Inorg. Chem. **2007**, *46*, 9425–9437

Inorganic Chemistry
Article

Syntheses, Solution Multi-NMR Characterization, and Reactivities of $[C_6F_5Xe]^+$ Salts of Weakly Coordinating Borate Anions, $[BY_4]^-$ (Y = CF_3, C_6F_5, CN, or $OTeF_5$)

Karsten Koppe,[†,‡] **Vural Bilir,**[†] **Hermann-J. Frohn,***[,†] **Hélène P. A. Mercier,**[‡] **and Gary J. Schrobilgen***[,‡]

Anorganische Chemie, Universität Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany,
and Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Received May 24, 2007

New examples of $[C_6F_5Xe]^+$ salts of the weakly coordinating anions $[B(CF_3)_4]^-$, $[B(C_6F_5)_4]^-$, $[B(CN)_4]^-$, and $[B(OTeF_5)_4]^-$ have been synthesized by metathesis reactions of $[C_6F_5Xe][BF_4]$ with the corresponding $M^I[BY_4]$ salts (M^I = K or Cs; Y = 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 $[BY_4]^-$ on the decomposition rate of $[C_6F_5Xe]^+$ as well as the presence of the weakly nucleophilic $[BF_4]^-$ ion has been studied. The electrophilic pentafluorophenylation of C_6H_5F by $[C_6F_5Xe][BY_4]$ 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 $[C_6F_5Xe]^+$ 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 $[C_6F_5Xe]^+$ 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 $B(C_6F_5)_3$ led to the syntheses and characterizations of $[C_6F_5Xe][(C_6F_5)_nBF_{4-n}]$ (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) [RXe][A], where $[A]^-$ 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 $[L]^-$ is a nucleophilic anion such as $[C_6F_5CO_2]^-$,[6] Cl^-,[7] or F^-[8,9] that forms a strong ion contact (donor−acceptor) interaction with $[RXe]^+$, 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, [RXe][A] (R = 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}.

---

* To whom correspondence should be addressed. E-mail: h-j.frohn@uni-due.de (H.-J.F.), schrobil@mcmaster.ca (G.J.S.).

[†] Universität Duisburg-Essen.

[‡] McMaster University.

(1) Naumann, D.; Tyrra, W. *J. Chem. Soc., Chem. Commun.* **1989**, 47−50.

(2) Frohn, H.-J.; Jakobs, S. *J. Chem. Soc., Chem. Commun.* **1989**, 625−627.

(3) Frohn, H.-J.; Jakobs, S.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1506−1507.

(4) Frohn, H.-J.; Bardin, V. V. *Organometallics* **2001**, *20*, 4750−4762.

(5) Tyrra, W.; Naumann, D. Organoxenon Compounds. In *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: Weinheim, Germany, 2002; pp 297−317.

(6) Frohn, H.-J.; Klose, A.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 99−100.

(7) Frohn, H.-J.; Schroer, T.; Henkel, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 2554−2556.

(8) Frohn, H.-J.; Theissen, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4591−4593.

(9) Maggiarosa, N.; Naumann, D.; Tyrra, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4588−4591.

(10) Frohn, H.-J.; Bardin, V. V. *J. Chem. Soc., Chem. Commun.* **1993**, 1072−1074.

(11) Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2465−2469.

(12) Frohn, H.-J.; Adonin, N. Yu.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2499−2508.

(13) Frohn, H.-J.; Bardin, V. V. *Mendeleev Commun.* **2007**, *17*, 137−138.

(14) Zhdankin, V. V.; Stang, P. J.; Zefirov, N. S. *J. Chem. Soc., Chem. Commun.* **1992**, 578−579.

(15) Frohn, H.-J.; Bardin, V. V. *Chem. Commun.* **2003**, 2352−2353.

(16) Frohn, H.-J.; Bardin, V. V. *Eur. J. Inorg. Chem.* **2006**, *19*, 3948−3953.

10.1021/ic7010138 CCC: $37.00

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 $[RXe]^+$ 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 $[RXe]^+$ 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 $[C_6F_5Xe]^+$ 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 $[C_6F_5Xe]^+$ salts having properties that approach those of the $[C_6F_5Xe]^+$ cation in the gas phase, a series of $[C_6F_5Xe]^+$ salts of the weakly coordinating borate anions, $[BY_4]^-$ (Y = 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 $[C_6F_5Xe][BY_4]$ (Y = 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 $[C_6F_5Xe]^+$ salt, which can serve as the starting material for other $[C_6F_5Xe]^+$ salts and is easy to handle at ambient temperature, is by means of the xenodeborylation reaction of XeF_2 with $C_6F_5BF_2$ (eq 1).[18] The reaction of equivalent amounts of XeF_2 and $C_6F_5BF_2$ in CH_2Cl_2 at −50 °C yields pure $[C_6F_5Xe][BF_4]$ 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, $CF_3CH_2CF_2CH_3$ (PFB), C_6H_5F, $ClCH_2CH_2Cl$ (DCE), and SO_2ClF.

$$XeF_2 + C_6F_5BF_2 \xrightarrow[-50\ ^\circ C]{CH_2Cl_2} [C_6F_5Xe][BF_4] \qquad (1)$$

$[C_6F_5Xe]^+$ Salts with Weakly Coordinating $[BY_4]^-$ (Y = 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, $[C_6F_5Xe][BF_4]$, and the products, $[C_6F_5Xe][BY_4]$, in combination with the low solubility of $M^I[BF_4]$ (M^I = 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 $[C_6F_5Xe][BY_4]$ salts and their isolation in nearly quantitative yields (90−100%) and very high purities. The salts, $[C_6F_5Xe][BY_4]$ (Y = CF_3 or CN) and $[C_6F_5XeNCCH_3][BY_4]$ (Y = C_6F_5), were obtained as pale-yellow solids, but attempts to isolate solid $[C_6F_5Xe][B(OTeF_5)_4]$ from CH_3CN/CH_2Cl_2, CH_2Cl_2, CH_3CN/PFB, or PFB solutions failed because the product separated as a yellow oil when the solutions were cooled.

$$[C_6F_5Xe][BF_4] + M^I[BY_4] \xrightarrow[20\ \text{to}\ -40\ ^\circ C]{CH_3CN} [C_6F_5Xe][BY_4] + M^I[BF_4]\downarrow \qquad (2)$$

Thermoanalytical studies showed that the $[B(C_6F_5)_4]^-$ and $[B(CF_3)_4]^-$ salts have significantly lower thermal stabilities in the solid state than the $[B(CN)_4]^-$, $[BF_4]^-$, and $[AsF_6]^-$ salts (Table 1). Both $[C_6F_5Xe][BF_4]$ and $[C_6F_5Xe][AsF_6]$ melt without decomposition, whereas the $[B(CN)_4]^-$, $[B(C_6F_5)_4]^-$, and $[B(CF_3)_4]^-$ salts decompose without melting.

The solubilities of $[C_6F_5Xe][BF_4]$ and $[C_6F_5Xe][BY_4]$ 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 $[C_6F_5Xe][BY_4]$). Among the series of $[C_6F_5Xe][BY_4]$ salts discussed here, the solubility behavior of the $[B(CN)_4]^-$ salt is most similar to that of the $[BF_4]^-$ salt. The solubility of $[C_6F_5Xe][B(CN)_4]$ is ~4.3 mmol mL^{-1} in CH_3CN at 20 °C compared with ~4.8 mmol mL^{-1} for the $[BF_4]^-$ salt, whereas both salts are insoluble in CH_2Cl_2, DCE, PFB, C_6H_5F, and SO_2ClF. Salts having four fluoroorganic groups in the anion such as $[C_6F_5Xe][B(CF_3)_4]$ and $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ have satisfactory solubilities in CH_3CN and low solubilities in halogenated hydrocarbons.

(b) Solution Stabilities of $[C_6F_5Xe][BY_4]$; Solvent and Counteranion Dependencies. The thermal stabilities of $[C_6F_5Xe][BY_4]$ solutions were compared for different borate salts in different solvent media at 20 °C. The $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ 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 $[C_6F_5Xe][BY_4]$ salts were compared with that of $[C_6F_5Xe][BF_4]$ in the same solvent. The extent of $[C_6F_5Xe]^+$ conversion, expressed in mole percent, was determined from the integrated ^{19}F NMR spectral intensities of $[C_6F_5Xe]^+$ 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) $[C_6F_5Xe][BF_4]$. The higher stabilities of $[C_6F_5Xe]^+$ 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 $[C_6F_5Xe][BF_4]$, the cation does not undergo significant solvolysis in aHF at −40 °C.

Among the $[C_6F_5Xe]^+$ salts examined in aprotic solvents during this comparative study, $[C_6F_5Xe][BF_4]$ solutions in CH_3CN are the most stable and solutions of $[C_6F_5Xe][BF_4]$ in aHF were found to be even more stable. After 54 days, only 15% of $[C_6F_5Xe]^+$ had decomposed to C_6F_6 in aHF (entry 5b), whereas a comparable conversion was only

---

(17) Frohn, H.-J.; Klose, A.; Schroer, T.; Henkel, G.; Buss, V.; Opitz, D.; Vahrenhorst, R. *Inorg. Chem.* **1998**, *37*, 4884−4890.

(18) Frohn, H.-J.; Franke, H.; Bardin, V. V. *Z. Naturforsch.* **1999**, *54b*, 1495−1498.

