Xenon difluoride was prepared by the thermal method described in the literature.⁴⁴ The starting materials, B(C₆F₅)₃^{45,46} (also see the Supporting Information), Cs[B(C₆F₅)₄]⁴⁶ (also see the Supporting

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Information), $C_6F_5B(OH)_2$,⁴⁷ $K[C_6F_5BF_3]$,⁴⁸ $C_6F_5BF_2$,⁴⁸ $B(OTeF_5)_3$,⁴⁹ $Cs[B(OTeF_5)_4]$,⁴⁹ and $[C_6F_5Xe][BF_4]$,¹⁸ were prepared as previously described. Samples of $K[B(CN)_4]$ ³⁸ and $M^I[B(CF_3)_4]$ ($M^I = K$ and Cs)³⁷ were obtained from Prof. Helge Willner (Bergische Universität Wuppertal, Wuppertal, Germany).

Syntheses of $[C_6F_5Xe][BY_4]$ ($Y = CF_3, C_6F_5, CN, \text{ or } OTeF_5$). Xenon difluoride (0.8734 g, 5.159 mmol) was suspended in cold ($-60^\circ C$) CH_2Cl_2 (25 mL) in a 23-mm i.d. FEP reaction tube. A freshly prepared $C_6F_5BF_2$ (5.15 mmol) solution in CH_2Cl_2 (7 mL) at $-80^\circ C$ was transferred onto the XeF_2 suspension with vigorous stirring of the latter at $-60^\circ C$. After 15 min, the temperature was raised to $-40^\circ C$. A pale-yellow solid precipitated. After 1.5 h of additional stirring, the suspension was centrifuged at $20^\circ C$ and the mother liquor was decanted. The near-white solid was dried for 4 h under dynamic vacuum (10^{-2} mbar) at $20^\circ C$, yielding $[C_6F_5Xe][BF_4]$ (1.65 g, 4.28 mmol, 83% yield) in high purity.

The salts, $[C_6F_5Xe][BY_4]$ ($Y = CF_3, C_6F_5, CN, \text{ or } OTeF_5$) were synthesized in CH_3CN by metatheses of $[C_6F_5Xe][BF_4]$ (~ 0.5 mmol) with equimolar amounts of either $Cs[BY_4]$ or $K[BY_4]$ at $-40^\circ C$. Both reactants were separately dissolved in CH_3CN (300 μL), and the solutions were combined at $20^\circ C$. A pale-yellow suspension resulted, which was stirred for 15 min, subsequently cooled to $-40^\circ C$, and centrifuged. The mother liquor was separated, and the solid, $M^I[BF_4]$ ($M^I = K$ or Cs), was washed with cold ($-40^\circ C$) CH_3CN (300 μL). Both CH_3CN extracts were combined and the solvent was subsequently removed under dynamic vacuum, yielding the pale-yellow solids $[C_6F_5Xe][B(CF_3)_4]$, $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, and $[C_6F_5Xe][B(CN)_4]$, which were dried for several hours under dynamic vacuum (5×10^{-3} mbar) at $20^\circ C$. Small amounts of $M^I[BF_4]$ contaminants were removed from $[C_6F_5Xe][B(CF_3)_4]$ and $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ by redissolving each salt in CH_2Cl_2 followed by centrifugation. The supernatants were removed and dried under dynamic vacuum (5×10^{-3} mbar) at 24 and $-50^\circ C$, respectively, yielding products that were free of $[BF_4]^-$ in their ^{19}F NMR spectra. It is important to note that $[C_6F_5Xe][B(CF_3)_4]$ tended to retain CH_3CN even after pumping under vacuum. It is only after repeated dissolutions ($\times 5$) in CH_2Cl_2 and evaporations under dynamic vacuum that $[C_6F_5Xe][B(CF_3)_4]$ was obtained free of CH_3CN (monitored by Raman and 1H NMR spectroscopies). When this procedure was applied to the salt containing the $[B(C_6F_5)_4]^-$ anion, $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ was obtained. The 1:1 stoichiometry of $[C_6F_5Xe]^+$ to CH_3CN was confirmed by $^1H/^{19}F$ NMR spectroscopy using the quantitative standard, $C_6H_5CF_3$, for integration. All $[C_6F_5Xe][BY_4]$ salts were obtained in essentially quantitative yields.

