Arylxenon Tetrafluoroborates: Compounds of Unexpected Stability

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The isolation and characterization of the new arylxenon tetrafluoroborates [XeAr][BF$_4$] (Ar = 2,6-F$_2$C$_6$H$_3$, 2-FC$_6$H$_4$, 4-FC$_6$H$_4$) are reported. Whereas [Xe(2,6-F$_2$C$_6$H$_3$)][BF$_4$] decomposes at 130 °C, the monofluorinated aryl derivatives are only stable up to 36 °C ([Xe(2-FC$_6$H$_4$)][BF$_4$]) and –14 °C ([Xe(4-FC$_6$H$_4$)][BF$_4$]). The differences in stability are discussed on the basis of hydrolysis rates and multinuclear (^{19}F, ^{13}C, ^{129}Xe) NMR techniques. The stabilizing effect of the fluorine atoms in the 2- and 6-positions of the aromatic ring is discussed.

Introduction

Since the discovery of the first noble gas compound in 1962, considerable effort was spent on the synthesis of compounds with noble gas–carbon bonds, but only few examples have been published before 1989. Papers concerning this subject were those[1] on [Xe(C$_6$H$_5$)]$^+$, which was postulated, on the basis of electrophoretic investigations, as an intermediate during the β-decay of [^{131}I(C$_6$H$_5$)$_2$][BF$_4$]. The Xe–C bond strength in the CH$_3$Xe$^+$ cation was determined as 55.2 ± 2.5 kcal mol^{-1} from methyl cation exchange equilibria by ion cyclotron resonance.[2] The formation of Xe(CF$_3$)$_2$ as an unstable solid with a half-life time of 30 min at room temperature was reported in 1979,[3] but this compound is still controversial. In 1980 Schmeisser, Walter, and Naumann reported[4] unsuccessful attempts to obtain Xe(CF$_3$)$_2$ from a glow discharge reaction of CF$_3$ radicals with elemental xenon. In 1989 Naumann and Tyrra successfully synthesized [Xe(C$_6$F$_5$)][B(C$_6$F$_5$)$_3$F],[5] the first example of a stable derivative with a xenon–carbon bond. Similar results were obtained by Frohn and Jakobs,[6] who also determined a crystal structure.[7] (Pentafluorophenyl)xenon fluoroborates are white crystalline solids which slowly decompose at room temperature. In a further paper[8] from our laboratory, the synthesis of [Xe(2,4,6-F$_3$C$_6$H$_2$)][BF$_4$] by an improved method was described. [Xe(2,4,6-F$_3$C$_6$H$_2$)][BF$_4$] is a stable colorless and air insensitive solid that decomposes at 128 °C. In 1992 Zhdankin, Stang, and Zefirov[9] reported the synthesis of alkynylxenon tetrafluoroborates from the reaction of intermediately formed Li[BF$_3$C≡CR] with XeF$_2$.

The present work was carried out to get further information about the influence of fluorine substituents at the aromatic ring on the stability of the corresponding xenon derivative. For this purpose three new partly fluorinated arylxenon tetrafluoroborates were prepared and investigated.

Experimental Section

Materials and Apparatus. Literature methods were used for the synthesis of B(2,6-F$_2$C$_6$H$_3$)$_3$,[10] B(4-FC$_6$H$_4$)$_3$,[10] B(2-FC$_6$H$_4$)$_3$,[10] and XeF$_2$.[11] Commercial BF$_3$·O(CH$_3$)$_2$ (Aldrich Co.) was freshly distilled before use. All solvents were purified by common methods.[12] CD$_3$CN was obtained from the Aldrich Co. and purified by the same method as described for CH$_3$CN.[12] Standard vacuum techniques were employed throughout all preparative procedures; all compounds were handled in a dry N$_2$ atmosphere by using Schlenk techniques.

The NMR spectra were recorded on a Bruker Model AC 200 spectrometer (^{19}F, 188.3 MHz; ^{1}H, 200.1 MHz) and on a Bruker Model AMX 300 spectrometer (^{13}C, 75.5 MHz; ^{11}B, 96.3 MHz; ^{129}Xe, 83.3 MHz) with positive shifts being downfield from the external standards CCl$_3$F (^{19}F), TMS (^{1}H, ^{13}C), BF$_3$·O(C$_2$H$_5$)$_2$ (^{11}B), and 1 M XeF$_2$ in CH$_3$CN (^{129}Xe).