Table 1. Melting Points and Decomposition Temperatures of $[C_6F_5Xe][BY_4]$ (Y = CF_3, C_6F_5, or CN), $[C_6F_5Xe][BF_4]$, and $[C_6F_5Xe][AsF_6]$

	mp, °C		decomp temp, °C	
$[C_6F_5Xe]^+$ salt	T_{onset}	T_{max}	T_{onset}	T_{max}
$[B(CF_3)_4]^-$			121.2	125.0
$[B(C_6F_5)_4]^{-\,a}$			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 $[C_6F_5XeNCCH_3]^+$ cation.

achieved in CH_3CN after 18 days and resulted in exclusive formation of C_6F_5H (entry 5c). Although the HF molecule can coordinate to the Xe^{II} center through fluorine, this interaction is expected to be weaker than CH_3CN coordination and leads to C_6F_6, Xe^0, and $[H(HF)_n][BF_4]$. Thus, the exclusive formation of C_6F_5H in CH_3CN is consistent with the initial coordination of CH_3CN to the positively charged xenon center and rapid homolytic cleavage of the Xe−C bond (eqs 3−7). The absence of HF and C_6F_6 shows that the main decomposition channel arose from CH_3CN coordination and not from $[BF_4]^-$ coordination (eqs 8−11).

$$[C_6F_5Xe]^+ + CH_3CN \rightarrow [C_6F_5Xe{-}NCCH_3]^+ \rightarrow C_6F_5^{\bullet} + [Xe{-}NCCH_3]^{\bullet+} \quad (3)$$

$$[XeNCCH_3]^{\bullet+} \rightarrow Xe^0 + [CH_3CN]^{\bullet+} \quad (4)$$

$$[CH_3CN]^{\bullet+} \rightarrow CH_2CN^{\bullet} + H^+_{solv} \quad (5)$$

$$C_6F_5^{\bullet} + CH_3CN \rightarrow C_6F_5H + {}^{\bullet}CH_2CN \quad (6)$$

$$2{}^{\bullet}CH_2CN \rightarrow NCCH_2CH_2CN \quad (7)$$

$$[C_6F_5Xe]^+ + [BF_4]^- \rightarrow C_6F_5XeFBF_3 \leftrightarrows C_6F_5XeF + BF_3 \quad (8)$$

$$C_6F_5XeF \rightarrow C_6F_6 + Xe \quad (9)$$

$$C_6F_5XeF \rightarrow C_6F_5^{\bullet} + XeF^{\bullet} \quad (10)$$

$$XeF^{\bullet} + CH_3CN \rightarrow HF + Xe^0 + {}^{\bullet}CH_2CN \quad (11)$$

(ii) $[C_6F_5Xe][B(CF_3)_4]$. The decomposition of $[C_6F_5Xe][B(CF_3)_4]$ was complete in CH_3CN after 43 days, and C_6F_5H, the only C_6F_5-containing product, and HF (56 mol % relative to C_6F_5H) were the sole products (entry 1a), whereas in CH_2Cl_2, 50% of the cation decomposed within 22 days, forming C_6F_5Cl (80%) and C_6F_5H (20%) (entry 1b). Decomposition in CH_3CN is likely initiated by coordination of CH_3CN, as previously described (eqs 3−6). The formation of HF is indicative of anion decomposition according to eq 12.

$$H^+_{solv}/[B(CF_3)_4]^- \leftrightarrows \langle (CF_3)_3BCF_2 \rangle + HF \quad (12)$$

The weakly coordinating solvent, CH_2Cl_2, is capable of coordinating to strong Lewis acid centers.[19] Thus, the decomposition sequence may be initiated by solvent coordination to $[C_6F_5Xe]^+$, subsequent homolytic cleavage of the Xe−C bond (eq 13), and electron transfer (eq 14) to give the observed products (eq 15). Abstraction of $[CF_3]^-$

$$[C_6F_5Xe]^+ + CH_2Cl_2 \rightarrow [C_6F_5Xe{-}ClCH_2Cl]^+ \rightarrow C_6F_5^{\bullet} + [Xe{-}ClCH_2Cl]^{\bullet+} \quad (13)$$

$$[XeClCH_2Cl]^{\bullet+} \rightarrow Xe^0 + [CH_2Cl_2]^{\bullet+} \rightarrow CHCl_2^{\bullet} + H^+_{solv} \quad (14)$$

$$C_6F_5^{\bullet} + CH_2Cl_2 \rightarrow C_6F_5Cl\ (C_6F_5H) + CH_2Cl^{\bullet}\ (CHCl_2^{\bullet}) \quad (15)$$

or F^- from $[B(CF_3)_4]^-$ by "$[C_6F_5]^+$" or $[C_6F_5Xe]^+$ is ruled out in CH_3CN or CH_2Cl_2 solvents because neither $C_6F_5CF_3$ nor C_6F_6 was detected. Clearly, $[C_6F_5Xe][B(CF_3)_4]$ is significantly more stable in PFB (entry 1c) than in CH_2Cl_2, with a decomposition rate that is approximately one-fourth of that in CH_2Cl_2. Two unidentified C_6F_5-containing products were formed in PFB (total, ~4 mol %) in addition to C_6F_6.

(iii) $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$. The stabilities and reaction pathways are markedly different in the case of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$. Acetonitrile solutions of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ were completely decomposed after 20 days with the formation of C_6F_5H (85%) and $(C_6F_5)_2$ (15%) (entry 2a). The stability of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ in CH_2Cl_2 was strongly dependent on the temperature. At 20 °C, the salt completely decomposed in less than 20 min, forming C_6F_5H (46%) and $(C_6F_5)_2$ (9%), and the balance (45%) was comprised of a mixture of $[(C_6F_5)_3BF]^-$, $B(C_6F_5)_3$, and $[C_6F_5BF_3]^-$ (superimposed spectra prevented integration), resulting from anion decomposition, whereas at −40 °C, only 4% of the cation was converted to C_6F_5H after 16 h (entry 2b). The stability of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ in DCE at 20 °C was significantly greater than that in CH_2Cl_2, with only 85% of the cation consumed after 1 h, forming only C_6F_5H (entry 2c). The solvent, CH_2ClCH_2Cl molecule [ϵ = 10.7 (20 °C); IP = 11.1 eV], is more polar than CH_2Cl_2 [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 $[C_6F_5Xe]^+$, after elimination of CH_3CN (eq 16), with nucleophilic sites of the $[B(C_6F_5)_4]^-$ anion and accounts for the absence of $(C_6F_5)_2$ at 20 °C.

The formation of $(C_6F_5)_2$ is clearly associated with the $[B(C_6F_5)_4]^-$ anion because none of the other $[C_6F_5Xe][BY_4]$ salts considered in this study give rise to this product, which most likely results from attack of $[C_6F_5Xe]^+$ on the anion (eq 17), with $(C_6F_5)_2$ resulting from decomposition of the intermediate, $Xe(C_6F_5)_2$ (eq 18). In contrast with the reversible step of Lewis acid elimination in eq 8, an irreversible elimination of $B(C_6F_5)_3$ is probable according to eq 17. The dominant product deriving from intrinsically unstable $Xe(C_6F_5)_2$ is, however, C_6F_5H (eqs 19 and 20). The relative

---

(19) Seggen, D. M. V.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 3453−3464.

Table 2. Solution Stabilities of $[C_6F_5Xe][BY_4]$ (Y = CF_3, C_6F_5, CN, or $OTeF_5$) and $[C_6F_5Xe][BF_4]$ at 20 °C and Their C_6F_5-Containing Decomposition Products

entry	$[C_6F_5Xe]^+$ salt	solvent	time,[a] days	% conversion[b]	C_6F_5 products (mol %)[c] derived from $[C_6F_5Xe]^+$
1a	$[B(CF_3)_4]^-$	CH_3CN	43	100	C_6F_5H (100)[d]
1b		CH_2Cl_2	22	50	C_6F_5H (20), C_6F_5Cl (80)
1c		PFB	8	4	C_6F_6 (6), C_6F_5X (31),[e] C_6F_5Y (63)[f]
2a	$[B(C_6F_5)_4]^{-}$[g]	CH_3CN	20	100	C_6F_5H (85), $(C_6F_5)_2$ (15)
2b		CH_2Cl_2	0.010(3)	100	C_6F_5H (46), $(C_6F_5)_2$ (9), C_6F_5-B species (45)
		CH_2Cl_2	0.667(6) (−40 °C)	4	C_6F_5H (100)
2c		DCE	0.042(3)	85	C_6F_5H (100)
3a	$[B(CN)_4]^-$	CH_3CN	71	100	C_6F_5H (100)[h]
4a	$[B(OTeF_5)_4]^-$	CH_3CN	25	72	C_6F_5H (94), C_6F_5Z (6)[i] and $OTeF_5$ compds
4b		CH_2Cl_2	24	81	C_6F_5H (81), C_6F_5Cl (14), C_6F_5Z (5)[j] and $OTeF_5$ compds
5a	$[BF_4]^-$	CH_3CN	58	79	C_6F_5H (100)
5b		aHF	54	15	C_6F_6 (100)
5c		CH_3CN	18	15	C_6F_5H (100)
6a	$[B(CF_3)_4]^- + [N(C_4H_9)_4][BF_4]$[k]	CD_3CN	2	100	C_6F_5H (~100), C_6F_5D (traces)
6b		CD_2Cl_2	18	100	C_6F_5H (64), C_6F_5D (18), C_6F_5Cl (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 $[C_6F_5Xe]^+$ cation and relative molar amounts of C_6F_5-containing products are in mole percent. [c] The integrated intensities given in parentheses are relative to the total C_6F_5-containing species in the sample. [d] HF (56). [e] Unknown product: $\delta(^{19}F) = -143.0$ (o), -154.7 (p), -163.1 (m) ppm. [f] Unknown product: $\delta(^{19}F) = -143.1$ (o), -155.2 (p), -162.5 (m) ppm. [g] This salt contains the $[C_6F_5XeNCCH_3]^+$ cation. [h] Unassigned singlets also occurred at −144.9 (0.10) and −181.3 (0.42) ppm. [i] Unknown C_6F_5 species: $\delta(^{19}F) = -138.1$ (o), -151.0 (p), -161.3 (m) ppm; unassigned resonances also occurred at −130.6 and −136.7 ppm. [j] Unknown C_6F_5 species: $\delta(^{19}F) = -137.5$ (o), -150.4 (p), -160.8 (m) ppm; unassigned resonances also occurred at −126.9 and −134.9 ppm. [k] Equimolar amounts of $[C_6F_5Xe][B(CF_3)_4]$ and $[N(C_4H_9)_4][BF_4]$ were used.

