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Two New Types of Xenon−Carbon Species: The Zwitterion, 1-(Xe^+)C_6F_4-4-(BF_3^-), and the Dication, $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$

Hermann-Josef Frohn,*[,†] Vural Bilir,[†] and Ulrich Westphal[†]

[†]Inorganic Chemistry, University of Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany

Supporting Information

ABSTRACT: In the 1:1 reaction of XeF_2 with 1,4-$(F_2B)_2C_6F_4$ in 1,1,1,3,3-pentafluoropropane the insoluble zwitterion 2,3,5,6-tetrafluorophenylene-1-xenonium-4-trifluoroborate, 1-(Xe^+)C_6F_4-4-(BF_3^-), was formed as the main product (77%) along with the zwitterion, 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-), the $[BF_4]^-$ salts of the dication, $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$, and the cation, [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$. The isolation of pure 1-(Xe^+)C_6F_4-4-(BF_3^-) was feasible after extraction of the byproduct with 27% aq HF. The zwitterion, 1-(Xe^+)C_6F_4-4-(BF_3^-), was characterized by multi-NMR and Raman spectroscopy and by DSC. The zwitterion, 1-(Xe^+)C_6F_4-4-(BF_3^-), reacted with halide nucleophiles (in excess) in 27% aq HF to form $[4\text{-}HalC_6F_4BF_3]^-$ (Hal = I, Br, Cl) along with $[2,3,5,6\text{-}C_6F_4HBF_3]^-$, whereas with fluoride ions $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ was obtained exclusively. Reactions of XeF_2 with 1,4-$(F_2B)_2C_6F_4$ in the molar ratio 2:1 did not allow for improving the yield of the tetrafluoroborate salt with the dication $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$. Instead, addition of fluorine to the phenylene unit was increased with the formation of 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-), [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$, and $[1,4\text{-}(Xe)_2$-*cyclo*-1,4-$C_6F_6]^{2+}$. After enrichment in an anhydrous hydrogen fluoride extract, the dication, $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$, was characterized by multi-NMR spectroscopy and by means of chemical proof (reaction with an excess of KI to 1,4-$I_2C_6F_4$).

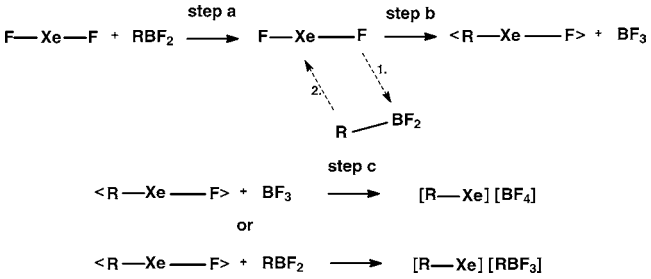
INTRODUCTION

Two types of xenon(II) compounds are described in the literature: xenonium salts, [RXe]Y (R = polyfluorinated aryl, alk-1-en-1-yl, and alk-1-yn-1-yl groups)[1−3] and molecular xenon compounds RXeY (R = polyfluorinated aryl groups, Y = Cl,[4] F,[5,6] CN,[6] R,[5−7] R′ = polyfluorinated aryl groups[7,8]). The "xenodeborylation" reaction is an efficient access to xenonium salts [RXe]Y and comprises the acid-assisted F/R substitution in XeF_2 using RBF_2 reagents.[1] Besides the specific syntheses of RXeF and R_2Xe,[5] RXeY molecules can generally be obtained by addition of Y^- nucleophiles to $[RXe]^+$.[6,7]

The xenodeborylation reaction can be described simplified by three steps: (a) interaction of one xenon-bonded fluorine of hypervalent XeF_2 with Lewis-acidic RBF_2 which results in an asymmetric fluorine moiety of Xe^{II} and an increased partial positive charge on Xe^{II}, (b) transfer of the carbon nucleophile R from the partially anionic organylboron transition state species to the Xe^{II} electrophile and of one fluorine atom from the Xe^{II} moiety to the boryl fragment, and (c) fluoride abstraction from RXeF by BF_3 or RBF_2 (Scheme 1). It is worth mentioning, that the fluoride acceptor property of RBF_2 increases from R = fluorine via perfluoroaryl, -alkenyl, and -alkynyl to -alkyl.[9] In the case of the perfluoroalkenyldifluoroboranes *cis*-$R_FCF{=}CFBF_2$ (R_F = F, CF_3, C_2F_5) the corresponding perfluoroalkenylxenonium salts contained mixtures of both anions: perfluoroalkenyltrifluoroborate and tetrafluoroborate.[10] No xenonium salts could be achieved with perfluoroalkyldifluoroboranes and 2,3,5,6-tetrafluoropyridyldifluoroborane.[9]

In the present work the 1:1 and 2:1 reaction of XeF_2 with the strong Lewis acidic reagent 1,4-$(F_2B)_2C_6F_4$ is investigated, with the intention to obtain the first Xe−C species with a zwitterionic structure and/or the salt with a dixenonium cation with two Xe−C bonds.

Scheme 1



RESULTS

Synthesis of the Zwitterion, 1-(Xe^+)C_6F_4-4-(BF_3^-) (1). The equimolar reaction of XeF_2 with 1,4-$(F_2B)_2C_6F_4$ in 1,1,1,3,3-pentafluoropropane ($CF_3CH_2CHF_2$, PFP) at −78 °C resulted in the spontaneous formation of a voluminous yellow precipitate (eq 1). The supernatant contained no XeF_2 but the oxidized borane 1,4-$(F_2B)_2$-*cyclo*-1,4-C_6F_6 (22% relative to the starting quantity of 1,4-$(F_2B)_2C_6F_4$).

$$XeF_2 + 1,4\text{-}(F_2B)_2C_6F_4 \xrightarrow{PFP,\,-78\,^\circ C} \underset{\mathbf{1}}{1\text{-}(Xe^+)C_6F_4\text{-}4\text{-}(BF_3^-)} \downarrow + BF_3 \quad (1)$$

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In the precipitate both target products, namely 1-(Xe^+)C_6F_4-4-(BF_3^-) (77%) and $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$ (3% as $[BF_4]^-$ salt), were present along with two products of fluorine addition to the 1,4-phenylene unit, 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) (**2**) (13%) and $[1\text{-Xe-}cyclo\text{-}1,4\text{-}C_6F_6\text{-}4\text{-}H]^+$ (7%), and $[BF_4]^-$ (51%). The byproduct in the precipitate could be extracted with cold (0 °C) 27% aq HF. After drying the residue under vacuum, pure 1-(Xe^+)C_6F_4-4-(BF_3^-) was isolated as a pale yellow solid. The yield of the isolated zwitterion **1** was always relatively low caused by the loss during the repeated extraction process.

Solid-State Stability, Solubility, and Solution Stability of 1-(Xe^+)C_6F_4-4-(BF_3^-). The zwitterion **1** can be stored in a glovebox under an atmosphere of dry Ar at 20 °C more than one month without decomposition. DSC measurements showed decomposition (exothermal effect: T_{onset} = 148 °C, T_{max} = 158 °C) without preceding melting.

The solubility of **1** was determined in 27% aq HF (16.5 μmol/mL at 0 °C and 15.7 μmol/mL at −60 °C) and was lower than in anhydrous HF (>90 μmol/mL at −78 °C). The solubility of **1** in CH_3CN was ca. half of that in 27% aq HF.

Solutions of **1** in CH_3CN showed no decomposition at −40 °C after 30 h. Whereas at 0 °C 2% were decomposed after 20 h with the formation of $[2,3,5,6\text{-}C_6F_4HBF_3]^-$. No decomposition of **1** was observed in aHF at −10 °C after 17 h and in 27% aq HF at 0 °C after 2 h. In a competitive study the stability of **1** and the related salt $[C_6F_5Xe][BF_4]$ (**3**) was examined in 27% aq HF at 20 °C. It was found that the stability of **1** exceeded that of **3**. Finally, after 3 d both salts were completely decomposed with the formation of $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ or $(C_6F_5)_2$ and $(C_6F_5)_2O$, respectively (Scheme 2(a),(b)).