The visible melting points were determined on a HWS Mainz melting point apparatus SG 2000 in one-end open glass capillaries.

The mass spectra were recorded on a modified Varian CH 5 mass spectrometer with a source temperature of 180 °C.

Preparation of [Xe(2,6-F$_2$C$_6$H$_3$)][BF$_4$]. B(2,6-F$_2$C$_6$H$_3$)$_3$ (2.8 mmol) and BF$_3$·O(CH$_3$)$_2$ (5.7 mmol) were dissolved in 30 mL of CH$_2$Cl$_2$ at –40 °C. A solution of XeF$_2$ (8.5 mmol) in 50 mL of CH$_2$Cl$_2$ cooled to –40 °C was slowly added to the well-stirred borane solution over a period of approximately 2 h. During this period a colorless solid began to precipitate. Precipitation was complete after 12 h. The solid residue was filtered from the solution at –78 °C and washed several times with cold dichloromethane. [Xe(2,6-F$_2$C$_6$H$_3$)][BF$_4$] was obtained in a yield of 57%. Its purity was checked by multinuclear NMR spectroscopy and was better than 99%.

Preparation of [Xe(4-FC$_6$H$_4$)][BF$_4$]. B(4-FC$_6$H$_4$)$_3$ (1.0 mmol) and BF$_3$·O(CH$_3$)$_2$ (2.0 mmol) were combined in 20 mL of dichloromethane at –40 °C. XeF$_2$ (3.0 mmol) dissolved in 30 mL of dichloromethane (–40 °C) was added dropwise to the well-stirred borane solution over a period of 30 min. From the reaction mixture crude [Xe(4-FC$_6$H$_4$)][BF$_4$] precipitated. After 5 h the precipitate was filtered off at –78 °C and washed several times with cold dichloromethane. After drying of the product at –30 °C in a high vacuum, colorless [Xe(4-FC$_6$H$_4$)][BF$_4$] was obtained in 53% yield. Although the solid is stable up to –14 °C, [Xe(4-FC$_6$H$_4$)][BF$_4$] slowly decomposes in CH$_3$CN/CH$_2$Cl$_2$ mixtures already at temperatures around –50 °C, whereas in CD$_3$CN solution the compound is stable up to –25 °C.

Preparation of [Xe(2-FC$_6$H$_4$)][BF$_4$]. After B(2-FC$_6$H$_4$)$_3$ (3.4 mmol) and BF$_3$·O(CH$_3$)$_2$ (6.5 mmol) were combined in 50 mL of dichloromethane at –40 °C, a cold solution of XeF$_2$ (9.8 mmol) in 60 mL of dichloromethane was added dropwise to the well-stirred solution of the boranes. The reaction mixture became first turbid and brown and after a short while transparent and dark red. After completion of the XeF$_2$ addition, the reaction mixture was stored for 2 days at dry ice temperature. During this period a white solid precipitated, which was filtered at –78 °C. After the precipitate was washed with cold dichloromethane and the residue was dried in vacuo, [Xe(2-FC$_6$H$_4$)][BF$_4$] was obtained as a colorless solid in 7% yield. The purity, as determined by multinuclear NMR spectroscopy, was better than 95%.

In all cases the ^{11}B NMR resonances of the tetrafluoroborate anions are located at δ 0 ± 0.5 ppm.

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Table I. ^{129}Xe NMR Data for (Fluoroaryl)xenon Tetrafluoroborates [ArXe][BF_4] in CD_3CN Solution and the Decomposition Points of the Solids

Ar in [ArXe][BF_4]	temp, °C	δ(^{129}Xe), ppm	dec pt, °C
4-FC_6H_4	−30	−1896	−14
C_6F_5[a]	−12	−1980	+14[b]
2-FC_6H_4	−30	−2039	+36
2,4,6-$F_3C_6H_2$	−30	−2073	+128[c,d]
2,6-$F_2C_6H_3$	−30	−2115	+130[e]

[a] From ref 5. [b] From ref 7. [c] From ref 8. [d] Complete decomposition at 162 °C. [e] Complete decomposition at 180 °C.

All attempts to obtain mass spectra exhibiting the cation peak failed. Only fragments and polymers of the aromatic ring and Xe^+ could be detected.