ratios of C_6F_5H to $(C_6F_5)_2$ in CH_3CN and CH_2Cl_2 at 20 °C are very similar, whereas C_6F_5H is formed exclusively in DCE.

$$[C_6F_5XeNCCH_3]^+ \leftrightarrows [C_6F_5Xe]^+ + CH_3CN \tag{16}$$

$$[C_6F_5Xe]^+ + [B(C_6F_5)_4]^- \rightarrow C_6F_5XeC_6F_5B(C_6F_5)_3 \rightarrow Xe(C_6F_5)_2 + B(C_6F_5)_3 \tag{17}$$

$$Xe(C_6F_5)_2 \rightarrow Xe^0 + (C_6F_5)_2 \tag{18}$$

$$Xe(C_6F_5)_2 \rightarrow Xe^0 + 2\ C_6F_5^{\bullet} \tag{19}$$

$$C_6F_5^{\bullet} + CH_3CN\ (CH_2Cl_2) \rightarrow C_6F_5H\ (C_6F_5H) + {}^{\bullet}CH_2CN\ ({}^{\bullet}CHCl_2) \tag{20}$$

The reaction pathway leading to $(C_6F_5)_2$ is supported by prior studies that have shown that, while the $[B(C_6F_5)_4]^-$ anion is generally classified as a weakly coordinating anion, this anion, with relatively open tetrahedral geometry and rigid C_6F_5 groups,[1] highly electron-withdrawing substituents, and decreased negative charge on the *ipso*-carbon atom, is still susceptible to $[C_6F_5]^-$ abstraction by metal cation centers.[20,21]

The proposed intermediate, $Xe(C_6F_5)_2$, is supported by its independent synthesis and characterization.[8,9] Acetonitrile solutions of $Xe(C_6F_5)_2$ have been shown to decompose within 24 h at −40 °C to mainly $(C_6F_5)_2$ and trace amounts of C_6F_5H.[9] Under these conditions, the $C_6F_5^{\bullet}$ radical does not readily abstract an acidic hydrogen from a basic solvent such as CH_3CN, indicating that radical solvation as well as resonance stabilization of the $C_6F_5^{\bullet}$ radical must be taken into account. In a weakly basic solvent such as CH_2Cl_2, the radical lifetime is very short at low temperatures, and solvent attack occurs with the exclusive formation of C_6F_5H.

(iv) $[C_6F_5Xe][B(CN)_4]$. The decomposition rate of $[C_6F_5Xe][B(CN)_4]$ in CH_3CN at 20 °C (entry 3a) was among the slowest encountered in this study and is similar to that of the $[BF_4]^-$ salt in CH_3CN (entry 5a). After 71 days, the cation had been consumed, with C_6F_5H being the only C_6F_5-containing product. In addition, two unassigned singlets were observed [$\delta(^{19}F) = -144.9$ and -181.3 ppm].

(v) $[C_6F_5Xe][B(OTeF_5)_4]$. The stability of $[C_6F_5Xe][B(OTeF_5)_4]$ (entries 4a and 4b) was significantly greater than that of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ (entries 2a and 2b), especially in CH_2Cl_2. The conversion of $[C_6F_5Xe][B(OTeF_5)_4]$ was 72% (81%) in CH_3CN (CH_2Cl_2) after 25 (24) days, with 94% (81%) C_6F_5H as the major product and 6% (5%) of an unknown C_6F_5- compound as the minor product. In addition, a significant amount of C_6F_5Cl (14%) was formed as a decomposition product in a CH_2Cl_2 (eqs 13−15). The decomposition pathway that led to C_6F_5H in CH_3CN is similar to that represented by eqs 3−6. The formation of C_6F_5Cl can be explained by analogy with the decomposition of $[C_6F_5Xe][B(CF_3)_4]$ (eqs 13−15) in CH_2Cl_2. Low-intensity overlapping AB_4 patterns corresponding to different $OTeF_5$-containing species were also obtained in CH_3CN and CH_2Cl_2.

(c) Reactions of $[C_6F_5Xe][BY_4]$ Salts with the π Nucleophile, C_6H_5F. The reactions of $[C_6F_5Xe][AsF_6]$ with monosubstituted benzenes, C_6H_5X (X = CH_3, F, CN, CF_3, or NO_2; 1.0−1.7 equiv), in CH_3CN at 20 °C have been previously reported.[22] In addition to isomeric mixtures of the polyfluorobiphenyls, $C_6F_5-C_6H_4X$, traces or minor amounts of C_6F_5H were obtained as products. Reaction rates

---

(20) Walker, D. A.; Woodman, T. J.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 3772−3776.

(21) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908−5912.

(22) Bardin, V. V.; Frohn, H.-J.; Klose, A. *J. Fluorine Chem.* **1993**, *64*, 201−215.

Table 3. Reactivities of $[C_6F_5Xe][BY_4]$ (Y = CF_3, C_6F_5, and CN), $[C_6F_5Xe][BF_4]$, and $[C_6F_5Xe][AsF_6]$ with C_6H_5F at 20 °C and Their C_6F_5-Containing Reaction Products

entry	$[C_6F_5Xe]^+$ salt	time,[a] days	solvent	equiv of C_6H_5F[b]	% conversion	$C_6F_5-C_6H_4F$[c]	C_6F_5H	C_6F_5X
1a	$[B(CF_3)_4]^-$	5	CH_3CN	20	100	31/29/38		
1b		0.010(3)	CH_2Cl_2		100	33/30/37		
2	$[B(C_6F_5)_4]^-$ [d]	6	CH_3CN		89	32/30/37	≤2	
3	$[B(CN)_4]^-$	6	CH_3CN		100	33/30/37		
4a	$[BF_4]^-$	15	CH_3CN		100	33/30/37		
4b		18	CH_3CN		100	32/30/38		
5a	$[AsF_6]^-$	4	CH_3CN		100	32/30/38		
5b	$[B(CF_3)_4]^-$	1.62(2)	CH_2Cl_2	1.2	82	18/19/22	41	
6a	$[B(CF_3)_4]^-$	0.069(3)	C_6H_5F	64	100	33/30/37		
6b	$[B(C_6F_5)_4]^-$ [d]	<0.010(3)	C_6H_5F	100	100	10/8/12	31	X = C_6F_5 (39)
7a	$[BF_4]^- + H_2O$[e]	0.250(6)	CH_3CN	20	100	32/30/38		
7b	$[BF_4]^- + 20\ H_2O$[e]	<0.017(3)	CH_3CN		100	32/30/38		
8a	$[AsF_6]^- + H_2O$[e]	0.792(6)	CH_3CN		96	32/30/38		
8b	$[AsF_6]^- + 20\ H_2O$[e]	0.017(3)	CH_3CN		88	32/30/38		
9a	C_6F_5XeF	0.021(3)	CH_2Cl_2, −40 °C	11	46	9/9/13	33	X = Cl (36)
9b	$[B(C_6F_5)_4]^-$ [d] + $[N(CH_3)_4]F$[f]	<0.010(3)	CH_2Cl_2, −55 °C[g]	20	100	22/32/26	15	X = C_6F_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 C_6H_5F that had been dried over P_4O_{10}. [c] The ratio of 2/3/4 isomers is given in mole percent. [d] This salt contains the $[C_6F_5XeNCCH_3]^+$ cation. [e] The relative molar amounts of the $[C_6F_5Xe]^+$ salt and H_2O are indicated. [f] Equimolar amounts of $[C_6F_5Xe][B(C_6F_5)_4]$ and $[N(CH_3)_4]F$ 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 $[C_6F_5Xe][AsF_6]$.

In the present study, the effects of the counteranion and the solvent (CH_3CN or CH_2Cl_2) on the reaction rates of $[C_6F_5Xe]^+$ with C_6H_5F 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 $[C_6F_5Xe]^+$ with C_6H_5F. The reaction of $[C_6F_5Xe][BY_4]$ with rigorously dried C_6H_5F (20 equiv) in CH_3CN proceeded slowly. To exclude the possibility of large uncertainties, a series of four identical experiments were carried out for the slowest reaction of $[C_6F_5Xe][BF_4]$ with C_6H_5F (20 equiv) in CH_3CN at room temperature. The result was comparable for all four experiments, ranging from 15 to 18 days for complete consumption of the $[C_6F_5Xe]^+$ cation.

The conversion times are similar for $[B(CF_3)_4]^-$ (ca. 5 days, entry 1a), $[B(C_6F_5)_4]^-$ (89% consumed after 6 days, entry 2), and $[B(CN)_4]^-$ (6 days, entry 3) but contrast with that of the less reactive $[BF_4]^-$ salt (15−18 days, entries 4a,b) and the somewhat more reactive $[AsF_6]^-$ salt (4 days, entry 5a) under the same conditions. In all cases, isomeric mixtures of polyfluorobiphenyls, $C_6F_5-C_6H_4F$, were obtained in nearly equimolar amounts of 2-, 3-, and 4-isomers, whereas C_6F_5H was only detected (≤2%) in the case of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$. It is noteworthy that the single 4-position of C_6H_5F is arylated twice as often as the two 2- and 3-positions to give $C_6F_5-C_6H_4F$, which is likely a consequence of the higher negative charge on carbon in the 4-position.