Scheme 2

(a) 1-(Xe^+)C_6F_4-4-(BF_3^-) —(27% aq HF < 3 d)→ $[2,3,5,6\text{-}C_6F_4HBF_3]^-$

(b) $[C_6F_5Xe][BF_4]$ —(27% aq HF ≤ 3 d)→ $(C_6F_5)_2$ + $(C_6F_5)_2O$

Reactivity of 1-(Xe^+)C_6F_4-4-(BF_3^-) toward Hal^- Nucleophiles in 27% aq HF. The zwitterion, 1-(Xe^+)C_6F_4-4-(BF_3^-), reacted with a 100-fold molar excess of KHal (Hal = I (a), Br (b), Cl (c), and F (d)) in 27% aq HF (Scheme 3) with different rates and formed mixtures of products. With iodide and bromide ions spontaneous reactions took place, and $[4\text{-}IC_6F_4BF_3]^-$ (87%) and $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (13%) (a) or $[4\text{-}BrC_6F_4BF_3]^-$ (72%) and $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (28%) (b) were formed, respectively. The reactions with chloride and fluoride ions proceeded markedly slower. After 1 d $[4\text{-}ClC_6F_4BF_3]^-$ (71%) and $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (29%) (c) or $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (100%) (d) were obtained, respectively. In case (d) of KF the participation of H^+ from aq HF under formation of $[HF_2]^-$ (equilibrium) has to be considered. In a competitive reaction with a large excess of chloride ions in 27% aq HF at 20 °C the different reactivity of 1-(Xe^+)C_6F_4-4-(BF_3^-) and $[C_6F_5Xe][BF_4]$ was exemplified. The reaction of $[C_6F_5Xe]$-$[BF_4]$ was completed after 7 h. Besides K$[BF_4]$ (precipitate) C_6F_5Cl was the only product which contained an aryl group. The transformation of 1-(Xe^+)C_6F_4-4-(BF_3^-) required 22 h and yielded $[4\text{-}ClC_6F_4BF_3]^-$ (88%) and $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (12%).

Attempted Addition of Fluorine to the Aromatic Moiety of 1-(Xe^+)C_6F_4-4-(BF_3^-) and/or Substitution of (BF_3^-) Using XeF_2 in aHF. A solution of 1-(Xe^+)C_6F_4-4-(BF_3^-) and 10 equiv XeF_2 in aHF showed no reaction at −78 °C within 15 min. Warming to −30 °C was accompanied by the complete conversion of 1-(Xe^+)C_6F_4-4-(BF_3^-) and the consumption of 3 equiv of XeF_2. Furthermore, ^{19}F NMR analysis of the solution confirmed the absence of $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$ and $[1,4\text{-}(Xe)_2\text{-}cyclo\text{-}1,4\text{-}C_6F_6]^{2+}$. From δ = −60 to −160 ppm numerous resonances were present. This range comprises the expected resonances of fluorine addition products to the aromatic C_6F_4 unit with *cyclo*-1,4-C_6F_6 and *cyclo*-1-C_6F_8 alkenyl structures.

The 2:1 Reaction of XeF_2 with 1,4-$(F_2B)_2C_6F_4$: Synthesis of $[1,4\text{-}(Xe)_2C_6F_4][BF_4]_2$ in a Low Yield. The reaction of a PFP solution of XeF_2 with 1,4-$(F_2B)_2C_6F_4$ in the molar ratio 2:1 at −78 °C resulted in a suspension with a voluminous yellow precipitate. After 1 h the mother liquor contained BF_3, 1,4-bis(difluoroboryl)-2,3,3,5,6,6-hexafluorocyclohexa-1,4-diene, 1,4-$(F_2B)_2$-*cyclo*-1,4-C_6F_6 (^{19}F NMR). The precipitate was separated and dried under vacuum at −78 °C. The solid was dissolved in aHF at −78 °C and consisted of a mixture of 1-(Xe^+)C_6F_4-4-(BF_3^-) (47%), 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) (42%), $[1\text{-}XeC_6F_4\text{-}4\text{-}H]^+$ (5%), $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$ (2%), $[1,4\text{-}(Xe)_2\text{-}cyclo\text{-}1,4\text{-}C_6F_6]^{2+}$ (1%), $[1\text{-}XeC_6F_4\text{-}4\text{-}R]^+$ (3%), 1-R′-*cyclo*-1,4-C_6F_6-4-R″ (5%), and $[BF_4]^-$ (45%).

Chemical Proof of the Dication, $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$ (4), in a Mixture by the Specific Conversion with Potassium Iodide in aHF. When the solid product of a 2:1 reaction in PFP was partially dissolved in cold (−78 °C) aHF enrichment of **4** was possible. Such a −78 °C cold aHF solution which contained, e.g., $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$ (8%), $[1,4\text{-}(Xe)_2\text{-}cyclo\text{-}1,4\text{-}C_6F_6]^{2+}$ (13%), 1-(Xe^+)C_6F_4-4-(BF_3^-) (23%), 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) (51%), and $[1\text{-Xe-}cyclo\text{-}1,4\text{-}C_6F_6\text{-}4\text{-}H]^+$ (5%) along with $[BF_4]^-$ was added to an excess of solid KI. Spontaneously a brown suspension resulted. After separation and drying, the major part of the yellowish solid was dissolved in CH_3CN at −40 °C. The ^{19}F NMR spectrum revealed a mixture of 1,4-$I_2C_6F_4$: $\delta(^{19}F)$ = −119.6 ppm (s, $\Delta\nu_{1/2}$ = 11 Hz), $[4\text{-}IC_6F_4BF_3]^-$: $\delta(^{19}F)$ = −122.8 ppm $F^{3,5}$, −133.3 ppm $F^{2,6}$, −135.5 ppm BF_3, and at least three new (presumably iodine-containing) compounds with partially overlapping signals. Addition of an authentic sample of 1,4-$I_2C_6F_4$ supported the assignment.

Scheme 3

1-(Xe^+)C_6F_4-4-(BF_3^-) + >>1 KHal —(27% aq HF)→ $[4\text{-HalC}_6F_4BF_3]^-$ + $[2,3,5,6\text{-}C_6F_4HBF_3]^-$

Hal =		
I	87%	13%
Br	72%	28%
Cl	71%	29%
F	0%	100%

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DISCUSSION

Synthesis of the Zwitterion, 1-(Xe^+)C_6F_4-4-(BF_3^-) (1), and the $[BF_4]^-$ Salt with the Dication $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$ (4). Reactions of XeF_2 and 1,4-$(F_2B)_2C_6F_4$ in PFP in the Molar Ratios 1:1 and 2:1. The xenodeborylation reaction of XeF_2 with RBF_2 is most effective in weakly coordinating solvents, e.g., PFP (or CH_2Cl_2 in case of less acidic boranes RBF_2) and ends generally with insoluble salts $[RXe][BF_4]$ or with few exceptions with $[RXe][RBF_3]$, depending on the nature of RBF_2, vide supra. Starting material, XeF_2, reacted spontaneously with the bifunctional and very acidic fluoroborane 1,4-$(F_2B)_2C_6F_4$ even at −78 °C. The gas phase fluoride affinity of 1,4-$(F_2B)_2C_6F_4$ (89.1 kcal/mol, cf. compilation in the Supporting Information) is comparable with that of PF_5 (89.2 kcal/mol) and BCl_3 (90.4 kcal/mol) and exceeds that of BF_3 (78.8 kcal/mol) significantly.[9] 1-FXeC_6F_4-4-BF_2 is the proposed intermediate after the first step in the xenodeborylation sequence (Scheme 1) and contains as well a fluoride donating substituent (XeF) as a fluoride accepting substituent (BF_2). The BF_2 group of 1-FXeC_6F_4-4-BF_2 is a stronger Lewis acid than BF_3, the coproduct in the first xenodeborylation step. The insoluble zwitterion **1** is probably formed from soluble 1-FXeC_6F_4-4-BF_2 on an intermolecular path.

In addition to the xenodeborylation route a second path has to be discussed which follows the interaction of XeF_2 with the strong fluoride acceptor 1,4-$(F_2B)_2C_6F_4$ (eq 2a) and ends with the oxidation of $[4\text{-}(F_2B)C_6F_4BF_3]^-$ by $[XeF]^+/XeF_2$ (eq 2b). The anion $[4\text{-}(F_2B)C_6F_4BF_3]^-$ is significantly easier to oxidize than the neutral precursor 1,4-$(F_2B)_2C_6F_4$. The electrophilic oxidizer $[XeF]^+$ can initiate the oxidation, and XeF_2 can serve as a source of fluoride. Subsequently, $[4\text{-}(F_2B)\text{-}cyclo\text{-}1,4\text{-}C_6F_6BF_3]^-$ may undergo xenodeboration (eq 2c) and form finally the cycloalkenylxenonium zwitterion **2** (eq 2d). The sequence of the second reaction channel is supported by the remarkable increase of the oxidized zwitterion, [1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-)] (**2**), from 13% to 42% when the stoichiometry (ratio XeF_2:1,4-$(F_2B)_2C_6F_4$) was changed from 1:1 to 2:1.

$$XeF_2 + 1,4\text{-}(F_2B)_2C_6F_4 \rightarrow [XeF]^+ + [4\text{-}(F_2B)C_6F_4BF_3]^- \quad (2a)$$

$$[XeF]^+/XeF_2 + [4\text{-}(F_2B)C_6F_4BF_3]^- \rightarrow [XeF]^+ + [4\text{-}(F_2B)\text{-}cyclo\text{-}1,4\text{-}C_6F_6BF_3]^- + Xe^0 \quad (2b)$$

$$[XeF]^+ + [4\text{-}(F_2B)\text{-}cyclo\text{-}1,4\text{-}C_6F_6BF_3]^- \rightarrow 1\text{-FXe-}cyclo\text{-}1,4\text{-}C_6F_6\text{-}4\text{-}BF_2 + BF_3 \quad (2c)$$

$$1\text{-FXe-}cyclo\text{-}1,4\text{-}C_6F_6\text{-}4\text{-}BF_2 \rightarrow \underset{\mathbf{2}}{1\text{-}(Xe^+)\text{-}cyclo\text{-}1,4\text{-}C_6F_6\text{-}4\text{-}(BF_3^-)} \quad (2d)$$