Alternative Synthesis of C_6F_5XeF . In the drybox, $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ (118.6 mg, 0.1165 mmol) was suspended in cold ($-80^\circ C$) CH_2Cl_2 (1000 μL). A solution of cold ($-80^\circ C$) CH_2Cl_2 (500 μL) and $[N(CH_3)_4]F$ (13.59 mg, 0.1459 mmol) was added and allowed to react for 1 h. A white suspension of $[N(CH_3)_4][B(C_6F_5)_4]$ immediately formed. The suspension was centrifuged at $-80^\circ C$, and the CH_2Cl_2 mother liquor was separated. The main product in the mother liquor was C_6F_5XeF (75.1%) in addition to C_6F_5H (4.0%), C_6F_5Cl (0.5%), $[B(C_6F_5)_4]^-$ (9.7%), $(C_6F_5)_2$ (2.0%), and several other unidentified C_6F_5 compounds (8.7%). Methylene chloride was then removed under vacuum (5×10^{-3} mbar) at temperatures below $-50^\circ C$, and the resulting yellow solid was

dried for several hours at temperatures not exceeding $-50^\circ C$. The solid was further purified by washing with dry pentane at $-60^\circ C$. The ^{19}F and ^{129}Xe NMR parameters of C_6F_5XeF (CH_2Cl_2 at $-80^\circ C$) prepared by the present method are in accordance with the previously reported values.⁸ ^{19}F NMR: $\delta(^{19}F) = -2.8$ ppm [$\Delta\nu_{1/2} = 129$ Hz, $^1J(^{19}F-^{129}Xe) = 4016$ Hz, XeF]; -129.6 ppm [$o-C_6F_5$]; -147.0 ppm [$^3J(^{19}F-^{19}F) = 20.1$ Hz, $p-C_6F_5$]; -157.2 ppm [$m-C_6F_5$]. ^{129}Xe NMR: $\delta(^{129}Xe) = -3793.4$ ppm [$^1J(^{19}F-^{129}Xe) = 4016$ Hz, XeF].

Reactivity Studies. Sample preparations are described below. All samples were prepared in 4.1-mm o.d. FEP NMR/reaction tubes, which were closed with PTFE stoppers. Samples were periodically monitored by ^{19}F NMR spectroscopy at $24^\circ C$ unless otherwise indicated. Initial concentrations of $[C_6F_5Xe]^+$ salts were 0.09–0.16 mol L^{-1} .

(a) Solubilities of $[C_6F_5Xe][BY_4]$ ($Y = CF_3$ or CN), $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, and $[C_6F_5Xe][BF_4]$ in Selected Solvents. The solubilities of $[C_6F_5Xe][BY_4]$ salts were determined in selected solvents (Table S1) prior to investigation of their solution stabilities. Each salt was loaded into a reaction tube and suspended in the solvent (CH_3CN , CH_2Cl_2 , DCE, PFB, SO_2ClF , or C_6H_5F). The saturated suspension was centrifuged, and the mother liquor was decanted into a second reaction tube. The amount of dissolved salt was determined by use of the internal quantitative standard for integration, $C_6H_5CF_3$.

(b) Stabilities of $[C_6F_5Xe][BY_4]$ ($Y = CF_3$ or CN), $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, and $[C_6F_5Xe][BF_4]$ in Solution. Each $[C_6F_5Xe][BY_4]$ salt (25–50 mg) was loaded into a reaction tube. The salts were dissolved in CH_3CN (500 μL) or CH_2Cl_2 (500 μL), in the case of $[C_6F_5Xe][B(CF_3)_4]$ and $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, outside the drybox under a blanket of argon.

(c) Influence of Equimolar Amounts of $[N(C_4H_9)_4][BF_4]$ on the Decomposition of $[C_6F_5Xe][B(CF_3)_4]$ in CD_2Cl_2 and CD_3CN . Equimolar amounts of $[C_6F_5Xe][B(CF_3)_4]$ (21.12 mg, 0.0361 mmol) and $[N(C_4H_9)_4][BF_4]$ (11.89 mg, 0.0361 mmol) were dissolved in CD_3CN (150 μL) in separate reaction tubes, and both solutions were combined (Table 2, entry 6a).

Similarly, $[C_6F_5Xe][B(CF_3)_4]$ (21.75 mg, 0.0372 mmol) and $[N(C_4H_9)_4][BF_4]$ (12.25 mg, 0.0372 mmol) were dissolved in CD_2Cl_2 (150 μL) at $20^\circ C$ and combined (Table 2, entry 6b).

(d) Solvolytic Behavior of $[C_6F_5Xe][BF_4]$ in aHF. The salt, $[C_6F_5Xe][BF_4]$ (39.00 mg, 0.1013 mmol), was loaded into a reaction tube and dissolved in aHF (~ 500 μL) at $-40^\circ C$ (Table 2, entry 5b).