The reaction rates with C_6H_5F are 4−8 times faster than the decomposition rates of $[C_6F_5Xe][BY_4]$ salts in CH_3CN in the absence of C_6H_5F, where C_6F_5H was the only (Y = CF_3 or CN) or main (Y = C_6F_5) reaction product (Table 2). The experimental results are therefore consistent with coordination of the π nucleophile, C_6H_5F, 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 $C_6F_5^{\bullet}$ radical can combine, in a cage, with a $C_6H_4F^{\bullet}$ radical, which results from a one-electron transfer, and is accompanied by the elimination of Xe^0 and H^+ from the intermediate radical cation, $[XeC_6H_5F]^{\bullet+}$ (eq 22). The ability of C_6H_5F to coordinate to $[C_6F_5Xe]^+$ is enhanced when the coordinating abilities of the $[BY_4]^-$ anion and solvent are weaker. From the reactivities of their $[C_6F_5Xe]^+$ cations in CH_3CN, it may be concluded that the coordination abilities of the $[BY_4]^-$ anions increase in the order $[B(CF_3)_4]^- < [B(CN)_4]^- < [B(C_6F_5)_4]^- \ll [BF_4]^-$.

$$[C_6F_5Xe]^+ + C_6H_5F \rightarrow [C_6F_5XeC_6H_5F]^+ \qquad (21)$$

$$[C_6F_5XeC_6H_5F]^+ \rightarrow C_6F_5C_6H_4F + Xe^0 + H^+_{solv} \qquad (22)$$

The reactivity of the $[C_6F_5Xe]^+$ cation toward C_6H_5F (20 equiv) was significantly enhanced when the strongly coordinating CH_3CN solvent was replaced by the weakly coordinating solvent, CH_2Cl_2. In CH_2Cl_2, $[C_6F_5Xe][B(CF_3)_4]$ was consumed in only 15 min (entry 1b), compared to 5 days in CH_3CN (entry 1a), forming only $C_6F_5-C_6H_4F$. The reaction proceeded more slowly in CH_2Cl_2 when only 1.2 equiv of C_6H_5F was used (82% conversion of $[C_6F_5Xe][B(CF_3)_4]$ after 1.62 days; entry 5b), showing that the reaction is not initiated by CH_2Cl_2 coordination to the cation because C_6F_5H (41%) is formed and C_6F_5Cl is absent (eqs 23 and 24).

$$C_6F_5^{\bullet} + C_6H_5F \rightarrow C_6F_5H + C_6H_4F^{\bullet} \qquad (23)$$

$$C_6F_5^{\bullet} + C_6H_4F^{\bullet} \rightarrow C_6F_5-C_6H_4F \qquad (24)$$

In contrast, only 50% of $[C_6F_5Xe][B(CF_3)_4]$ reacted after 22 days in CH_2Cl_2 in the absence of C_6H_5F, yielding C_6F_5Cl as the major product (80%) and C_6F_5H (20%) (Table 2, entry 1b). The rapid reaction of $[C_6F_5Xe][A]$ with C_6H_5F in CH_2Cl_2 and the dependence of the reaction rate on the C_6H_5F concentration clearly demonstrate that the interaction of $[C_6F_5Xe]^+$ with the π nucleophile is favored in the presence of a weakly coordinating anion and solvent. The $[C_6F_5Xe][B(CF_3)_4]$ and $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ salts have solubilities comparable to those of CH_3CN in C_6H_5F and react rapidly with neat C_6H_5F, whereas $[C_6F_5Xe][B(CN)_4]$, $[C_6F_5Xe][BF_4]$, and $[C_6F_5Xe][AsF_6]$ are insoluble in C_6H_5F. The $[C_6F_5Xe]^+$ cation of $[C_6F_5Xe][B(CF_3)_4]$ is completely reacted within 100 min in C_6H_5F (64 equiv), exclusively yielding an isomeric mixture of hexafluorobiphenyls (entry 6a), which supports the proposed reaction path (eqs 21 and 22). The reaction between $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ and C_6H_5F (100 equiv) proceeded more than 4 times faster, but the product distribution differed. In addition to $C_6F_5{-}C_6H_4F$ (30%), C_6F_5H (31%), and $(C_6F_5)_2$ (39%) were formed (entry 6b). The latter product again supports attack by the $[C_6F_5Xe]^+$ cation at the nucleophilic *ipso*-carbon of the anion (eqs 17 and 18) as a significant competing reaction pathway, with the formation of C_6F_5H arising from $C_6F_5^{\bullet}$ radical attack on C_6H_5F (eq 23) or coordinated CH_3CN (eqs 3−6).

(ii) Effects of H_2O and F^- on the Reactivity of $[C_6F_5Xe]^+$ with C_6H_5F. When the reactions of $[C_6F_5Xe][BY_4]$ salts in CH_3CN were initially carried out with freshly distilled, but not rigorously dried C_6H_5F (1.2 equiv), the reaction rates accelerated for the $[BF_4]^-$, $[B(CF_3)_4]^-$, and $[AsF_6]^-$ salts but were less affected for the $[B(C_6F_5)_4]^-$ salt. In all cases, minor amounts of C_6F_5H were detected in addition to $C_6F_5{-}C_6H_4F$.

In order to evaluate the influence of water on this reaction in a controlled manner, the reactions of $[C_6F_5Xe][BF_4]$ and $[C_6F_5Xe][AsF_6]$ with rigorously dried C_6H_5F (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 $[BF_4]^-$ salt reacting slightly faster than the $[AsF_6]^-$ salt. In the presence of 1 equiv of H_2O, the $[C_6F_5Xe]^+$ cation of the $[AsF_6]^-$ 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 $C_6F_5{-}C_6H_4F$ isomers, the only C_6F_5-containing products, were not noticeably influenced by the presence of H_2O. The absence of C_6F_5H in experiments where H_2O was added confirms that C_6F_5H formed during the decomposition of $[C_6F_5Xe]^+$ 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 $[C_6F_5Xe]^+$ and subsequent solvent-assisted deprotonation to give the presently unknown C_6F_5XeOH molecule (eq 25) as an unstable reaction intermediate may account for the products and enhanced reactivities (cf. the reaction of C_6F_5XeF with C_6H_5F in CH_2Cl_2 discussed below). The $C_6F_5^{\bullet}$ radical, resulting from the

$$[C_6F_5Xe]^+ + H_2O \rightarrow [C_6F_5Xe{-}OH_2]^+ \rightarrow C_6F_5XeOH + H^+_{solv} \quad (25)$$

$$C_6F_5XeOH \rightarrow C_6F_5^{\bullet} + {}^{\bullet}XeOH \quad (26)$$

decomposition of C_6F_5XeOH (eq 26), may add preferentially to C_6H_5F without attacking CH_3CN. The $C_6F_5{-}C_6H_4F$ products, in the absence of C_6F_5H, agree with this interpretation.

In order to compare the relative influences of water and fluoride ion, the reactivities of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ in CH_2Cl_2 in the presence of both C_6H_5F and a “naked” fluoride ion, $[N(CH_3)_4]F$, which yields C_6F_5XeF,[8,23] were also studied. As a result of the strong interaction between $[C_6F_5Xe]^+$ and F^-, which leads to the 3c−4e-bonded C_6F_5XeF molecule, C_6H_5F coordination to xenon is expected to be inhibited, so that the rate of $C_6F_5{-}C_6H_4F$ formation decreases. In order to test this hypothesis, C_6F_5XeF 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]

$$[C_6F_5XeNCCH_3][B(C_6F_5)_4] + [N(CH_3)_4]F \xrightarrow[-80\ °C]{CH_2Cl_2} C_6F_5XeF + [N(CH_3)_4][B(C_6F_5)_4]\downarrow + CH_3CN \quad (27)$$

At −40 °C, 46% of C_6F_5XeF reacted in CH_2Cl_2 in the presence of C_6H_5F (11 equiv) within 30 min, forming C_6F_5Cl (36%), C_6F_5H (33%), and $C_6F_5{-}C_6H_4F$ (31%) (entry 9a). The products, C_6F_5Cl and C_6F_5H, likely result from $C_6F_5^{\bullet}$ radical attack on CH_2Cl_2 (eqs 13−15). A reaction mixture consisting of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, C_6H_5F (20 equiv), and $[N(CH_3)_4]F$ (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 $C_6F_5{-}C_6H_4F$ (80%), $(C_6F_5)_2$ (5%), and C_6F_5H (15%) (see Table 3, entry 9b).

Characterization of $[C_6F_5Xe][BY_4]$ ($Y = CF_3$, C_6F_5, CN, or $OTeF_5$) and $[C_6F_5Xe][BF_4]$ by Multi-NMR Spectroscopy. Since the discovery of the $[C_6F_5Xe]^+$ cation, NMR data for $[C_6F_5Xe]^+$ salts having different counteranions such as $[AsF_6]^-$,[17,24,25] $[PF_6]^-$,[24] $[SiF_5]^-$,[26] $[BF_4]^-$,[18] $[(C_6F_5)_nBF_{4-n}]^-$,[1,2,25,27,28] $[E(SO_2CF_3)_{n-1}]^-$ (E = O, N, and C),[24] and $[HF_2]^-$ [29] have been reported.[4,5] However, only two of the six possible $^{19}F{-}^{19}F$ couplings in the aryl group have

---

(23) Frohn, H. -J.; Theissen, M. *J. Fluorine Chem.* **2004**, *125*, 981−988.

(24) Franke, H. Doctoral Dissertation, Gerhard-Mercator Universität, Duisburg, Germany, 2000.

(25) Schroer, T. Doctoral Dissertation, Gerhard-Mercator Universität, Duisburg, Germany, 1996.

(26) Scholten, T. Doctoral Dissertation, Gerhard-Mercator Universität, Duisburg, Germany, 1996.