Both zwitterions 1-(Xe^+)C_6F_4-4-(BF_3^-) (**1**) and 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) (**2**) are insoluble in PFP. Furthermore, the (BF_3^-)-substituent of both zwitterions is a negligible fluoride donor. E.g., in the conjugated borane $[1\text{-}XeC_6F_4\text{-}4\text{-}BF_2]^+$, the electron-withdrawing effect of the 1-(Xe^+)C_6F_4 group is significantly higher than that of the C_6F_5-group in $C_6F_5BF_2$, because the partial positive charge on Xe polarizes the π-system in the aromatic unit and reduces the p(C)-p(B)-π-backbond of the C(4)-B bond. There is no fluoride acceptor in the reaction mixture, which is strong enough to abstract a fluoride ion from the zwitterions 1-(Xe^+)C_6F_4-4-(BF_3^-) or 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-). As a consequence, a second xenodeborylation cannot proceed to a remarkable extent, even in the case of a 2:1 ratio of the starting materials (XeF_2:1,4-$(F_2B)_2C_6F_4$). Furthermore, after the first xenodeborylation step there are heterogeneous reaction conditions. All aforementioned arguments explain (a) why in case of all applied stoichiometries only mixtures of **1**, **2**, and **4** resulted and (b) why the fraction of $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$ was only 2−3% and practically independent of the stoichiometry and the applied reaction conditions.

In the case of the 1:1 reaction the byproduct in the reaction mixture could be separated from zwitterion **1** by extraction. It was found that 27% aq HF was the best medium which fulfilled both demands for **1**: relative low solubility and good stability. The main component besides **1** was the anion $[BF_4]^-$ which belonged to different cations of the byproduct. The counterion, $[BF_4]^-$, of these salts was well solvated by 27% aq HF. Repeated extraction steps were necessary for the purification and were accompanied by a significant loss of zwitterion **1**, caused by its solubility (5.73 mg/mL at 0 °C).

The salt $[1,4\text{-}(Xe)_2C_6F_4][BF_4]_2$ contains the first organyldixenonium cation, $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$, which was characterized in mixtures by multi-NMR spectroscopy and by chemical proof in the specific conversion with KI to 1,4-$I_2C_6F_4$.

Solid-State and Solution Stability of 1-(Xe^+)C_6F_4-4-(BF_3^-). The zwitterion **1** was stable in a dry atmosphere of Ar at 20 °C for more than one month. The DSC measurement of **1** in an Al pan showed decomposition at 148 °C (T_{onset}, exothermal effect) without preceding melting. The temperature of decomposition was of the same magnitude as that of the salt $[C_6F_5Xe][BF_4]$ (**3**) with 157 °C, but the latter underwent melting at 80 °C before decomposition.[11]

Solutions of **1** showed no decomposition in aHF at −10 °C after 17 h and in 27% aq HF at 0 °C after 2 h. In a competitive study in 27% aq HF at 20 °C the stability of **1** exceeded that of salt $[C_6F_5Xe][BF_4]$ (**3**). After 20 h the ratio **1**:**3** changed from 33:67 to 44:56 caused by slow decomposition. The complete decomposition of both salts was found latest after 3 d with the formation of $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ or $(C_6F_5)_2$ and $(C_6F_5)_2O$, respectively (Scheme 2(a),(b)). The nucleophilicity of water in 27% aq HF seems to be still high enough that coordination to Xe^+ takes place accompanied by weakening the Xe−C bond. In the case of **1**, homolytic cleavage of the Xe−C bond generates a $[2,3,5,6\text{-}C_6F_4BF_3]^{-\bullet}$ radical anion which abstracts a hydrogen atom from water and forms the $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ anion. In the case of **2** the coordinated water molecule is able to release a proton and the intermediate C_6F_5XeOH can eliminate Xe^0. Phenol, C_6F_5OH, on its part is able to coordinate to cation **3**. The base coordinated cation, $[C_6F_5XeO(H)C_6F_5]^+$, is able to undergo (a) a homolytic cleavage of the Xe−C bond and the $C_6F_5^\bullet$ radical forms $(C_6F_5)_2$ and (b) deprotonation and finally elimination of Xe^0 results in the ether $(C_6F_5)_2O$.

In contrast to **3** the zwitterion **1** is only poorly soluble in CH_3CN at 0 °C. Solutions of **1** in CH_3CN showed no decomposition at −40 °C after 30 h and only 2% decomposition at 0 °C after 20 h with the formation of $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (cf. the coordination of CH_3CN with the before discussed coordination of water).

Reactivity of 1-(Xe^+)C_6F_4-4-(BF_3^-) toward Hal^- Nucleophiles in 27% aq HF. The satisfactory stability of **1** in 27% aq HF allowed the investigation of fast reactions in this medium. Reactions with negatively charged nucleophiles were chosen, and 1-(Xe^+)C_6F_4-4-(BF_3^-) reacted with a 100-fold molar excess

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Table 1. ^{19}F, ^{129}Xe, and ^{13}C NMR Spectroscopic Data of 1-(Xe^+)C_6F_4-4-(BF_3^-), [1,4-$(Xe)_2C_6F_4$]$^{2+}$, and the Related Compound $[C_6F_5Xe][BF_4]$ (δ in ppm, J in Hz)

			aromatic C_6F_4-unit				$-Xe^+$		aromatic C_6F_4-unit			
compound	solvent	T (°C)	$\delta(F^{2,6})$	$^3J^a$	$\delta(F^{3,5})$	$-BF_3^-$ $\delta(F)$	$\delta(Xe)$	$^3J^b$	$\delta(C^1)$	$\delta(C^{2,6})$	$\delta(C^{3,5})$	$\delta(C^4)$
1-(Xe^+)C_6F_4-4-(BF_3^-)	aHF	−10	−126.8	53	−124.7	−133.6	−3982	53	83.7	149.4	143.1	111.5[c]
1-(Xe^+)C_6F_4-4-(BF_3^-)	aHF	−30	−127.0	53	−124.8	−133.6						
1-(Xe^+)C_6F_4-4-(BF_3^-)	aHF	−80	−127.4	54	−125.4	−133.6	−3998	53				
1-(Xe^+)C_6F_4-4-(BF_3^-)	27% aq HF	24	−129.3	59	−128.6	−133.1						
1-(Xe^+)C_6F_4-4-(BF_3^-)	CH_3CN	24	−129.9	60	−126.8	−134.0						
1-(Xe^+)C_6F_4-4-(BF_3^-)	CH_3CN	0	−129.9	61	−127.2	−133.9	−3858	60	n.o.[d]	149.5	143.3	n.o.[d]
1-(Xe^+)C_6F_4-4-(BF_3^-)	CH_3CN	−40	−130.0	61	−127.9	−133.7						
$[C_6F_5Xe][BF_4]$[19]	aHF[e]	−10	−123.3		−151.5		−3941	59				
$[C_6F_5Xe][BF_4]$[11]	aHF[f]	−40	−123.6	58	−151.8		−3935[g]	58				
$[C_6F_5Xe][BF_4]$	27% aq HF[h]	24	−125.8	67	−154.1							
$[C_6F_5Xe][BF_4]$	CH_3CN[i]	24	−124.9	67	−154.2		−3803	67	84.8	144.9	139.2	146.2
$[C_6F_5Xe][BF_4]$[11]	CH_3CN[j]	−40	−125.5	68	−155.1		−3783	68				
[1,4-$(Xe)_2C_6F_4$]$^{2+}$	aHF	−30	−113.8		−113.8							
[1,4-$(Xe)_2C_6F_4$]$^{2+}$	aHF	−80	−114.6		−114.6		−3823	60				

[a] $^3J(^{19}F^{2,6}-^{129}Xe)$. [b] $^3J(^{129}Xe-^{19}F^{2,6})$. [c] $\Delta\nu_{1/2}$ > 1000 Hz. [d] n.o. = not observed within 15 h (during longer term measurements decomposition proceeded). [e] $\delta(F^4)$ = −137.9 ppm. [f] $\delta(F^4)$ = −138.2 ppm. [g] $[C_6F_5Xe][AsF_6]$[18]. [h] $\delta(F^4)$ = −141.8 ppm. [i] $\delta(F^4)$ = −141.9 ppm. [j] $\delta(F^4)$ = −142.3 ppm.

of KHal (Hal = I (a), Br (b), Cl (c), and F (d) in 27% aq HF (Scheme 3). With iodide and bromide ions spontaneous reactions took place, and $[4\text{-}IC_6F_4BF_3]^-$ (87%) and $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (13%) (a) or $[4\text{-}BrC_6F_4BF_3]^-$ (72%) and $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (28%) (b) were formed, respectively. The reactions with chloride and fluoride ions proceeded slower. With chloride $[4\text{-}ClC_6F_4BF_3]^-$ (71%) and $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (29%) (c) were yielded, and with fluoride $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (100%) (d) was obtained exclusively.