Hydrolysis of [XeAr][BF$_4$]. A solution of 1% water in acetonitrile was poured into the well-stirred solution of the xenon derivative in the appropriate solvent. The reactions proceeded under evolution of elemental xenon. The end of hydrolysis was determined by ^{19}F NMR spectroscopy. The formation of H_2O_2 was established qualitatively by the oxidation of iodide in an acetate medium. ArH and HBF_4 were identified by their ^{19}F NMR spectra.

Results and Discussion

Synthesis of the Arylxenon Tetrafluoroborates. In analogy to [Xe(C_6F_5)][BF_4] and [Xe(2,4,6-$F_3C_6H_2$)][BF_4],[8] the new xenon derivatives are formed according to eq 1. This reaction can be explained by the assumption of the following two steps (eqs 2 and 3). In the primary step, $ArBF_2$ is formed as an intermediate

$$\mathrm{BAr_3 + 2BF_3{\cdot}O(CH_3)_2 + 3XeF_2 \rightarrow 3[XeAr][BF_4] + 2(CH_3)_2O} \quad (1)$$

solvent CH_2Cl_2; Ar = 2,6-$F_2C_6H_3$, 4-FC_6H_4, 2-FC_6H_4

$$\mathrm{BAr_3 + 2BF_3{\cdot}O(CH_3)_2 \rightleftharpoons 3ArBF_2 + 2(CH_3)_2O} \quad (2)$$

$$\mathrm{XeF_2 + ArBF_2 \rightarrow [XeAr][BF_4]} \quad (3)$$

which then reacts quantitatively with xenon difluoride to form the salts described above. Although the intermediately formed aryldifluoroborane could not be detected during the reaction by ^{19}F NMR spectroscopy, comparative studies on the reaction behavior of fluorinated triarylboranes with boron trifluoride adducts in the absence of XeF_2 showed that the formation of aryldifluoroboranes is the primary step. However, it cannot be excluded that [XeF][BF_4] is an intermediate which has previously been observed in the reaction of XeF_2 with $BF_3{\cdot}O(CH_3)_2$ in acetonitrile.[13] BAr_3 reacts with the [XeF]$^+$ cation undergoing a stepwise aryl–fluorine exchange to yield the arylxenon tetrafluoroborate as the final product.

Dichloromethane has been chosen as the solvent because of its inertness toward XeF_2 at temperatures below 0 °C and the extremely low solubility of the arylxenon tetrafluoroborates in this solvent. Therefore, the xenon derivative precipitates from the reaction mixture and can be easily separated by low-temperature filtration. By this method the arylxenon tetrafluoroborate is obtained in a nonsolvated form.

Properties and NMR Spectra of [XeAr][BF$_4$]. All compounds obtained are colorless solids which decompose between 36 and 130 °C (see Table I). They are air insensitive but are readily hydrolyzed by aqueous acetonitrile under formation of ArH (eq 4).

$$\mathrm{[XeAr][BF_4] + 2H_2O \rightarrow ArH + Xe + H_2O_2 + HBF_4} \quad (4)$$

The hydrolysis rate decreases with the thermal stability of [XeAr][BF_4] (see Table I). [Xe(4-FC_6H_4)][BF_4] is completely hydrolyzed within a few minutes by a solution of 1% water in acetonitrile, whereas hydrolyses of [Xe(2,6-$F_2C_6H_3$)][BF_4] and [Xe(2,4,6-$F_3C_6H_2$)][BF_4] require 1 week for completion.

All compounds readily dissolve in acetonitrile solution but decompose in the presence of Lewis bases of greater spatial requirement such as ethers, pyridine, or dimethylformamide. E.g., in the system [Xe(C_6F_5)][BF_4]/pyridine the *N*-(pentafluorophenyl)pyridinium tetrafluoroborate, [C_5H_5N-C_6F_5][BF_4], is formed and has fully been characterized by Frohn and Jakobs.[14]

The ^{19}F NMR spectra (Table II) show that the resonances of the (fluoroaryl)xenon cations are deshielded by comparison with the resonances of the isoelectronic neutral iodine or bromine species. This can be explained by a cation effect as always observed in the ^{19}F NMR spectra of (fluoroaryl)element cations (compare e.g. ref 8).