(27) Jakobs, S. Doctoral Dissertation, Gerhard-Mercator Universität, Duisburg, Germany, 1991.

(28) Klose, A. Doctoral Dissertation, Gerhard-Mercator Universität, Duisburg, Germany, 1993.

(29) Frohn, H.-J.; Schroer, T. *J. Fluorine Chem.* **2001**, *112*, 259−264.

been extracted from the ^{19}F spectra in the course of these studies, namely, $^3J(^{19}F_o-^{19}F_p)$ (J_{24}) and $^4J(^{19}F_m-^{19}F_p)$ (J_{34}), but all three possible ^{129}Xe−^{19}F couplings, $^3J(^{19}F_o-^{129}Xe)$, $^4J(^{19}F_m-^{129}Xe)$, and $^5J(^{19}F_p-^{129}Xe)$, have been reported.[1,2] Moreover, the relative signs of the reported couplings have not been assigned. The availability of new $[C_6F_5Xe][BY_4]$ (Y = CF_3, C_6F_5, CN, or $OTeF_5$) salts that are soluble in neutral polar solvents provided an opportunity to characterize these salts by ^{19}F, ^{11}B, ^{13}C, and ^{129}Xe NMR spectroscopy (Table 4) with the view to provide, for the first time, a complete determination of the ^{19}F and ^{129}Xe NMR parameters of the $[C_6F_5Xe]^+$ cation and to correlate the nature of the $[C_6F_5Xe]^+$ cation−solvent interaction with its NMR parameters.

(a) Simulation of $[C_6F_5Xe]^+$ ^{19}F and ^{129}Xe NMR Spectra. The ^{19}F NMR spectra of $[C_6F_5Xe][BY_4]$ are well-resolved at 7.0463 T, exhibiting complex multiplet structures for the *o*- and *m*-C_6F_5 fluorine resonances and a triplet (J_{34}) of triplets (J_{24}) for the *p*-C_6F_5 fluorine resonance (Figure 1). All C_6F_5 resonances are accompanied by ^{129}Xe satellites ($I = ^1/_2$, 26.44%) arising from $^3J(^{19}F_o-^{129}Xe)$, $^4J(^{19}F_m-^{129}Xe)$, and $^5J(^{19}F_p-^{129}Xe)$ spin−spin couplings. The improved resolution afforded in the present circumstances provided the first fully resolved ^{129}Xe NMR spectra of $[C_6F_5Xe]^+$ (Figure 2), showing all of the expected ^{19}F−^{129}Xe spin−spin couplings as a triplet (o) of triplets (m) of doublets (p). The $^3J(^{19}F_o-^{129}Xe)$ and $^5J(^{19}F_p-^{129}Xe)$ spin−spin coupling constants were found to be identical, within experimental error, to those obtained in previous studies, whereas the $^4J(^{19}F_m-^{129}Xe)$ coupling was found to be significantly smaller (8.8 Hz) than that published earlier from ^{19}F NMR spectra (18.7−19.5 Hz).[1−3]

The present ^{19}F and ^{129}Xe NMR spectral simulations for $[C_6F_5Xe][B(CN)_4]$ have yielded the first complete set of $J(^{19}F-^{19}F)$ couplings and assignments of their relative signs for $[C_6F_5Xe]^+$. The ^{19}F and ^{129}Xe NMR spectra of the $[B(CN)_4]^-$ salt in CH_3CN solution were better resolved and therefore were used for spectral simulations. The spectrum of isoelectronic C_6F_5I was also compared and, in this case, chemical shifts and *J* couplings were remeasured in CD_3CN at 24 °C and used for simulation of the ^{19}F NMR spectrum. The ^{19}F ($[C_6F_5Xe]^+$ and C_6F_5I) and ^{129}Xe ($[C_6F_5Xe]^+$) 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 ^{19}F (100%) and ^{129}Xe (26.44%). In the case of C_6F_5I, complete quadrupolar collapse of the ^{127}I−^{19}F couplings was assumed. Full spectral simulations were achieved under C_{2v} symmetry for both $[C_6F_5Xe]^+$ and C_6F_5I. In the case of $[C_6F_5Xe]^+$, only the values of J_{24} and J_{34} were readily available from the $^{19}F_p$ multiplet, while $^3J(^{129}Xe-^{19}F_o)$ (67.7 Hz), $^4J(^{129}Xe-^{19}F_m)$ (8.8 Hz), and $^5J(^{129}Xe-^{19}F_p)$ (3.7 Hz) were obtained from the ^{129}Xe NMR spectrum. Preliminary values for J_{24}, J_{26}, J_{35}, and J_{25} were calculated from empirical relationships between $\delta(^{19}F_p) = -140.9$ ppm and the fluorine−fluorine coupling constants of the C_6F_5 group (eqs 28−31)[31,32] and were then manually iterated to give the best spectral fits.

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

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

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

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

The signs of the coupling constants used for the simulations are relative and have not been experimentally determined; however, extensive studies made on C_6F_5 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 C_6F_5I as well as for most other C_6F_5 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 C_6F_5I (−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 C_6F_5I), and (3) the J_{34} and J_{23} couplings are negative and similar in magnitude for both $[C_6F_5Xe]^+$ and C_6F_5I.

When $[C_6F_5Xe]^+$ and isoelectronic C_6F_5I 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 C_6F_5I, but comparable negative values have been observed for $C_6F_5SO_2Cl$[33,34] and $C_6F_5NO_2$.[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 $[C_6F_5Xe]^+$. Two sets of conditions may be distinguished: (1) the anions are weakly coordinating when compared with CH_3CN and (2) both the anion and the solvent are weakly coordinating.

In the first case, very similar ^{19}F NMR chemical shifts are obtained for $[C_6F_5Xe][BY_4]$, $[C_6F_5Xe][BF_4]$, and $[C_6F_5Xe][AsF_6]$ when dissolved in CH_3CN (Table 4). This is consistent with $[C_6F_5XeNCCH_3]^+$ formation and counter-

---

(30) Santry, D. P.; Mercier, H. P. A.; Schrobilgen, G. J. *ISOTOPOMER, A Multi-NMR Simulation Program*, version 3.02NTF; Snowbird Software, Inc.: Hamilton, Ontario, Canada, 2000.

(31) Pushkina, L. N.; Stepanov, A. P.; Zhukov, V. S.; Naumov, A. D. *J. Org. Chem. USSR* **1972**, *8*, 586−597.

(32) Pushkina, L. N.; Stepanov, A. P.; Zhukov, V. S.; Naumov, A. D. *Org. Magn. Reson.* **1972**, *4*, 607−623.

(33) Bruce, M. I. *J. Chem. Soc. A* **1968**, 1459−1464.

(34) Moniz, W. B.; Lustig, E.; Hanzen, E. A. *J. Chem. Phys.* **1969**, *51*, 4666−4669.

(35) Fields, R.; Lee, J.; Mowthorpe, D. J. *J. Chem. Soc. B* **1968**, 308−312.

Table 4. ^{19}F, ^{13}C, ^{11}B, ^{10}B, and ^{129}Xe NMR Parameters for $[C_6F_5Xe]^{+}$ [a] in $[C_6F_5Xe][BY_4]$ (Y = CF_3, C_6F_5, CN, or $OTeF_5$), $[C_6F_5Xe][BF_4]$, $[C_6F_5Xe][AsF_6]$, $[C_6F_5Xe][SiF_5]$, and $[C_6F_5Xe][HF_2]$

^{19}F NMR spectra

$[C_6F_5Xe]^+$ salt	o-C_6F_5 (ppm)	$^3J(^{19}F-^{129}Xe)$ (Hz)	p-C_6F_5 (ppm)	$^3J(^{19}F-^{19}F)$ (Hz)	$^4J(^{19}F-^{19}F)$ (Hz)	$^5J(^{19}F-^{129}Xe)$ (Hz)	m-C_6F_5 (ppm)	$^4J(^{19}F-^{129}Xe)$ (Hz)	anion in ^{11}B [^{10}B] (ppm)	solvent	T (°C)
$[BF_4]^-$	−124.8	66.6	−141.9	20.0	5.6	4.2	−154.7	8.6	−148.4 [n.o.]	CH_3CN	24
$[B(C_6F_5)_4]^-$	−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)		
$[B(CN)_4]^-$	−124.5	67.7	−140.9	20.0	5.6	3.7	−153.8	8.8	–		
$[B(CF_3)_4]^-$	−124.8	67.5	−141.0	19.9	5.6	3.6	−154.0	8.8	−61.3 [−61.3]		
$[B(OTeF_5)_4]^-$	−125.5	68	−141.8	20	6	4	−154.7	9	−38.8 (F_A) −45.4 (F_B)		
$[AsF_6]^-$	−124.8	67.8	−141.3	20.0	5.6	n.r.	−154.2	8.6	−64.1 ($[AsF_6]^-$)		
$[SiF_5]^-$ [b]	−126.8	n.r.	−143.0	n.r.	n.r.	n.r.	−154.9	n.r.	–		
$[HF_2]^-$ [c]	−127.1	73	−144.6	n.r.	n.r.	n.r.	−156.1	n.r.	–		
$[B(CF_3)_4]^-$	−123.4	66.5	−135.3	20.9	6.6	2.2	−149.6	8.8	−63.9 [−63.9]	CH_2Cl_2	24
$[BF_4]^-$	−125.5	68.1	−142.3	20.5	5.3	n.r.	−155.1	n.r.	−148.7 [n.o.]	CH_3CN	−40
$[B(C_6F_5)_4]^-$	−125.5	68.9	−141.7	20.5	5.5	n.r.	−154.5	n.r.	−132.9 (o) −162.2 (p) −166.7 (m)		
$[B(CN)_4]^-$	−125.2	69.3	−141.4	20.5	5.4	n.r.	−154.2	n.r.	–		
$[B(CF_3)_4]$	−125.5	68.9	−141.6	20.4	5.4	n.r.	−154.5	n.r.	−61.9 [−61.8]		
$[B(CF_3)_4]^-$	−124.6	68.3	−137.1	21.9	5.5	n.r.	−150.8	n.r.	−63.9 [−63.9]	CH_2Cl_2	−80
$[B(CF_3)_4]^-$	−124.3	62.9	−138.9	18.9	6.2	n.r.	−152.3	n.r.	−60.1 [−60.1]	PFB	24
$[BF_4]^-$	−123.6	58.1	−138.2	18.8	6.4	n.r.	−151.8	n.r.	−148.6 [−148.6]	aHF	−40