In case (d) a strong interaction of the electrophilic site in 1-(Xe^+)C_6F_4-4-(BF_3^-) with the nucleophiles F^- or $[F(HF)_n]^-$ can be discussed without electron transfer from the anion to Xe^+. As a result of this interaction the Xe−C bond becomes weakened, and after homolysis the radical anion $[2,3,5,6\text{-}C_6F_4BF_3]^{-\bullet}$ abstracts hydrogen from water (eq 3a). Formally, the reactions with Hal^- (Hal = I, Br, Cl) can be described as an elimination of Xe^0 from the intermediate anion $[4\text{-}HalXeC_6F_4BF_3]^-$. The increase of $[4\text{-}HalC_6F_4BF_3]^-$ with smaller ionization potentials of Hal^- from Cl^- to I^- refers to a single electron transfer step (SET) from Hal^- to 1-(Xe^+)C_6F_4-4-(BF_3^-). After elimination of Xe^0 in 1-($Xe^\bullet$)C_6F_4-4-(BF_3^-) the coupling of the radicals $[2,3,5,6\text{-}C_6F_4BF_3]^{-\bullet}$ and $Hal^\bullet$ proceeds in cage and yields $[4\text{-}HalC_6F_4BF_3]^-$, whereas the escaping radical anion $[2,3,5,6\text{-}C_6F_4BF_3]^{-\bullet}$ abstracts hydrogen from water molecules (eq 3b).

$$1\text{-}(Xe^+)C_6F_4\text{-}4\text{-}(BF_3^-) + F^- \rightarrow [4\text{-}(F\text{-}Xe)\text{-}C_6F_4BF_3]^- \rightarrow [F\text{-}Xe]^\bullet + [C_6F_4BF_3]^{-\bullet}$$
$$[C_6F_4BF_3]^{-\bullet} + H_2O \rightarrow [2,3,5,6\text{-}C_6F_4HBF_3]^- + [HO]^\bullet \quad (3a)$$

$$1\text{-}(Xe^+)C_6F_4\text{-}4\text{-}(BF_3^-) + Hal^- \rightarrow [4\text{-}(Hal\text{-}Xe)\text{-}C_6F_4BF_3]^- \rightarrow [Hal]^\bullet + 1\text{-}(Xe^\bullet)C_6F_4\text{-}4\text{-}(BF_3^-) \rightarrow Xe^0 + <[Hal]^\bullet[C_6F_4BF_3]^{-\bullet}>_{\text{in cage}} \rightarrow Xe^0 + [4\text{-}HalC_6F_4BF_3]^-$$
$$Hal = Cl, Br, I \quad (3b)$$

In a competitive reaction with a large excess of KCl in 27% aq HF at 20 °C the different reactivity of 1-(Xe^+)C_6F_4-4-(BF_3^-) and $[C_6F_5Xe][BF_4]$ was exemplified. The reaction of $[C_6F_5Xe][BF_4]$ (cf. the reactivity in CH_3CN)[12] was completed after 7 h. Besides $K[BF_4]$ (precipitate) C_6F_5Cl was the only product which contained an C_6F_5 group. The transformation of 1-(Xe^+)C_6F_4-4-(BF_3^-) required 22 h and yielded $[4\text{-}ClC_6F_4BF_3]^-$ (88%) and $[2,3,5,6\text{-}C_6F_4HBF_3]^-$ (12%). The lower reactivity of **1** is in agreement with the σ-electron donating character of the (BF_3^-)-substituent (σ_I = −0.33, σ_R = −0.05)[13] in the 4-position which causes a lower acceptor property of (Xe^+) and a lower oxidation potential of **1**.

Attempted Addition of Fluorine to the Aromatic Moiety of 1-(Xe^+)C_6F_4-4-(BF_3^-) and/or Substitution of (BF_3^-) Using XeF_2 in aHF. Previously, it was shown that in the superacidic medium aHF, the boranes $B(C_6F_5)_3$ and $C_6F_5BF_2$ underwent xenodeborylation with XeF_2. Besides, in some extent fluorine addition to the aryl group of $[C_6F_5Xe]^+$ and $[C_6F_5BF_3]^-$ took place.[14,15] In independent experiments it was shown that XeF_2 in aHF was a suitable reagent to add fluorine to the aromatic ring of $[C_6F_5Xe][BF_4]$ and $[2,3,4,5\text{-}C_6F_4HXe][BF_4]$ to form the corresponding cyclohexa-1,4-dien-1-yl and cyclohex-1-en-1-ylxenonium salts.[16,17] In the present work it was found that a solution of 1-(Xe^+)C_6F_4-4-(BF_3^-) and 10 equiv XeF_2 in aHF did not react at −78 °C within 15 min. When warmed to −30 °C, the complete conversion of 1-(Xe^+)C_6F_4-4-(BF_3^-) proceeded and ca. 3 equiv of XeF_2 were consumed. But neither defined fluorination of the zwitterion **1** to 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) nor xenodeboration to [1,4-$(Xe)_2C_6F_4$]$^{2+}$ nor fluorine addition to the latter with the formation of [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$ took place. It is worth mentioning, that xenodeboration of $[C_6F_5BF_3]^-$ with XeF_2 in aHF was performed successfully in the past.[15]

The ^{19}F NMR spectrum of the interaction of 1-(Xe^+)C_6F_4-4-(BF_3^-) with XeF_2 in aHF revealed numerous resonances between δ = −60 and −160 ppm, the range which includes fluorine addition products to the aromatic C_6F_4 unit, but an unambiguous assignment of the partially overlapping signals was not possible. Nevertheless, the formation of 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-), [1,4-$(Xe)_2C_6F_4$]$^{2+}$, and [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$ can be excluded.

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Table 2. ^{19}F and ^{129}Xe NMR Spectroscopic Data of 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-), [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$, and the Related Compounds [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$ and [1-Xe-*cyclo*-1,4-C_6F_7]$^+$ (δ in ppm, J in Hz)

			cyclo-1,4-C_6F_6 unit				$-BF_3^-$	$-Xe^+$	
compound	solvent	T (°C)	$\delta(F^2)$	$\delta(F^{3,3})$	$\delta(F^5)$	$\delta(F^{6,6})$	$\delta(F)$	$\delta(Xe)$	$J(Xe)^a$
1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-)	aHF	−30	−88.5	−96.0	−115.5	−94.9	−135.1		
1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-)	aHF	−80	−89.3	−96.8	−116.0	−95.7	−135.1	−4004	68
[1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$	aHF	−80	−83.7	−93.2	−83.7	−93.2	-	−3865	69
[1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$	aHF	−30	−84.1	−109.3	−116.1	−107.3	-		
[1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$	aHF	−80	−84.9	−110.1	−116.5	−108.1	-	−3970	73
[1-Xe-*cyclo*-1,4-C_6F_7]$^+$ [18]	aHF[b]	−30	−90.6	−107.9	−147.4	−93.6	-	−3907	69
[1-Xe-*cyclo*-1,4-C_6F_7]$^+$ [16]	CH_3CN[c]	−30	−95.8	−110.0	−147.9	−95.8	-	−3763	82

[a] $^3J(^{129}Xe-F^2)$. [b] $\delta(F^4) = -151.5$ ppm. [c] $\delta(F^4) = -153.0$ ppm.

^{13}C, ^{11}B, ^{19}F, and ^{129}Xe NMR Spectra of 1-(Xe^+)C_6F_4-4-(BF_3^-) and ^{19}F and ^{129}Xe NMR Spectra of [1,4-$(Xe)_2C_6F_4$]$^{2+}$ and Related Compounds. Solutions of 1-(Xe^+)C_6F_4-4-(BF_3^-) (**1**) in aHF, 27% aq HF, and CH_3CN were stable enough to obtain NMR spectral data. But only the solubility in aHF allowed to measure ^{13}C and ^{129}Xe NMR spectra with a satisfactory signal-to-noise ratio. Table 1 comprises NMR data of **1** in aHF, 27% aq HF, and CH_3CN at different temperatures. No significant temperature dependence of the δ- (^{19}F) and ^3J-values ($^{129}Xe-^{19}F$) was found in aHF and CH_3CN. The temperature dependence of the ^{129}Xe NMR shift of **1** and **3** in aHF is of comparable magnitude and is significantly lower than that of XeF_2.[18] The observed solvent dependence reflects the individual coordination property of the three solvents to the electrophilic xenon center as shown for $F^{2,6}$ ($\delta(^{19}F) = -126.8$ ppm (aHF, −10 °C), −129.3 ppm (27% aq HF, 24 °C), and −129.9 ppm (CH_3CN, 24 °C) and Xe ($\delta(^{129}Xe) = -3982$ ppm, aHF, −10 °C, $^3J(^{129}Xe-^{19}F) = 53$ Hz) and (−3858 ppm, CH_3CN, 0 °C, $^3J(^{129}Xe-^{19}F) = 60$ Hz). Stronger coordination to Xe is accompanied by the shielding of $\delta(^{19}F^{2,6})$, the deshielding of $\delta(^{129}Xe)$, and the increase of the $^3J(^{129}Xe-^{19}F)$ coupling constant. The (BF_3^-)-substituent in **1** is a strong σ-donor. Its influence can be compared with that of F^4 in [C_6F_5Xe][BF_4] (**3**). Shielding of $\delta(^{19}F^{2,6})$ and $\delta(^{129}Xe)$ in **1** relative to **3** was observed in aHF and CH_3CN solutions. Opposite to **1** the $F^{2,6}$ resonance of **3** appears deshielded from $F^{3,5}$. A comparison of the ^{19}F NMR spectral data of the dication, [1,4-$(Xe)_2C_6F_4$]$^{2+}$ (**4**), with that of the zwitterion **1** shows the significant σ-withdrawing influence of the second (Xe^+) substituent combined with a polarization of the C_6F_4-π-system in direction to C(1) and C(4). Thus, a low π-electron density on $C^{2,3,5,6}$ results from the polarization and enables an intense p-p-π-backbond from the four attached fluorine atoms $F^{2,3,5,6}$ to $C^{2,3,5,6}$. As well $F^{2,6}$ and $F^{3,5}$ as $Xe^{1,4}$ show deshielded resonances in **4** with respect to **1**.