(e) Reactions of $[C_6F_5Xe][BY_4]$ ($Y = CF_3$ or CN), $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, $[C_6F_5Xe][BF_4]$, and $[C_6F_5Xe][AsF_6]$ with the π Nucleophile, C_6H_5F . (i) Rigorously Dried C_6H_5F in CH_3CN . The salts $[C_6F_5Xe][BF_4]$ (**1**; 25.55 mg, 0.0663 mmol), $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ (**2**; 61.51 mg, 0.0604 mmol), $[C_6F_5Xe][B(CN)_4]$ (**3**; 28.98 mg, 0.0701 mmol), $[C_6F_5Xe][B(CF_3)_4]$ (**4**; 34.88 mg, 0.0596 mmol), and $[C_6F_5Xe][AsF_6]$ (**5**; 30.93 mg, 0.0635 mmol) were loaded into separate reaction tubes and dissolved in CH_3CN (500 μL). Freshly dried and distilled C_6H_5F (20 equiv) was added under argon to the pale-yellow $[C_6F_5Xe]^+$ salt solutions: 125 μL (**1**; 128 mg, 1.33 mmol), 118 μL (**2**; 121 mg, 1.26 mmol); 130 μL (**3**; 133 mg, 1.38 mmol); 127 μL (**4**; 130 mg, 1.35 mmol); 112 μL (**5**; 115 mg, 1.20 mmol) (Table 3, entries 1a–5a).

(ii) C_6H_5F (20 equiv) and H_2O (1 and 20 equiv) in CH_3CN . Two portions of the salts, **1** and **5** were loaded into separate reaction tubes and dissolved in CH_3CN (500 μL): **1a** (31.66 mg, 0.0822 mmol), **5a** (27.07 mg, 0.0556 mmol), **1b** (30.13 mg, 0.0782 mmol), and **5b** (26.86 mg, 0.0551 mmol). Freshly dried and distilled C_6H_5F

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(20 equiv) was added to the pale-yellow [C₆F₅Xe]⁺ salt solutions: 155 μL (**1a**; 158.7 mg, 1.651 mmol); 110 μL (**5a**; 112.6 mg, 1.172 mmol); 155 μL (**1b**; 158.7 mg, 1.651 mmol); 110.0 μL (**5b**; 112.6 mg, 1.172 mmol). This was followed by the addition of 1 or 20 equiv of triply distilled H₂O: **1a** (1.5 μL, 0.083 mmol); and **5a** (1.0 μL, 0.056 mmol); **1b** (29 μL, 1.61 mmol) and **5b** (20 μL, 1.11 mmol) (Table 3, entries 7a–8b).

(iii) **C₆H₅F and Fluoride in CH₂Cl₂**. In the drybox, [C₆F₅XeNCCH₃][B(C₆F₅)₄] (26.04 mg, 0.0256 mmol) was loaded into a reaction tube and suspended in cold (–55 °C) CH₂Cl₂ (1000 μL). Freshly dried and distilled C₆H₅F (45 μL, 45.9 mg, 0.478 mmol, 20 equiv) was added to the [C₆F₅XeNCCH₃]⁺ salt suspension. The resulting solution was divided into two equal samples (A and B), and a portion (250 μL, 0.015 mmol) of a solution of [N(CH₃)₄]F (5.72 mg, 0.0614 mmol) in cold (–55 °C) CH₂Cl₂ (1000 μL) was added to sample A (Table 3, entry 9b). Sample B served as a reference.

(iv) **Reaction of C₆F₅XeF with C₆H₅F in CH₂Cl₂**. Freshly prepared C₆F₅XeF (16.3 mg, 0.0514 mmol) containing [N(CH₃)₄]-[B(C₆F₅)₄] (9%) as an impurity was loaded into a reaction tube and dissolved in cold (–80 °C) CH₂Cl₂ (1200 μL). Freshly dried and distilled C₆H₅F (50 μL, 51.2 mg, 0.533 mmol, 11 equiv) was added to the pale-yellow solution at –80 °C. The solution was warmed to –40 °C, stirred for 30 min, and periodically monitored by ¹⁹F NMR spectroscopy at –40 °C (Table 3, entry 9a).

(v) **Reaction of [C₆F₅Xe][B(CF₃)₄] with C₆H₅F in CH₂Cl₂**. Two portions of salt **4a** (35.11 mg, 0.0600 mmol) and **4b** (34.83 mg, 0.0595 mmol), were loaded into separate reaction tubes, and each was dissolved in CH₂Cl₂ (500 μL). Freshly dried and distilled C₆H₅F, **4a** (20 equiv) and **4b** (1.2 equiv) was added to the pale-yellow [C₆F₅Xe]⁺ salt solutions: **4a**, 113 μL (115.4 mg, 1.201 mmol); **4b**, 6 μL (6.92 mg, 0.0720 mmol) (Table 3, entries 1b and 5b).