^{13}C NMR spectra

	$[C_6F_5Xe]^+$ cation												anion		
	C(3,5)			C(4)				C(2,6)			C(1)				
$[C_6F_5Xe^+]$ salt	δ (ppm)	$^1J(^{13}C-^{19}F)$ (Hz)	$^2J(^{13}C-^{19}F)$ (Hz)	δ (ppm)	$^1J(^{13}C-^{19}F)$ (Hz)	$^2J(^{13}C-^{19}F)$ (Hz)	$^3J(^{13}C-^{19}F)$ (Hz)	δ (ppm)	$^1J(^{13}C-^{19}F)$ (Hz)	$^2J(^{13}C-^{19}F)$ (Hz)	δ (ppm)	$^1J(^{13}C-^{129}Xe)$ (Hz)	anion in ^{11}B [^{10}B] (ppm)	$^1J(^{13}C-^{11}B)$ [$^1J(^{13}C-^{10}B)$] [Hz]	solvent T (°C)
$[BF_4]^-$	139.7	260.1	15.3	146.9	260.2	13.4	4.5	145.4	257.8	14.9	84.3	113.0	–	–	CH_3CN 24
$[B(C_6F_5)_4]^-$	140.1	259.1	14.6	147.2	262.4	13.3	4.5	145.5	258.2	14.9	84.7	114.4	149.5, C(2,6)[d] 137.8, C(3,5)[e] 139.7, C(4)[f] 125.3, C(1)	51.9, C(1) [17.2, C(1)]	
$[B(CN)_4]^-$	140.0	259.1	15.0	147.1	262.4	13.3	4.5	145.4	257.0	14.9	84.6	114.2	123.5	71.0	
$[B(CF_3)_4]^-$	140.0	258.2	15.2	147.1	262.4	13.3	4.5	145.4	259.1	15.2	84.4	114.4	133.2[g]	73.4	
$[AsF_6]^-$	140.0	257.0	15.3	147.0	261.8	13.3	4.5	145.4	259.2	13.1	83.9	n.r.	–	–	
$[BF_4]^-$	139.0	–	–	146.0	–	–	–	144.6	–	–	83.8	117.2	–	–	CH_3CN −40
$[B(C_6F_5)_4]^-$	139.2	–	–	146.2	–	–	–	144.6	–	–	84.0	118.7	148.6, C(2,6) 136.9, C(3,5) 138.9, C(4) 124.2, C(1)	50.8, C(1) [17.7, C(1)]	
$[B(CN)_4]^-$	139.2	–	–	146.3	–	–	–	144.6	–	–	84.0	118.1	122.8 [122.8]	71.4 [23.8]	
$[B(CF_3)_4]^-$	139.1	–	–	146.2	–	–	–	144.5	–	–	83.7	119.1	n.r.	n.r.	
$[AsF_6]^-$	139.1	–	–	146.2	–	–	–	144.6	–	–	83.7	118.6	–	–	

anions that are less basic than CH_3CN. 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 $[C_6F_5Xe][B(CF_3)_4]$ has sufficient stability and solubility in the weakly coordinating solvents CH_2Cl_2 and PFB (stable at 20 °C for more than 3 and 5 days, respectively, contrasting with CH_2Cl_2 solutions of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ and $[C_6F_5Xe][B(OTeF_5)_4]$, which must be maintained below −40 °C to avoid rapid decomposition) to allow NMR studies in these media. A comparison of the ^{19}F NMR chemical shifts of $[C_6F_5Xe][B(CF_3)_4]$ in CH_2Cl_2, PFB, and CH_3CN at 24 °C (Table 4) shows that the fluorine resonances of the C_6F_5 group are shifted to higher frequencies (deshielded) in CH_2Cl_2 (~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 CH_3CN, consistent with a more weakly coordinated $[C_6F_5Xe]^+$ cation and significant polarization of the C_6F_5 group by Xe^{II}.

A more weakly coordinated $[C_6F_5Xe]^+$ cation was also achieved by dissolution of $[C_6F_5Xe][BF_4]$ in aHF. The ^{19}F NMR chemical shifts at −40 °C are similar to those obtained for $[C_6F_5Xe][B(CF_3)_4]$ in PFB at 24 °C (Table 4). Hydrogen fluoride presumably solvates the anion, resulting in a much larger $[BF_4{\bullet}(HF)_n]^-$ anion, which disperses the negative charge over more than four fluorine atoms, rendering it less basic. The $[BF_4{\bullet}(HF)_n]^-$ anion exhibits a broadened 1:1:1:1 quartet in the ^{19}F NMR spectrum at −148.6 ppm and a quintet splitting in the ^{11}B NMR spectrum at −1.3 ppm that arises from $^1J(^{19}F-^{11}B) = 11.5$ Hz. The quartet in the ^{19}F NMR spectrum arises because the electric field gradient at the quadrupolar ^{11}B 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 $^1J(^{19}F-^{10}B)$ was insufficiently resolved to provide a directly measured value for this coupling constant (calcd, 3.9 Hz).

The ^{129}Xe NMR chemical shifts of $[C_6F_5Xe][BY_4]$ and $[C_6F_5Xe][BF_4]$ in CH_3CN at 24 °C differ only slightly, ranging from −3792.6 ($[B(CN)_4]^-$) to −3802.8 ppm ($[BF_4]^-$), having spin−spin coupling constants of $^3J(^{19}F_o-^{129}Xe) = 66.6$ ($[BF_4]^-$) to 67.6 Hz ($[B(C_6F_5)_4]^-$), $^4J(^{19}F_m-^{129}Xe) = 8.6$ ($[BF_4]^-$) to 9.1 Hz ($[B(C_6F_5)_4]^-$), and $^5J(^{19}F_p-^{129}Xe) = 3.6$ ($[B(CF_3)_4]^-$) to 4.2 Hz ($[BF_4]^-$) (Table 4). The temperature dependencies of the ^{129}Xe NMR chemical shifts of $[C_6F_5Xe]^+$ salts are in good agreement with the previously published results for $[C_6F_5Xe][AsF_6]$ in CD_3CN/C_2H_5CN (1:3, v/v) of -0.35 ppm K^{-1}.[36] The ^{129}Xe NMR chemical shifts of the $[C_6F_5Xe][BY_4]$ salts in CH_3CN at −40 °C (−3772.2 to −3783.0 ppm) are only slightly shifted to higher frequency when compared with that of C_6F_5XeF (−3793.4 ppm) in CH_2Cl_2 at −40 °C. The chemical shifts

	^{11}B NMR spectra			^{129}Xe NMR spectra					
$[C_6F_5Xe]^-$ salt	$\delta(^{11}B)$ (ppm)	$J(^{11}B-^{19}F)$ (Hz)	$^1J(^{11}B-^{13}C)$ (Hz)	$\delta(^{129}Xe)$ (ppm)	$^3J(^{19}F-^{129}Xe)$ (Hz)	$^4J(^{19}F-^{129}Xe)$ (Hz)	$^5J(^{19}F-^{129}Xe)$ (Hz)	solvent	T (°C)
$[BF_4]$	−1.5	n.r.	n.r.	−3802.8	66.6	8.6	4.2	CH_3CN	24
$[B(C_6F_5)_4]^-$	−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		
$[B(CF_3)_4]^-$	−19.1	25.9	73.4	−3802.0	67.5	8.8	3.6		
$[AsF_6]^-$	–	–	–	−3802.3	67.8	8.6	n.r.		
$[B(CF_3)_4]^-$	−19.1	25.9	73.2	−3821.1	62.9	8.7	n.r.	PFB	24
$[BF_4]$	−1.3	11.5	–	−3831.5	58.1	n.r.	n.r.	aHF	−40
$[BF_4]^-$	–	–	–	−3783.0	68.1	n.r.	n.r.	CH_3CN	−40
$[B(C_6F_5)_4]^-$	–	–	–	−3772.2	68.9	n.r.	n.r.		
$[B(CN)_4]^-$	–	–	–	−3776.7	69.3	n.r.	n.r.		
$[B(CF_3)_4]^-$	–	–	–	−3779.6	68.9	n.r.	n.r.		
$[AsF_6]$	–	–	–	−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] $^1J(^{13}C(2,6)-^{19}F) = 241.1$ Hz; $^2J(^{13}C(2,6)-^{19}F)$ was not resolved. [e] $^1J(^{13}C(3,5)-^{19}F) = 243.8$ Hz; $^2J(^{13}C(3,5)-^{19}F) = 13.9$ Hz. [f] $^1J(^{13}C(4)-^{19}F) = 244.7$ Hz; $^2J(^{13}C(4)-^{19}F) = 14.0$ Hz. [g] $^1J(^{13}C(1)-^{11}B) = 73.4$ Hz; $^3J(^{13}C(1)-^{19}F) = 3.8$ Hz; $^1J(^{13}C-^{19}F) = 304.3$ Hz.

---

(36) Bardin, V. V.; Frohn, H.-J. *Magn. Reson. Chem.* **2006**, *44*, 648−650.

(37) Bernhardt, E.; Henkel, G.; Willner, H.; Pawelke, G.; Bürger, H. *Chem.*−*Eur. J.* **2001**, *7*, 4696−4705.