In the ^{13}C NMR spectra of the [Xe(C_6F_5)]$^+$, [Xe(2,4,6-$F_3C_6H_2$)]$^+$, and [Xe(2,6-$F_2C_6H_3$)]$^+$ series (Table III), the coupling constants $^1J(^{129}\mathrm{Xe}-^{13}\mathrm{C})$ decrease in the same manner as measured for the $^3J(^{129}\mathrm{Xe}-^{19}\mathrm{F})$ couplings. However, no obvious correlation between the coupling constants $^1J(^{129}\mathrm{Xe}-^{13}\mathrm{C})$ and any other properties of these compounds could be established.

With increasing fluorination of the aromatic ring, the shielding of the 1-C resonance increases in the ^{13}C NMR spectra (Table III). Two fluorine atoms in 2- and 6-positions increase the electron density at the 1-C atom, whereas a single fluorine atom in the 2-position causes a deshielding of the 1-C resonance of approximately 17 ppm. The resonance of the 1-C atom in [Xe(4-FC_6H_4)][BF_4] is located even 10 ppm further downfield from the resonance of the 1-C atom in [Xe(2-FC_6H_4)][BF_4]. This effect may be explained by a transfer of electron density from the 2,6-fluorine atoms to the xenon nucleus. The more the electron deficiency at the xenon nucleus is compensated by the lone electron pairs of the fluorine atoms, the more shielded is the 1-C resonance, and as a consequence the stability of the Xe–C bond increases.

In the same manner effects on the shielding of the ^{129}Xe nucleus are observed (Table I). Increasing electron density at the Xe–C bond is reflected by a higher shielding of the xenon nucleus in the ^{129}Xe NMR spectra. As expected, the decomposition points of the pure solids increase with increasing electron density in the Xe–C bond. However, it should be mentioned that properties of solids are not neccessarily comparable with data obtained from their solutions. The effect of back-donation, as it is also observed for Li[2,4,6-$(CF_3)_3C_6H_2$]·TMEDA,[15] may cause the differences in stability described above.

The thermal stability must be connected with the relative Lewis acid–Lewis base strength of BF_3 and ArXeF, or [ArXe]$^+$ and [BF_4]$^-$. The thermal decomposition in solution proceeds through eqs 5 and 6.

$$\underset{\text{Lewis acid}}{\mathrm{[XeAr]^+}}\ \underset{\text{Lewis base}}{\mathrm{[BF_4]^-}} \rightleftharpoons \underset{\text{Lewis base}}{\mathrm{ArXeF}} + \underset{\text{Lewis acid}}{\mathrm{BF_3}} \quad (5)$$

$$\mathrm{ArXeF \rightarrow ArF + Xe} \quad (6)$$

The differences in the Lewis acid strengths of the cations are expressed by the following characteristic features: An increased Lewis acidity causes (i) a lower decomposition point due to a strong competition of the cation with boron trifluoride to abstract the fluoride ion, (ii) a deshielding of the ^{129}Xe resonance, and

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Table II. ^{19}F NMR Data for (Fluoroaryl)xenon Tetrafluoroborates $[ArXe][BF_4]$[a]

Ar in $[ArXe][BF_4]$	solvent	temp, °C	δ(2-F)	δ(3-F)	δ(4-F)	δ(5-F)	δ(6-F)	$\delta(BF_4^-)$	$^3J(^{129}Xe-^{19}F)$, Hz
C_6F_5[b]	CH_3CN/CH_2Cl_2	r.t.	−125.2	−154.8	−142.0	−154.8	−125.2	−149.5	68
2,4,6-$F_3C_6H_2$[c]	CD_3CN	r.t.	−96.3		−96.0		−96.3	−149.8	54
2,6-$F_2C_6H_3$	CD_3CN	−30	−99.6				−99.6	−149.7	52
4-FC_6H_4	CD_3CN/CH_2Cl_2	−60			−104.6			−149.2	
2-FC_6H_4	CD_3CN	−30	−100.6					−149.5	48

[a] δ in ppm. [b] From ref 5. [c] From ref 8.