(vi) **Reactions of [C₆F₅XeNCCH₃][B(C₆F₅)₄] and [C₆F₅Xe]-[B(CF₃)₄] with Neat C₆H₅F**. The salts **2** (45.0 mg, 0.0442 mmol) and **4** (38.7 mg, 0.0661 mmol) were each loaded into a reaction tube and dissolved in freshly dried and distilled C₆H₅F (400 μL, 4.2 mmol) (Table 3, entries 6a,b).

NMR Spectroscopy. (a) Instrumentation and Acquisition Parameters. NMR samples were measured in 4.1-mm o.d. FEP tubes placed inside a thin-walled precision glass NMR tube (Wilmad 537 PPT), which contained CD₂Cl₂ or CD₃CN in the annular space, or internally as dry solvents in precision glass NMR tubes (Wilmad 528 PPT). Ambient and low-temperature NMR spectra were recorded in the deuterium-locked mode on a Bruker Avance 300 spectrometer equipped with a 7.0463 T cryo-magnet. For low-temperature work, the NMR probe was cooled using a nitrogen flow and a variable-temperature controller (BVT 3000).

The ¹H and ¹⁹F NMR spectra were acquired using a 5 mm combination ¹H/¹⁹F probe operating at 300.14 and 282.40 MHz, respectively. The ¹¹B, ¹³C, and ¹²⁹Xe NMR spectra were obtained using a 5 mm broad-band inverse probe operating at 96.29, 75.47, and 83.02 MHz, respectively. Pulse widths, corresponding to bulk magnetization tip angles of ~90°, were 11.9 (¹H), 9.3 (¹¹B), 8.0

(¹³C), 14.6 (¹⁹F), and 8.5 (¹²⁹Xe) μs. Line-broadening parameters used in exponential multiplication of the free induction decays were set equal to or less than their respective data-point resolutions or the natural line widths of the resonances. All line-shape functions were Lorentzian unless specified otherwise. In some cases, the free induction decays were multiplied by Gaussian functions for resolution enhancement on Fourier transformation. Spectra were recorded using various memory sizes, optimal acquisition times, and relaxation delays (0.5–2 s).

The ¹H NMR chemical shifts were referenced with respect to tetramethylsilane (TMS) using the chemical shifts for the solvents CH₂Cl₂ (5.32 ppm) and CH₃CN (1.95 ppm). The ¹³C NMR chemical shifts were referenced with respect to TMS using the chemical shifts for the solvents CH₂Cl₂ (53.5 ppm) and CH₃CN (118.7 ppm). The ¹⁹F NMR spectra were referenced with respect to CFCl₃ using either the internal standards C₆F₆ (–162.9 ppm) or C₆H₅CF₃ (–63.9 ppm) or externally to a neat CFCl₃ reference sample at 24 °C. The ¹²⁹Xe NMR spectra were directly referenced with respect to neat liquid XeOF₄ or indirectly by use of the secondary external reference XeF₂/CD₃CN extrapolated to zero concentration, yielding an XeF₂ chemical shift of –1813.3 ppm with respect to external XeOF₄ at 24 °C.⁵⁰ The ¹¹B NMR spectra were referenced either to an external BF₃·Et₂O (neat) at 24 °C or to an external BF₃·Et₂O/CD₃Cl solution (15% v/v) at 24 °C. A positive (negative) sign denotes a chemical shift to high (low) frequency of the reference compound.

(b) **Simulation of NMR Spectra.** The ¹⁹F and ¹²⁹Xe NMR spectra of the [C₆F₅Xe]⁺ cation ([B(CN)₄][–] salt in CH₃CN at 24 °C) and C₆F₅I were simulated on a PC using the program *ISOTO-POMER*.³⁰ The program provides a full heteronuclear simulation that takes into account second-order effects. Spectra in the present study were not iterated.

Differential Scanning Calorimetry (DSC). Thermal analyses were performed using previously described instrumentation and procedures.⁵¹ Samples were typically 2–5 mg (4–40 μmol).

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Supporting Information Available: Solubilities of [C₆F₅Xe]-[BY₄] (Y = CF₃ or CN), [C₆F₅XeNCCH₃][B(C₆F₅)₄], and [C₆F₅Xe][BF₄] (Table S1) and solution decomposition rates and products (20 °C) for [C₆F₅Xe][BY₄] (Y = CF₃, CN, or OTeF₅), [C₆F₅XeNCCH₃][B(C₆F₅)₄], and [C₆F₅Xe][BF₄] (Table S2), experimental and simulated ¹⁹F NMR spectra of C₆F₅I (Figure S1), and the syntheses of B(C₆F₅)₃ and Cs[B(C₆F₅)₄]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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