(38) Bernhardt, E.; Henkel, G.; Willner, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 560−568.

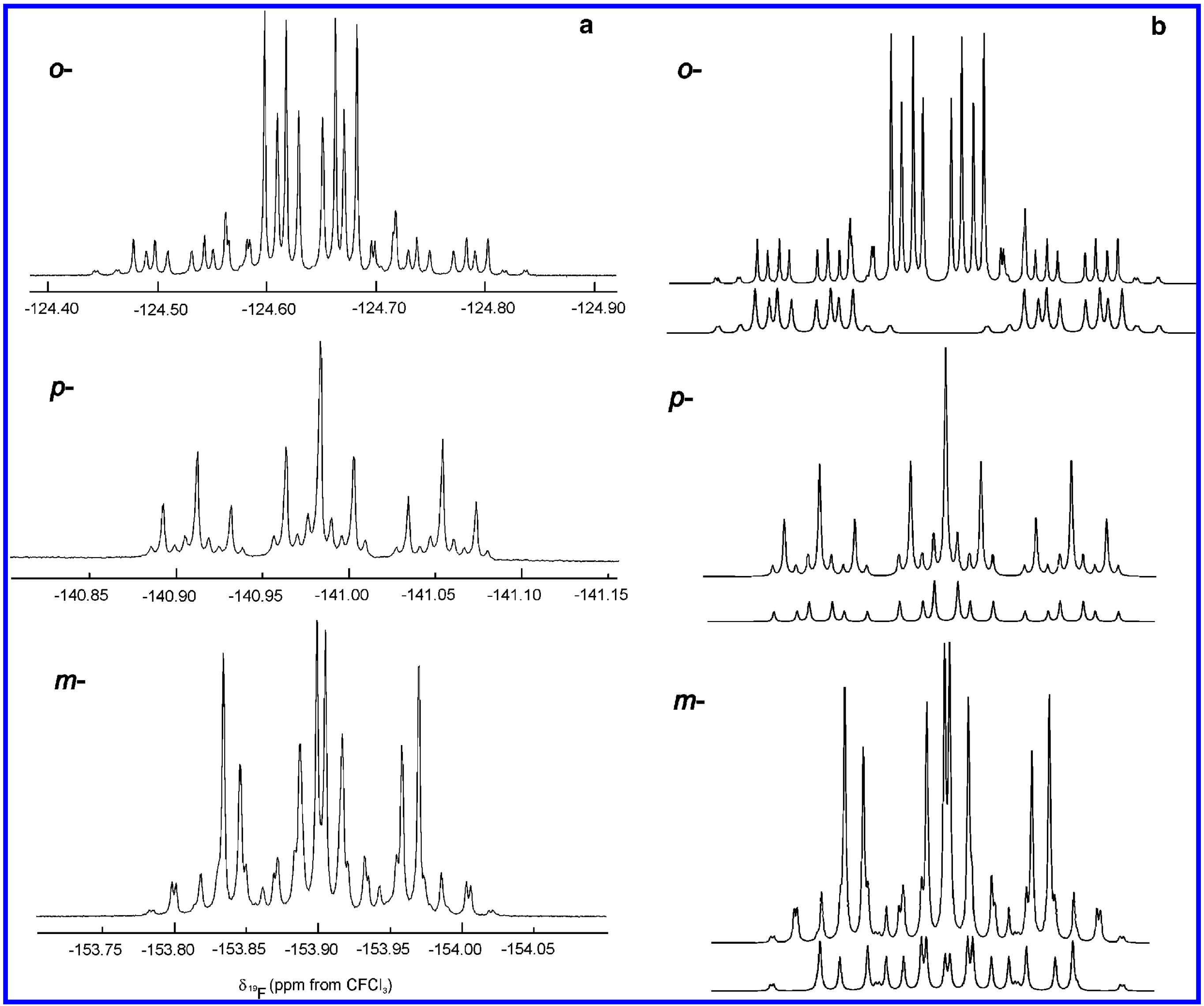

Figure 1. ^{19}F NMR spectra (282.40 MHz) of the *o*-, *p*- and *m*-C_6F_5 fluorine resonances of the $[C_6F_5Xe]^+$ cation in $[C_6F_5Xe][B(CN)_4]$ recorded in CH_3CN at 24 °C. Spectra were resolution-enhanced by Gaussian multiplication (**a** traces). The simulated spectra (**b** traces) are provided 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 $[C_6F_5XeNCCH_3]^+$ formation and are very similar to those reported previously for $[B(CF_3)_4]^-$,[37] $[B(CN)_4]^-$,[38] and $[B(C_6F_5)_4]^-$ [39] and are therefore not discussed.

Generally, the nature of the counteranion influences the $^3J(^{19}F_o{-}^{129}Xe)$ coupling constant, which is 68 ± 1 Hz for $[C_6F_5XeNCCH_3]^+$ in the presence of weakly coordinating $[BY_4]^-$ anions and 70 and 73 Hz in the case of more nucleophilic anions such as $[SiF_5]^-$ [26] and $[HF_2]^-$,[29] respectively. The more strongly coordinating the anion is, the greater the magnitude of the $^3J(^{19}F_o{-}^{129}Xe)$ coupling, trending toward 80 Hz in C_6F_5XeF (CH_2Cl_2, −80 °C; see the Experimental Section) and 94.2 Hz in C_6F_5XeCl (CH_2Cl_2, −60 °C).[7]

Conclusions

The $[C_6F_5Xe]^+$ salts of the weakly coordinating $[BY_4]^-$ (Y = CF_3, C_6F_5, CN, or $OTeF_5$) anions, which were obtained by the metatheses of $[C_6F_5Xe][BF_4]$ and $M^I[BY_4]$ 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, $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, was the least stable among the $[C_6F_5Xe]^+$ salts considered in both the solid state and in weakly coordinating CH_2Cl_2 and strongly coordinating CH_3CN solvents.

In all cases except $[B(C_6F_5)_4]^-$, the only decomposition product was C_6F_5H in CH_3CN, whereas the decomposition of $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ in CH_2Cl_2 yielded significant amounts of $(C_6F_5)_2$, which resulted from cation attack at the nucleophilic *ipso*-carbon of the anion. The decompositions of $[C_6F_5Xe][BY_4]$ (Y = CF_3 or $OTeF_5$) in CH_2Cl_2 result in hydrogen and chlorine abstraction by the $C_6F_5^\bullet$ radical, whereas $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ also forms significant quantities of $(C_6F_5)_2$.

In general, $[C_6F_5Xe][BY_4]$ salts exhibited a range of stabilities, which were not leveled by coordination of the

---

(39) Jutzi, P.; Müller, C.; Stammler, A.; Stammler, H.-G. *Organometallics* **2000**, *19*, 1442−1444.

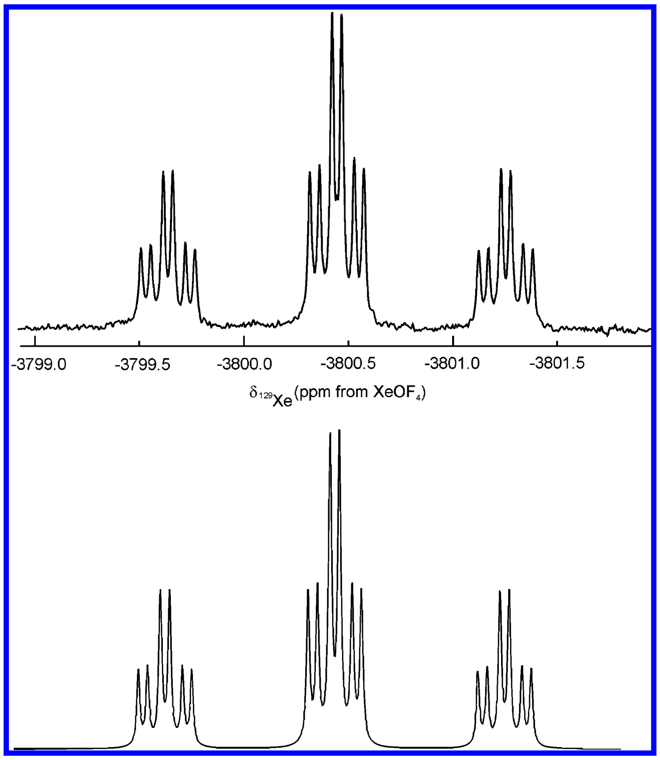

Figure 2. ^{129}Xe NMR spectrum (83.02 MHz) of the $[C_6F_5Xe]^+$ cation in $[C_6F_5Xe][B(CN)_4]$ recorded in CH_3CN at 24 °C. The spectrum was resolution-enhanced by Gaussian multiplication. The simulated spectrum is provided for comparison (bottom trace).

nucleophile, CH_3CN. Accordingly, the reactivities of $[C_6F_5Xe][BY_4]$ with an excess of the π nucleophile, C_6H_5F, differed in CH_3CN. All reactions of $[C_6F_5Xe][BY_4]$ with C_6H_5F 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., H_2O) or anionic (e.g., F^-) nucleophiles. The major products in all of these reactions were isomeric mixtures of hexafluorobiphenyls, $C_6F_5-C_6H_4F$. Their formation proceeded faster in weakly coordinating CH_2Cl_2 than in strongly coordinating CH_3CN. The factors that influence the rates of pentafluorophenylation and the product distributions are in accordance with the intermediate coordination of C_6H_5F at $[C_6F_5Xe]^+$ and the subsequent radical attack of C_6H_5F by $C_6F_5\bullet$.