Table III. $^{13}C\{^1H\}$ NMR Data for (Fluoroaryl)xenon Tetrafluoroborates $[ArXe][BF_4]$[a]

Ar in $[ArXe][BF_4]$	solvent	temp, °C	δ(1-C)	δ(2-C)	δ(3-C)	δ(4-C)	δ(5-C)	δ(6-C)	$^1J(^{129}Xe-^{13}C)$, Hz
C_6F_5[b]	CH_3CN/CH_2Cl_2	−12	83.5	144.2	138.3	142.5	138.3	144.2	119
2,4,6-$F_3C_6H_2$[c]	CD_3CN	−30	83.8	158.4	105.0	167.8	105.0	158.4	104
2,6-$F_2C_6H_3$	CD_3CN	−30	88.8	156.8	115.2	137.8	115.2	156.8	99
4-FC_6H_4	CD_3CN/CH_2Cl_2	−30	115.6	133.3	122.7	165.1	122.7	133.3	104
2-FC_6H_4	CD_3CN	−30	105.5	155.3	120.6	136.9	130.7	133.2	78

[a] δ in ppm. [b] From ref 5. [c] From ref 8.

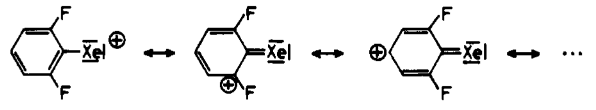

Figure 1.

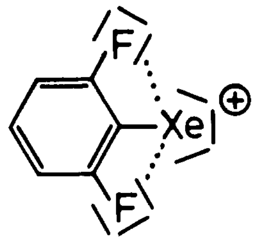

Figure 2.

(iii) a decrease of the $^1J(^{129}Xe-^{13}C)$ coupling constant as an effect of a lower electron density in the Xe–C bond.

The stability of the arylxenon cations may additionally be explained by the following effects: (i) the resonance effect, (ii) the general electron-withdrawing effect by fluorine substituents, (iii) the back-donation of electrons from fluorine atoms in the 2- and 6-positions, and (iv) the chelating effect.

The formation of resonance structures (Figure 1), by formation of a partial Xe–C π-bond, influences the stability of these compounds as discussed in ref 8. Electron-withdrawing groups in general are essential for the formation of stable xenon compounds. Back-donation of electrons from fluorine atoms in the 2- or 2- and 6-positions and a chelate effect (Figure 2) additionally increase the stability of arylxenon cations. On the basis of these suggestions, a classification of the aromatic substituents into three different groups can be made.

The C_6F_5 group may be classified as an electron-poor aromatic system with the possibility of a fluorine–xenon back-donation by formation of a chelate. The 2-FC_6H_4, 2,6-$F_2C_6H_3$, and 2,4,6-$F_3C_6H_2$ groups can be classified as electron-rich aromatic systems with the possibility of a fluorine–xenon back-donation and an additional chelate effect in the cases of the 2,6-$F_2C_6H_3$ and 2,4,6-$F_3C_6H_2$ groups. The 4-FC_6H_4 group is an electron-rich aromatic system without the possibility of an additional stabilizing effect.

These results agree in many aspects with those obtained by Zhdankin, Stang, and Zefirov.[9] If the ^{129}Xe NMR chemical shifts of the alkynylxenon tetrafluoroborates are compared with those of $[Xe(4\text{-}FC_6H_4)][BF_4]$, it is obvious that the resonances are located in the same region ($[Xe(C{\equiv}CSi(CH_3)_3)][BF_4]$, $\delta(^{129}Xe)$ −1818 ppm; $[Xe(4\text{-}FC_6H_4)][BF_4]$, $\delta(^{129}Xe)$ −1896 ppm). The alkynyl derivatives decompose at temperatures above −30 °C; $[Xe(4\text{-}FC_6H_4)][BF_4]$ decomposes at −14 °C. This example provides further support for the suggestion that the ^{129}Xe NMR chemical shifts of these compounds are a good measure of their thermal stabilities. Both ligands, the alkynyl group and the 4-fluorophenyl group, have in common that they are electron-rich substituents which enable resonance stabilization but do not allow further stabilization by formation of a chelate.

Conclusion

The thermal stability of arylxenon tetrafluoroborates strongly depends on the nature of the substituents at the aromatic ring: First, an electron-rich aromatic system is required for the stabilization. Second, small electron-rich substituents in ring positions 2 and 6 are essential to increase stability by formation of a chelate. Third, the formation of resonance structures should be possible.

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