A comparison of the three related cyclohexa-1,4-diene species, the zwitterion, 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) (**2**), the dication, [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$ (**5**), and the cation, [1-Xe-*cyclo*-1,4-C_6F_7]$^+$[16] (Table 2) shows the following sequence of shielding for $\delta(^{19}F^2)$ (and $\delta(^{19}F^5)$ in **5**) in neighborhood to Xe^+: [1-Xe-*cyclo*-1,4-C_6F_7]$^+$ > 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) > [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$. The ^{129}Xe resonance in (Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) appears more shielded than in [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$ and [1-Xe-*cyclo*-1,4-C_6F_7]$^+$. Additionally, the ^{19}F and ^{129}Xe NMR spectroscopic data of the new cycloalkenylxenonium cation [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$ are reported. The latter resulted from 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) by protodeboration with aHF (cf. the protodeboration of [1,4-$(F_3B)_2C_6F_4$]$^{2-}$ in the Supporting Information). The ^{129}Xe shielding and the $^3J(^{129}Xe-^{19}F)$ coupling constant of [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$ is slightly larger than in the [1-Xe-*cyclo*-1,4-C_6F_7]$^+$ cation.

Solid-State Raman Spectrum of 1-(Xe^+)C_6F_4-4-(BF_3^-). The solid-state Raman spectrum of the zwitterion 1-(Xe^+)C_6F_4-4-(BF_3^-) at 20 °C revealed the most intense Raman band at 187 cm^{-1}. This frequency is lower than in [C_6F_5Xe][BF_4] (205 cm^{-1}) and the corresponding isoelectronic molecule C_6F_5I (204 cm^{-1}).[20] In the former study it was shown that these frequencies correspond to Xe−C and I−C stretches, respectively, which are coupled to in-plane bending modes of the C_6F_5 group. In analogy, the vibration at 187 cm^{-1} was assigned to the Xe−C stretch in **1**. The lower frequency in **1** compared to **3** is supported by a weaker bond (longer Xe−C distance) in **1** relative to **3** (see computational results in the Supporting Information). The polarity of the Xe−C bond is one important factor for the strength of the bond. Electron-withdrawing substituents bonded to the C_6-ring are necessary to establish relatively strong Xe−C bonds. In contrast, the electron-donating (BF_3^-)-substituent in the *para*-position to Xe^+ lowers the Xe−C bond strength and explains the reported frequency shift to lower energy in the Raman spectrum.

CONCLUSIONS

The Lewis acidity of 1,4-bis(difluoroboryl)tetrafluorobenzene, 1,4-$(F_2B)_2C_6F_4$, exceeds that of the related (difluoroboryl)-pentafluorobenzene, $C_6F_5BF_2$. The combination of high acidity and bifunctionality in 1,4-$(F_2B)_2C_6F_4$ constrained the xenodeborylation reaction of the diboryl compound with XeF_2 in PFP. Only one of the two potential xenodeborylation steps could be realized with 1,4-$(F_2B)_2C_6F_4$ in a satisfactory conversion. Instead of the xenonium salt [$XeC_6F_4BF_2$][BF_4] the zwitterion 1-(Xe^+)C_6F_4-4-(BF_3^-) was formed in the 1:1 reaction. The zwitterion, 1-(Xe^+)C_6F_4-4-(BF_3^-) was insoluble under the experimental conditions (PFP). The insolubility of the product and the conversion of the second BF_2 group into (BF_3^-) in the first xenodeborylation step hampered a further xenodeborylation step. While xenodeborylation is a unique methodical approach to [RXe][BF_4] salts, it is not the optimal method to prepare xenonium salts with *two* or *more* Xe−C bonds.

Besides the desired formation of the Xe−C bond in 1-(Xe^+)C_6F_4-4-(BF_3^-), fluorine addition to the aromatic C_6F_4 unit proceeded in the highly acidic system with the formation of 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) and depended on the ratio of XeF_2 applied in the reaction with 1,4-$(F_2B)_2C_6F_4$.

The zwitterion 1-(Xe^+)C_6F_4-4-(BF_3^-) and the xenonium tetrafluoroborate salt with the dication, [1,4-$(Xe)_2C_6F_4$]$^{2+}$ (a low yield byproduct), revealed two types of opposite influence

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on the stability and reactivity of the Xe−C bond in a perfluoroaryl xenonium moieties (a) that of a strong electron-donating substituent (BF_3^-) and (b) that of a strong electron-withdrawing substituent (second Xe^+).

EXPERIMENTAL SECTION

Apparatus and Materials. The NMR spectra were measured on the Bruker spectrometer AVANCE 300 (^1H at 300.13 MHz, ^{19}F at 282.40 MHz, ^{11}B at 96.29 MHz, ^{129}Xe at 83.02 MHz, ^{13}C at 75.46 MHz). The chemical shifts are referenced to TMS (^1H, ^{13}C), CCl_3F (^{19}F, with C_6F_6 as secondary external reference (−162.9 ppm)), and $XeOF_4$ (^{129}Xe, with XeF_2 in CH_3CN (extrapolated to zero concentration) as secondary external reference (−1818.3 ppm),[21] respectively. The composition of the reaction mixtures and the yields of products in solution were determined by ^{19}F NMR spectroscopy using internal integral standards. Differential Scanning Calorimetry (DSC) was performed using a Netzsch 204 Phoenix instrument. In a glovebox, samples (ca. 5 mg) were weighed in Al pans with lids which contained a ca. 1 mm bore hole allowing gaseous decomposition products to escape. The furnace of the DSC instrument was flushed with dry nitrogen and heating proceeded with a rate of 10 K/min. The Raman spectra were recorded at 20 °C on powders in glass capillaries on a Bruker RFS 100/S FT Raman spectrometer using 1064 nm excitation, a resolution of 4 cm^{-1}, a laser power of ca. 250 mW, and a total of 512 scans.

1,1,1,3,3-Pentafluoropropane (PFP) was supplied by Honeywell and dried over molecular sieves 3 Å. Anhydrous hydrogen fluoride, aHF, was obtained by electrolysis (stainless steel cell, Ni electrodes). The salt, $[C_6F_5Xe][BF_4]$,[11,19] was prepared as described. The synthesis of $K_2[1,4\text{-}(F_2B)_2C_6F_4]$ is described in the Supporting Information.

All manipulations with organylxenonium salts in aHF and 27% aq HF were performed in FEP (a block copolymer of tetrafluoroethylene and hexafluoropropylene) vessels under an atmosphere of dry argon. ***Caution**: Adequate precaution is necessary when handling anhydrous hydrogen fluoride (aHF).*[22]

Synthesis of 1,4-$(F_2B)_2C_6F_4$. The salt, $K_2[1,4\text{-}(F_3B)_2C_6F_4]$ (432.45 mg; 1.1950 mmol), was suspended in PFP (8 mL) in an FEP trap (inner diameter = 23 mm) and cooled to −50 °C. Under vigorous stirring a large excess of BF_3 gas (4.5 mmol, HF was removed by passing the gas through a cold NaF/PFP suspension) was bubbled into the borate suspension within 40 min. Subsequently, the trap with the suspension was closed with a Teflon stopper and stirred for 35 min before warming to 0 °C. Two alternatives were checked to remove the excess of BF_3 gas: (a) removal under dynamic vacuum ($5\bullet10^{-2}$ hPa) at −78 °C was incomplete and combined with a loss of larger amounts of PFP and (b) distillation under Ar protection from the opened trap at 0 °C in a well-ventilated hood with a gas scrubber. After sedimentation of the slightly red solid and centrifugation at 0 °C the colorless mother liquor (8 mL) was separated. A sample (350 μL; 0 °C) was taken, and 1,1,1,3,3-pentafluorobutane (PFB, 8.02 mg; 0.0542 mmol) was added as an internal integral standard to determine the quantity of 1,4-$(F_2B)_2C_6F_4$ by ^{19}F NMR. The total amount of 1,4-$(F_2B)_2C_6F_4$ was 224 mg; 0.91 mmol; 76%. Attempts to separate low boiling PFP from volatile 1,4-$(F_2B)_2C_6F_4$ were not successful. Consequently, for all xenodeborylation reactions 1,4-$(F_2B)_2C_6F_4$/PFP solutions with a defined content were used.