The ^{19}F NMR parameters of the $[C_6F_5Xe]^+$ cation in the present series of salts are shown to reflect the relative degrees of cation−solvent interactions. The high-frequency shifts of the ^{19}F NMR resonances of $[C_6F_5Xe]^+$ in CH_2Cl_2 and PFB are consistent with a more weakly coordinated $[C_6F_5Xe]^+$ cation and significant polarization of the C_6F_5 group by Xe^{II} relative to the ^{19}F NMR chemical shifts obtained for $[C_6F_5Xe]^+$ in CH_3CN solutions of $[C_6F_5Xe][BY_4]$ ($Y = CF_3$, C_6F_5, CN, or $OTeF_5$) and $[C_6F_5Xe][BF_4]$. In the latter case, the enhanced shielding and narrow chemical shift range are consistent with $[C_6F_5XeNCCH_3]^+$ formation. The ^{19}F NMR chemical shifts of $[C_6F_5Xe][BF_4]$ in aHF are similar to those obtained for $[C_6F_5Xe][B(CF_3)_4]$ in a PFB solution and are also indicative of a weakly coordinated $[C_6F_5Xe]^+$ cation. Hydrogen fluoride presumably solvates the anion, resulting in a much larger $[BF_4\bullet(HF)_n]^-$ anion, which disperses the negative charge over more than four fluorine atoms, rendering it less basic. Simulations of the ^{19}F and ^{129}Xe NMR spectra of $[C_6F_5Xe]^+$ have provided the complete set of aryl $^{19}F-^{19}F$ and $^{129}Xe-^{19}F$ coupling constants and their relative signs, which are in accord with those of isoelectronic C_6F_5I.

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; $H_2O < 1$ 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 $KMnO_4$ (5 g L^{-1} of CH_3CN), distilled, repeatedly refluxed with P_4O_{10} and distilled until the P_4O_{10} suspension was colorless. Finally, CH_3CN 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 P_4O_{10}, distilled, and stored over dry 3 Å molecular sieves. Two grades of C_6H_5F (Fluorochem Ltd.) were used in this study: (1) redistilled C_6H_5F that had been stored under argon and (2) C_6H_5F that had been freshly refluxed with P_4O_{10}, distilled, and stored over 3 Å molecular sieves. Benzotrifluoride, $C_6H_5CF_3$ (Aldrich; >99%, anhydrous), was stored over dry 3 Å molecular sieves.

Sulfuryl chloride fluoride, SO_2ClF (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 described[42] 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 ^{19}F NMR spectroscopy at 24 °C.

Xenon difluoride was prepared by the thermal method described in the literature.[44] The starting materials, $B(C_6F_5)_3$[45,46] (also see the Supporting Information), $Cs[B(C_6F_5)_4]$[46] (also see the Supporting

---

(40) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.
(41) Schrobilgen, G. J.; Holloway, J. H.; Granger, P.; Brevard, C. *Inorg. Chem.* **1978**, *17*, 980−987.
(42) Emara, A. A. A.; Schrobilgen, G. J. *Inorg. Chem.* **1992**, *31*, 1323−1332.
(43) Ignatév, N.; Sartori, P. *J. Fluorine Chem.* **2000**, *103*, 57−61.
(44) Mercier, H. P. A.; Sanders, J. C. P.; Schrobilgen, G. J.; Tsai, S. S. *Inorg. Chem.* **1993**, *32*, 386−393.
(45) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc., London* **1963**, 212.
(46) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250.

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, or $OTeF_5$). Xenon difluoride (0.8734 g, 5.159 mmol) was suspended in cold (−60 °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 °C was transferred onto the XeF_2 suspension with vigorous stirring of the latter at −60 °C. After 15 min, the temperature was raised to −40 °C. A pale-yellow solid precipitated. After 1.5 h of additional stirring, the suspension was centrifuged at 20 °C and the mother liquor was decanted. The near-white solid was dried for 4 h under dynamic vacuum (10^{-2} mbar) at 20 °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, 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 °C. Both reactants were separately dissolved in CH_3CN (300 μL), and the solutions were combined at 20 °C. A pale-yellow suspension resulted, which was stirred for 15 min, subsequently cooled to −40 °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 °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 °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 °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 (×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 °C) CH_2Cl_2 (1000 μL). A solution of cold (−80 °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 °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 °C, and the resulting yellow solid was dried for several hours at temperatures not exceeding −50 °C. The solid was further purified by washing with dry pentane at −60 °C. The ^{19}F and ^{129}Xe NMR NMR parameters of C_6F_5XeF (CH_2Cl_2 at −80 °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 °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 °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 °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

---

(47) Frohn, H.-J.; Adonin, N. Y.; Bardin, V. V.; Starichenko, V. F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2827−2833.

(48) Frohn, H.-J.; Franke, H.; Fritzen, P.; Bardin, V. V. *J. Organomet. Chem.* **2000**, *598*, 127−135.

(49) Kropshofer, H.; Leitzke, O.; Peringer, P.; Sladky, F. *Chem. Ber.* **1981**, *114*, 2644−2648.

(20 equiv) was added to the pale-yellow $[C_6F_5Xe]^+$ 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 H_2O: **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) C_6H_5F and Fluoride in CH_2Cl_2. In the drybox, $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ (26.04 mg, 0.0256 mmol) was loaded into a reaction tube and suspended in cold (−55 °C) CH_2Cl_2 (1000 μL). Freshly dried and distilled C_6H_5F (45 μL, 45.9 mg, 0.478 mmol, 20 equiv) was added to the $[C_6F_5XeNCCH_3]^+$ 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 $[N(CH_3)_4]F$ (5.72 mg, 0.0614 mmol) in cold (−55 °C) CH_2Cl_2 (1000 μL) was added to sample A (Table 3, entry 9b). Sample B served as a reference.

(iv) Reaction of C_6F_5XeF with C_6H_5F in CH_2Cl_2. Freshly prepared C_6F_5XeF (16.3 mg, 0.0514 mmol) containing $[N(CH_3)_4]$-$[B(C_6F_5)_4]$ (9%) as an impurity was loaded into a reaction tube and dissolved in cold (−80 °C) CH_2Cl_2 (1200 μL). Freshly dried and distilled C_6H_5F (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 ^{19}F NMR spectroscopy at −40 °C (Table 3, entry 9a).

(v) Reaction of $[C_6F_5Xe][B(CF_3)_4]$ with C_6H_5F in CH_2Cl_2. Two portions of salt **4**, **a** (35.11 mg, 0.0600 mmol) and **b** (34.83 mg, 0.0595 mmol), were loaded into separate reaction tubes, and each was dissolved in CH_2Cl_2 (500 μL). Freshly dried and distilled C_6H_5F, **4a** (20 equiv) and **4b** (1.2 equiv) was added to the pale-yellow $[C_6F_5Xe]^+$ 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 $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$ and $[C_6F_5Xe]$-$[B(CF_3)_4]$ with Neat C_6H_5F. 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 C_6H_5F (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 CD_2Cl_2 or CD_3CN 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 cryomagnet. For low-temperature work, the NMR probe was cooled using a nitrogen flow and a variable-temperature controller (BVT 3000).

The ^1H and ^{19}F NMR spectra were acquired using a 5 mm combination $^1H/^{19}F$ probe operating at 300.14 and 282.40 MHz, respectively. The ^{11}B, ^{13}C, and ^{129}Xe 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 (^{11}B), 8.0 (^{13}C), 14.6 (^{19}F), and 8.5 (^{129}Xe) 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 CH_2Cl_2 (5.32 ppm) and CH_3CN (1.95 ppm). The ^{13}C NMR chemical shifts were referenced with respect to TMS using the chemical shifts for the solvents CH_2Cl_2 (53.5 ppm) and CH_3CN (118.7 ppm). The ^{19}F NMR spectra were referenced with respect to $CFCl_3$ using either the internal standards C_6F_6 (−162.9 ppm) or $C_6H_5CF_3$ (−63.9 ppm) or externally to a neat $CFCl_3$ reference sample at 24 °C. The ^{129}Xe NMR spectra were directly referenced with respect to neat liquid $XeOF_4$ or indirectly by use of the secondary external reference XeF_2/CD_3CN extrapolated to zero concentration, yielding an XeF_2 chemical shift of −1813.3 ppm with respect to external $XeOF_4$ at 24 °C.[50] The ^{11}B NMR spectra were referenced either to an external $BF_3{\cdot}Et_2O$ (neat) at 24 °C or to an external $BF_3{\cdot}Et_2O/CD_3Cl$ 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 ^{19}F and ^{129}Xe NMR spectra of the $[C_6F_5Xe]^+$ cation ($[B(CN)_4]^-$ salt in CH_3CN at 24 °C) and C_6F_5I were simulated on a PC using the program *ISOTOPOMER*.[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).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada (G.J.S.) and the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie (H.-J.F.) for support in the form of research grants and Prof. Helge Willner for providing samples of $M^I[B(CF_3)_4]$ (M^I = K or Cs) and $K[B(CN)_4]$.

Supporting Information Available: Solubilities of $[C_6F_5Xe]$-$[BY_4]$ (Y = CF_3 or CN), $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, and $[C_6F_5Xe][BF_4]$ (Table S1) and solution decomposition rates and products (20 °C) for $[C_6F_5Xe][BY_4]$ (Y = CF_3, CN, or $OTeF_5$), $[C_6F_5XeNCCH_3][B(C_6F_5)_4]$, and $[C_6F_5Xe][BF_4]$ (Table S2), experimental and simulated ^{19}F NMR spectra of C_6F_5I (Figure S1), and the syntheses of $B(C_6F_5)_3$ and $Cs[B(C_6F_5)_4]$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7010138

---

(50) Schumacher, G. A.; Schrobilgen, G. J. *Inorg. Chem.* **1984**, *23*, 2923–2929.

(51) NETZSCH, Proteus, Messung, version 4.2.1 ed.; Netzsch Gerätebau GmbH: Selb, Germany, 2002.