1,4-$(F_2B)_2C_6F_4$. ^{19}F NMR spectrum (PFP, 0 °C): $\delta(^{19}F)$ = −72.0 ppm (br, $\Delta\nu_{1/2}$ = 110 Hz, 4F, BF_2), −128.9 ppm (s, $\Delta\nu_{1/2}$ = 14 Hz, $^1J(^{19}F-^{13}C)$ = 256 Hz, 4F, $F^{2,3,5,6}$); ^{11}B NMR spectrum (PFP, 0 °C): $\delta(^{11}B)$ = 21.7 ppm (br, $\Delta\nu_{1/2}$ = 179 Hz); $^{13}C\{^{19}F\}$ NMR spectrum (PFB, 0 °C): $\delta(^{13}C)$ = 150.2 ppm (s, $C^{2,3,5,6}$), 98.4 ppm (s, $C^{1,4}$).

Synthesis of 1-$(Xe^+)C_6F_4$-4-(BF_3^-) (Optimized Procedure). A cold (−78 °C) solution of 1,4-$(F_2B)_2C_6F_4$ (0.121 mmol) in PFP (1.5 mL) was added under vigorous stirring to a cold (−78 °C) solution of XeF_2 (20.24 mg; 0.120 mmol) in 5 mL of PFP in an FEP trap (inner diameter = 23 mm). Spontaneously a voluminous yellow precipitate resulted. After 55 min the ^{19}F NMR spectrum of the mother liquor confirmed that XeF_2 and 1,4-$(F_2B)_2C_6F_4$ were completely converted. The only byproduct was 1,4-$(F_2B)_2$-*cyclo*-1,4-C_6F_6 {$\delta(^{19}F)$ = −73.6 ppm (br, $\Delta\nu_{1/2}$ = 401 Hz, 4F, BF_2), −97.6 ppm (m, 2F, $F^{2,5}$), −98.3 ppm (m, 2F, $F_a^{3,6}$), −98.4 ppm (m, 2F, $F_b^{3,6}$)}, which was formed in 22% yield. The suspension was centrifuged (−78 °C), and the mother liquid separated. The solid residue was dried under vacuum ($7\bullet10^{-2}$ hPa, 1 h; −78 °C), and the yellow product was dissolved in aHF (500 μL; −78 °C, FEP inliner) to determine the products and their fraction.

^{19}F NMR spectrum (aHF, −30 °C): $\delta(^{19}F)$ = −124.8 ppm (br, $\Delta\nu_{1/2}$ = 39 Hz, 2F, $F^{3,5}$), −127.0 ppm (m, $^3J(^{19}F^{2,6}-^{129}Xe)$ = 53 Hz, 2F, $F^{2,6}$), −133.6 ppm (br, $\Delta\nu_{1/2}$ = 138 Hz, 3F, BF_3) 1-$(Xe^+)C_6F_4$-4-(BF_3^-); −88.5 ppm (m, 1F, F^2), −94.9 ppm (m, 2F, $F^{6,6}$), −96.0 ppm (m, 2F, $F^{3,3}$), −115.5 ppm (m, 1F, F^5), −135.1 ppm (br, $\Delta\nu_{1/2}$ = 135 Hz, 3F, BF_3) 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-); −84.1 ppm (m, 1F, F^2), −107.3 ppm (m, 2F, $F^{6,6}$), −109.3 ppm (m, 2F, $F^{3,3}$), −116.1 ppm (m, 1F, F^5) [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$; −113.8 ppm (s, $\Delta\nu_{1/2}$ = 6 Hz, 4F, $F^{2,3,5,6}$) $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$; −148.8 ppm (q(1:1:1:1), $^1J(^{19}F-^{11}B)$ = 12 Hz, 4F) $[BF_4]^-$; molar fraction (The sum of all 1,4-C_6F_4- and *cyclo*-1,4-C_6F_6-compounds was fixed to 100%.): 1-$(Xe^+)C_6F_4$-4-(BF_3^-) (77%); 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) (13%); [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$ (7%); $[1,4\text{-}(Xe)_2C_6F_4]^{2+}$ (3%); $[BF_4]^-$ (51%).

Purification of the Solid Mixture of a 1:1 Reaction Product. The dried solid mixture of products (120 mg from a larger scale experiment) was warmed under vacuum to 20 °C within 10 min. The solid was extracted repeatedly with cold (0 °C) 27% aq HF, total amount 9 mL. With proceeding extraction steps the quantity of $[BF_4]^-$ and the corresponding cations decreased. The extraction was accompanied by a significant loss of 1-$(Xe^+)C_6F_4$-4-(BF_3^-) because of its partial solubility in 27% aq HF. Therefore the extraction was stopped when the fraction of $[BF_4]^-$ relative to **1** in the 27% aq HF phase fell below 1%. Purified and vacuum-dried ($4\bullet10^{-2}$ hPa; 20 °C; 2 h) 1-$(Xe^+)C_6F_4$-4-(BF_3^-) showed a pale yellow color. The isolated yield was 31.6 mg; 0.091 mmol; 13%. The zwitterion, 1-$(Xe^+)C_6F_4$-4-(BF_3^-), was stored in a glovebox at 20 °C more than one month without decomposition.

Solubility of 1-$(Xe^+)C_6F_4$-4-(BF_3^-). The solubility of 1-(Xe^+)-C_6F_4-4-(BF_3^-) was determined in 27% aq HF (550 μL) using the internal integral standard $(CF_3)_2CHOH$ (4.85 mg; 0.0289 mmol) to 5.73 mg/mL; 0.0165 mmol/mL at 0 °C and to 5.46 mg/mL; 0.0157 mmol/mL at −60 °C, respectively. The solubility in aHF (>90 μmol/mL at −78 °C) was higher than in 27% aq HF.

1-$(Xe^+)C_6F_4$-4-(BF_3^-). DSC: 148 °C (T_{onset}, exothermic, dec), 158 °C ($T_{maximum}$).

Raman (250 mW; 512 Scans; 20 °C), $\tilde{\nu}$(cm^{-1}) = 55 (3), 120 (12), 187 (100), 202 (19), 274 (6), 302 (21), 376 (11), 394 (17), 420 (21), 439 (23), 466 (6), 499 (66), 631 (30), 752 (8), 857 (5), 1027 (2), 1148 (5), 1239 (3), 1385 (5), 1616 (5).

^{19}F NMR spectrum (27% aq HF, 24 °C): $\delta(^{19}F)$ = −128.6 ppm (m, 2F, $F^{3,5}$), −129.3 ppm (m, $^3J(^{19}F^{2,6}-^{129}Xe)$ = 59 Hz, 2F, $F^{2,6}$), −133.1 ppm (m, 3F, BF_3); ^{11}B NMR spectrum (27% aq HF, 24 °C): $\delta(^{11}B)$ = 0.9 ppm (q(1:1:1:1), $^1J(^{11}B-^{19}F)$ = 43 Hz); ^{19}F NMR spectrum (aHF, −10 °C): $\delta(^{19}F)$ = −124.7 ppm (m, $^1J(^{19}F^3-^{13}C^3$, $^{19}F^5-^{13}C^5)$ = 250 Hz, 2F, $F^{3,5}$), −126.8 ppm (m, $^1J(^{19}F^2-^{13}C^2$, $^{19}F^6-^{13}C^6)$ = 262 Hz, $^3J(^{19}F^{2,6}-^{129}Xe)$ = 53 Hz, 2F, $F^{2,6}$), −133.6 ppm (br, $\Delta\nu_{1/2}$ = 145 Hz, 3F, BF_3); ^{11}B NMR spectrum (aHF, −10 °C): $\delta(^{11}B)$ = 1.9 ppm (br, $\Delta\nu_{1/2}$ = 90 Hz); $^{13}C\{^{19}F\}$ NMR (aHF, −10 °C): $\delta(^{13}C)$ = 149.4 ppm (s, $C^{2,6}$), 143.1 ppm (s, $C^{3,5}$), 111.5 ppm (s, $\Delta\nu_{1/2}$ > 1000 Hz, C^4), 83.7 ppm (s, $^1J(^{13}C^1-^{129}Xe)$ = 82 Hz, C^1); ^{129}Xe NMR spectrum (aHF, −10 °C): $\delta(^{129}Xe)$ = −3982 ppm (t, $^3J(^{129}Xe-^{19}F^{2,6})$ = 53 Hz); ^{19}F NMR spectrum (CH_3CN, 0 °C): $\delta(^{19}F)$ = −127.2 ppm (m, 2F, $F^{3,5}$), −129.9 ppm (m, $^3J(^{19}F^{2,6}-^{129}Xe)$ = 60 Hz, 2F, $F^{2,6}$), −133.9 (q(1:1:1:1)t, $^1J(^{19}F-^{11}B)$ = 40 Hz, $^4J(^{19}F-^{19}F^{3,5})$ = 12 Hz, 3F, BF_3); ^{11}B NMR spectrum (CH_3CN, 0 °C): $\delta(^{11}B)$ = 1.2 ppm (q, $^1J(^{11}B-^{19}F)$ = 41 Hz); $^{13}C\{^{19}F\}$ NMR spectrum (CH_3CN, 0 °C): $\delta(^{13}C)$ = 149.5 ppm (s, $C^{2,6}$), 143.3 ppm (s, $C^{3,5}$), the resonances of C^1 and C^4 were not observed within 15 h time of measuring; ^{129}Xe NMR spectrum (CH_3CN, 0 °C): $\delta(^{129}Xe)$ = −3858 ppm (t, $^3J(^{129}Xe-F^{2,6})$ = 60 Hz); ^{19}F NMR spectrum (CH_3CN, −40 °C): $\delta(^{19}F)$ = −127.9 ppm (m, 2F, $F^{3,5}$), −130.0 ppm (m, $^3J(^{19}F^{2,6}-^{129}Xe)$ = 61 Hz, 2F, $F^{2,6}$), −133.7 ppm (m, 3F, BF_3); ^{19}F NMR spectrum (CH_3CN, 24 °C): $\delta(^{19}F)$ = −126.8 ppm (m, 2F, $F^{3,5}$), −129.9 ppm (m,

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$^3J(^{19}F^{2,6}-^{129}Xe)$ = 60 Hz, 2F, $F^{2,6}$), −134.0 ppm (q(1:1:1:1)t, $^1J(^{19}F-^{11}B)$ = 40 Hz, $^4J(^{19}F-^{19}F^{3,5})$ = 13 Hz, 3F, BF_3).

Thermal Stabiliy of 1-(Xe^+)C_6F_4-4-(BF_3^-) in CH_3CN and aHF Solutions. The decomposition of a saturated mother liquor (ca. 500 μL) of 1-(Xe^+)C_6F_4-4-(BF_3^-) in cold (−40 °C) CH_3CN was monitored by ^{19}F NMR spectroscopy in an FEP inliner. After 30 h at −40 °C no decomposition was detected. After 20 h at 0 °C only 2% of 1-(Xe^+)C_6F_4-4-(BF_3^-) was converted to [2,3,5,6-$C_6F_4HBF_3$]$^-$. ^{19}F NMR spectrum (CH_3CN, 0 °C): $\delta(^{19}F)$ = −133.1 ppm (m, 3F, BF_3), −135.2 ppm (m, 2F, $F^{3,5}$), −142.7 ppm (m, 2F, $F^{2,6}$) [2,3,5,6-$C_6F_4HBF_3$]$^-$. A solution of 1-(Xe^+)C_6F_4-4-(BF_3^-) in cold aHF (−10 °C, FEP inliner) showed no decomposition after 17 h at −10 °C (^{19}F NMR).

The Competitive Comparison of the Thermal Stability of 1-(Xe^+)C_6F_4-4-(BF_3^-) and [C_6F_5Xe][BF_4] in 27% aq HF. A solution of 1-(Xe^+)C_6F_4-4-(BF_3^-) in 27% aq HF (500 μL) was added to solid [C_6F_5Xe][BF_4] in an FEP inliner. ^{19}F NMR spectrum (27% aq HF, 24 °C): $\delta(^{19}F)$ = −128.6 ppm (m, 2F, $F^{3,5}$), −129.3 ppm (m, $^3J(^{19}F^{2,6}-^{129}Xe)$ = 60 Hz, 2F, $F^{2,6}$), −133.1 ppm (m, 3F, BF_3) 1-(Xe^+)C_6F_4-4-(BF_3^-); −125.8 ppm (m, $^3J(^{19}F^{2,6}-^{129}Xe)$ = 67 Hz, 2F, $F^{2,6}$), −141.8 ppm (tt, $^3J(^{19}F^4-^{19}F^{3,5})$ = 20 Hz, $^4J(^{19}F^4-^{19}F^{2,6})$ = 5 Hz, 1F, F^4), −154.1 ppm (m, 2F, $F^{3,5}$), −149.1 (q(1:1:1:1), $^1J(^{19}F-^{11}B)$ = 1 Hz, 4F, BF_4) [C_6F_5Xe][BF_4]. After 80 min at 20 °C no products of decomposition were detected, and the molar ratio of 1-(Xe^+)C_6F_4-4-(BF_3^-):[C_6F_5Xe][BF_4] was determined to 33:67. The decomposition was monitored by ^{19}F NMR spectroscopy. After 20 h at 20 °C the ratio **1**:**3** changed to 44:56. Finally, after 3 d both compounds were decomposed completely by solvolysis and formed a suspension of [2,3,5,6-$C_6F_4HBF_3$]$^-$ along with $(C_6F_5)_2$ and $(C_6F_5)_2O$, respectively. ^{19}F NMR spectrum (solid decomposition products in CH_3CN, 24 °C): $\delta(^{19}F)$ = −138.0 ppm ($F^{2,6}$) −150.6 ppm (F^4), −160.9 ppm ($F^{3,5}$), $(C_6F_5)_2$; −156.2 ppm ($F^{2,6}$), −159.9 ppm (F^4), −162.3 ppm ($F^{3,5}$), $(C_6F_5)_2O$.

Reaction of 1-(Xe^+)C_6F_4-4-(BF_3^-) with a ca. 100-Fold Excess of KHal (Hal = I, Br, Cl, F). Each of the FEP inliners was loaded with KHal (Hal = I (**A**), 141 mg, 0.849 mmol; Br (**B**), 92 mg, 0.77 mmol; Cl (**C**), 62 mg, 0.83 mmol; F (**D**), 48 mg; 0.83 mmol before the pale yellow solution of 1-(Xe^+)C_6F_4-4-(BF_3^-) (**A**−**D**: 2.9 mg; 0.0084 mmol) in 27% aq HF (500 μL) was added at 20 °C. Solution **A** changed its color to yellow orange. The progress of reactions **A**−**D** was monitored by ^{19}F NMR spectroscopy (27% aq HF, 24 °C). In **A** and **B** 1-(Xe^+)C_6F_4-4-(BF_3^-) was converted completely within <10 min, whereas **C** and **D** required 1 d.

A: ^{19}F NMR spectrum: $\delta(^{19}F)$ = −123.4 ppm (m, 2F, $F^{3,5}$), −133.2 ppm (m, 3F, BF_3), −135.4 (m, 2F, $F^{2,6}$), [4-$IC_6F_4BF_3$]$^-$; −133.2 ppm (m, 3F, BF_3), −138.0 ppm (m, 2F, $F^{2,6}$), −140.9 ppm (m, 2F, $F^{3,5}$) [2,3,5,6-$C_6F_4HBF_3$]$^-$; molar ratio [4-$IC_6F_4BF_3$]$^-$:[2,3,5,6-$C_6F_4HBF_3$]$^-$ 87:13.

B: ^{19}F NMR spectrum: $\delta(^{19}F)$ = −133.2 ppm (m, 3F, BF_3), −135.8 ppm (m, 2F, $F^{3,5}$), −135.8 ppm (m, 2F, $F^{2,6}$) [4-$BrC_6F_4BF_3$]$^-$; −133.2 (m, 3F, BF_3), −138.0 (m, 2F, $F^{2,6}$), −141.0 ppm (m, 2F, $F^{3,5}$) [2,3,5,6-$C_6F_4HBF_3$]$^-$; molar ratio [4-$BrC_6F_4BF_3$]$^-$:[2,3,5,6-$C_6F_4HBF_3$]$^-$ 72:28.

C: ^{19}F NMR spectrum: $\delta(^{19}F)$ = −133.3 ppm (m, 3F, BF_3), −136.3 ppm (m, 2F, $F^{2,6}$), −143.4 (m, 2F, $F^{3,5}$) [4-$ClC_6F_4BF_3$]$^-$; −133.2 ppm (m, 3F, BF_3), −138.0 ppm (m, 2F, $F^{2,6}$), −141.0 ppm (m, 2F, $F^{3,5}$) [2,3,5,6-$C_6F_4HBF_3$]$^-$; molar ratio [4-$ClC_6F_4BF_3$]$^-$:[1-[2,3,5,6-$C_6F_4HBF_3$]$^-$ 71:29.

D: ^{19}F NMR spectrum: $\delta(^{19}F)$ = −133.2 ppm (m, 3F, BF_3), −138.0 ppm (m, 2F, $F^{2,6}$), −141.2 ppm (m, 2F, $F^{3,5}$) [2,3,5,6-$C_6F_4HBF_3$]$^-$.

The Competitive Reaction of 1-(Xe^+)C_6F_4-4-(BF_3^-) and [C_6F_5Xe][BF_4] with KCl in a ca. 100-Fold Excess. The salt, KCl (64 mg, 0.86 mmol), was loaded in an FEP inliner, and the pale yellow solution of 1-(Xe^+)C_6F_4-4-(BF_3^-) (2.9 mg; 0.0084 mmol) and [C_6F_5Xe][BF_4] (2.5 mg; 0.0065 mmol) in 27% aq HF (500 μL) was added. A solid product precipitated. The progress of the reaction was monitored by ^{19}F NMR spectroscopy. After 7 h [C_6F_5Xe]$^+$ was completely converted into C_6F_5Cl. The complete conversion of 1-(Xe^+)C_6F_4-4-(BF_3^-) to [4-$ClC_6F_4BF_3$]$^-$ (88%) and [2,3,5,6-$C_6F_4HBF_3$]$^-$ (12%) took 22 h. At the end, the solid product was separated, dissolved in $(CH_3)_2SO$ (300 μL), and identified as K[BF_4].

Treatment of 1-(Xe^+)C_6F_4-4-(BF_3^-) with an Excess of XeF_2 in aHF. Solid XeF_2 (9.8 mg; 0.058 mmol) was added to a solution of 1-(Xe^+)C_6F_4-4-(BF_3^-) (2.0 mg; 0.0057 mmol) in cold aHF (300 μL; −78 °C) in an FEP inliner. After 15 min at −78 °C no reaction could be observed in the solution. The sample was warmed up (−30 °C) and after 80 min 1-(Xe^+)C_6F_4-4-(BF_3^-) was completely consumed and 17 μmol of XeF_2. Neither 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) nor [1,4-$(Xe)_2C_6F_4$]$^{2+}$ and [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$ were detected. Besides the resonance of [BF_4]$^-$ (main signal) a large number of unknown signals with ^{19}F resonances between −60 and −160 ppm were present. This range comprises inter alia fluorine addition products to the C_6F_4 unit.

The 2:1 Reaction of XeF_2 with 1,4-$(F_2B)_2C_6F_4$, a Typical Experiment in a Series of Attempts To Optimize the Synthesis of [1,4-$(Xe)_2C_6F_4$][BF_4]$_2$. A solution of XeF_2 (50.86 mg; 0.3004 mmol) in PFP (6 mL; −78 °C) in an FEP trap (inner diameter = 23 mm) was vigorously stirred when a solution of 1,4-$(F_2B)_2C_6F_4$ (0.1478 mmol) in PFP (1.5 mL; −78 °C) was added dropwise. A voluminous yellow precipitate was formed instantly. After 1 h the supernatant was investigated by ^{19}F NMR. The coproduct, BF_3, was detected along with 1,4-$(F_2B)_2$-*cyclo*-1,4-C_6F_6. The cold (−78 °C) suspension was centrifuged, the mother liquor was separated, and the solid residue was dried under vacuum (65 min; −78 °C). The pale yellow solid was dissolved in aHF (700 μL; −78 °C) and transferred into an FEP inliner for the NMR spectroscopic characterization.

^{19}F NMR spectrum (aHF, −80 °C): $\delta(^{19}F)$ = −125.4 ppm (br, $\Delta\nu_{1/2}$ = 59 Hz, 2F, $F^{3,5}$), −127.4 ppm (m, $^3J(^{19}F^{2,6}-^{129}Xe)$ = 54 Hz, 2F, $F^{2,6}$), −133.6 ppm (br, $\Delta\nu_{1/2}$ = 146 Hz, 3F, BF_3) 1-(Xe^+)C_6F_4-4-(BF_3^-); −89.3 ppm (m, 1F, F^2), −95.7 ppm (m, 2F, $F^{6,6}$), −96.8 ppm (m, 2F, $F^{3,3}$), −116.0 ppm (m, 1F, F^5), −135.1 ppm (br, $\Delta\nu_{1/2}$ = 149 Hz, 3F, BF_3) 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-); −84.9 ppm (m, 1F, F^2), −108.1 ppm (m, 2F, $F^{6,6}$), −110.1 ppm (m, 2F, $F^{3,3}$), −116.5 ppm (m, 1F, F^5) [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$; −114.6 ppm (s, $\Delta\nu_{1/2}$ = 5 Hz, 4F, $F^{2,3,5,6}$) [1,4-$(Xe)_2C_6F_4$]$^{2+}$; −83.7 ppm (m, 2F, $F^{2,5}$), −93.2 ppm (m, 4F, $F^{3,3,6,6}$) [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$; −122.4 ppm (m, 2F, $F^{3,5}$), −124.4 ppm (m, $^3J(^{19}F^2-^{129}Xe)$ = 54 Hz, 2F, $F^{2,6}$) [1−Xe-C_6F_4-4-R]$^+$; −102.5 ppm (m, 1F), −106.8 ppm (m, 2F), −118.9 ppm (m, 1F), −129.0 ppm (m, 2F) 1-R′-*cyclo*-1,4-C_6F_6-4-R″; −148.5 ppm (br, $\Delta\nu_{1/2}$ = 63 Hz, 4F) [BF_4]$^-$; molar fraction (The sum of all 1,4-C_6F_4- and *cyclo*-1,4-C_6F_6-compounds was fixed to 100%): 1-(Xe^+)C_6F_4-4-(BF_3^-) (47%); 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) (42%); [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$ (5%); [1,4-$(Xe)_2C_6F_4$]$^{2+}$ (2%); [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$ (1%); [1−Xe-C_6F_4-4-R]$^+$ (3%); 1-R′-*cyclo*-1,4-C_6F_6-4-R″ (5%); [BF_4]$^-$ (45%).

^{129}Xe NMR spectrum (aHF, −80 °C): $\delta(^{129}Xe)$ = −3998 (t, $^3J(^{129}Xe-^{19}F^{2,6})$ = 53 Hz) 1-(Xe^+)C_6F_4-4-(BF_3^-); −4004 (d, $^3J(^{129}Xe-^{19}F^2)$ = 68 Hz) 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-); −3970 (d, $^3J(^{129}Xe-^{19}F^2)$ = 73 Hz) [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$; −3823 (t, $^3J(^{129}Xe-^{19}F^{2,6})$ = 60 Hz) [1,4-$(Xe)_2C_6F_4$]$^{2+}$; −3865 (d, $^3J(^{129}Xe-^{19}F^2)$ = 69 Hz) [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$; from another experiment after enrichment of 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-): ^{129}Xe NMR (CH_3CN, −30 °C): $\delta(^{129}Xe)$ = −3834 (d, $^3J(^{129}Xe-F^{2,6})$ = 71 Hz).

Chemical Proof of [1,4-$(Xe)_2C_6F_4$]$^{2+}$ in a Mixture of Products by the Definite Conversion with Potassium Iodide in aHF. The salt, KI (17 mg, 0.10 mmol), was loaded in an FEP inliner before a cold (−78 °C) reaction mixture with an enriched amount of [1,4-$(Xe)_2C_6F_4$]$^{2+}$ (8%), [1,4-$(Xe)_2$-*cyclo*-1,4-C_6F_6]$^{2+}$ (13%), 1-(Xe^+)C_6F_4-4-(BF_3^-) (23%), 1-(Xe^+)-*cyclo*-1,4-C_6F_6-4-(BF_3^-) (51%), and [1-Xe-*cyclo*-1,4-C_6F_6-4-H]$^+$ (5%) in aHF (500 μL) was added. A brown suspension resulted which was vigorously shaken. The mother liquor was separated, and the precipitate was dried under vacuum. The color of the solid changed to yellow. The solid product was suspended in cold CH_3CN (500 μL; −40 °C). 1,4-$I_2C_6F_4$ (s, $\Delta\nu_{1/2}$ = 11 Hz, −119.6 ppm) and [4-$IC_6F_4BF_3$]$^-$ (m, −122.8 ppm $F^{3,5}$, m, −133.3 ppm $F^{2,6}$, br, −135.5 ppm BF_3) were assigned, and at least three unidentified compounds with partially overlapping signals were additionally present (^{19}F) which presumably belonged to iodo compounds with I−C_6F_4- and I-*cyclo*-1,4-C_6F_6-fragments without reference data in literature. The

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product, 1,4-$I_2C_6F_4$, was additionally proven by adding an authentic sample of 1,4-$I_2C_6F_4$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calculated bond distances, natural population analysis charges, and σ- and π-orbital natural population analysis charges of $(Xe^+)C_6F_4(BF_3^-)$ and related species (Table S1), the Raman spectrum of $(Xe^+)C_6F_4(BF_3^-)$ (Figure S1), fluoride affinities of selected fluoroboranes (Table S2), the synthesis of 2,3,5,6-tetrafluorophenylene-1,4-bis(magnesiumbromide), the synthesis of 1,4-bis(dimethoxyboryl)-2,3,5,6-tetrafluorobenzene, the synthesis of dipotassium 2,3,5,6-tetrafluorobenzene-1,4-bis(trifluoroborate), the protodeboration of $K_2[1,4\text{-}(F_3B)_2C_6F_4]$ in 48% aq HF, and the protodeboration of $K_2[1,4\text{-}(F_3B)_2C_6F_4]$ in aHF at −40 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: h-j.frohn@uni-due.de.

Notes

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