# The First Hydrogen Containing (Polyfluorocycloalken-1-yl)xenon(II) Salts

H.-J. Frohn<sup>\*,a</sup>, V. V. Bardin<sup>b</sup>

<sup>a</sup> Fachgebiet Anorganische Chemie, Gerhard-Mercator-Universität Duisburg,

Lotharstr. 1, D-47048 Duisburg, Germany

<sup>b</sup> Institute of Organic Chemistry, Russian Academy of Sciences, 630090 Novosibirsk, Russia

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(2-H-Hexafluoro-1,4-cyclohexadien-1-yl)xenon(II) and (2-H-octafluorocyclohexen-1-yl)xe-non(II) hexafluoroarsenates and tetrafluoroborates were obtained together with their perfluorinated analogues on reacting the corresponding (2,3,4,5-tetrafluorophenyl)xenon(II) salts with XeF<sub>2</sub> in anhydrous HF (aHF). The fluorinated (cyclohexen-1-yl)xenon(II) cations react with bromide and iodide anions in MeCN and aHF under alkenylation of the halide anions.

## Introduction

In 1993 we have reported the first preparation of perfluorinated cycloalken-1-ylxenon(II) compounds.  $[1-Xe^+-1,4-C_6F_7]$  [AsF<sub>6</sub>]<sup>-</sup> and  $[1-Xe^+-C_6F_9]$  [AsF<sub>6</sub>]<sup>-</sup> were formed by fluorine addition to [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> [AsF<sub>6</sub>]<sup>-</sup> using XeF<sub>2</sub> in anhydrous HF [1]. Until recently hydrogen-containing alkenylxenon(II) derivatives were unknown. Their preparation is of interest in order to study the relative influence of hydrogen versus fluorine in vicinal position to xenon [2], here in a vinylic moiety. This study gives inter alia an experimental answer to the proposed Xe-C bond stabilisation by "through-space" or chelate-like *vic*-F-Xe interactions (see [3]).

#### Results

The addition of XeF<sub>2</sub> in small portions (*ca.* 1.5 equivalents) into a solution of (2,3,4,5-tetrafluorophenyl)xenon(II) hexafluoroarsenate **1a** or tetrafluoroborate **1b** [4] in anhydrous HF at -15 °C and warming to room temperature resulted in Xe° evolution and formation of (3,3,4,5,6,6-hexafluoro-1,4-cyclohexadien-1-yl)xenon(II) (**2a**, **b**), minor amounts of (pentafluorophenyl)xenon(II) (**3a**, **b**), and (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) (**4a**, **b**) salts. Further fluorine addition using excess XeF<sub>2</sub> gave (3,3,4,4,5,5,6,6-octafluorocyclohexen-1-yl)xenon(II) (**5a**, **b**) and (nonafluorocyclohexen-1-yl)xenon(II) (**5a**, **b**) and (nonafluorocyclohexen-1-yl)xeno(II) (**5a**, **b**) and (nonafluorocyclohexen

1-yl)xenon(II) (**6a**, **b**) salts as final products in a *ca*. 2 : 1 molar ratio.

The formation of the perfluorinated compounds 3, 4, and 6 is in agreement with the general picture of fluorination of tetrafluorobenzenes C<sub>6</sub>HF<sub>4</sub>R by xenon difluoride *via* 1-R-hexafluorocvclohexadiene and its dehydrofluorination [5]. Indeed, NMR monitoring of the reaction mixture of 1b and  $XeF_2$  (1.3) to 1.7 equivalents) showed, besides the resonances of compounds 2, 4, 5 and 6 [1], signals at 6.5 ppm (<sup>1</sup>H, d 47 Hz, H-C-F), at *ca.* -186 ppm (<sup>19</sup>F, d 40-45 Hz, F-C-H) and at -2235 ppm (<sup>129</sup>Xe, d ca. 70 Hz,  ${}^{3}J(Xe, F-2)$  which are assigned to one of the isomeric cations  $[C_6HF_6Xe]^+$  7 with a geminal CHF-fragment: the (2,3,3,4,5,6-hexafluoro-1,4-cyclohexadien-1-yl)xenon(II) or (2,3,4,5,5,6hexafluoro-1,3-cvclohexadien-1-vl)xenon(II) cation. After further XeF<sub>2</sub> addition (2.53 equivalents in total) the oxidative fluorination was complete and compounds 5 and 6 were the only products. It is necessary to emphasize that no conversion of hexene 5 into hexene 6 was observed in the presence of XeF<sub>2</sub> during one week at room temperature.

In the couples of cyclohexadienylxenon(II) **4b**, **2b** and cyclohexenylxenon(II) **6b**, **5b** tetrafluoroborates the hydrogen-containing alkenylxenon cation shows a substantial shift of the <sup>129</sup>Xe resonance to higher frequency with corresponding  $\Delta$ (<sup>129</sup>Xe) values of 131 and 137 ppm, respectively. The deshielding of the xenon nucleus is comparable with the one observed for the transition from cation **3** to [X-C<sub>6</sub>H<sub>4</sub>Xe]<sup>+</sup> (X = m-CF<sub>3</sub> [6], p-CF<sub>3</sub>, m-F, p-F) [7]. Substitution of F by H in the perfluorophenyl or

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<sup>\*</sup> Reprint requests to Prof. Dr. H.-J. Frohn.



-vinyl group bonded to Xe(II) leads to a stronger polarisation of the phenyl or vinyl group by the positively charged Xe atom and weakens the Xe-C bond [8].

However, the weakening of the Xe-C bond in 2 and 5 is probably not very significant, since there is no direct correspondence of the large difference in the <sup>129</sup>Xe NMR chemical shift of the couple 5/6 to the reactivity or thermal stability in the solid state or in solution. A mixture of (cyclohexenvl)xenon(II) hexafluoroarsenates 5a and 6a could be stored at room temperature (FEP container under argon) over more than 2 months without decomposition. No changes were observed in the solution of the tetrafluoroborates 5b and 6b in anhydrous HF after one week (<sup>19</sup>F NMR). The treatment of a mixture of 5 and 6 (2:1, molar) with NaBr or NaI in anhydrous HF as well as in MeCN solution resulted in the fast quantitative conversion of both alkenylxenon cations into the corresponding polyfluorinated 1-bromo- or 1-iodocyclohexenes in the same molar ratio (cf. [9]).

The close similarity of the hydrogen-containing cycloalkenylxenon(II) cations **2**, **5** and the perfluorinated analogues **4**, **6** indicates the absence of a specific participation of the vinylic fluorine atom in neighbourhood to xenon in a "'through space"' or chelate-like stabilisation of the carbon-xenon bond.

## Experimental

The NMR spectra were measured on Bruker spectrometers WP 80 SY (<sup>1</sup>H at 80.13 and <sup>19</sup>F at 75.39 MHz) and Avance DRX 500 (<sup>1</sup>H at 500.130, <sup>19</sup>F at 470.593 and <sup>129</sup>Xe at 138.338 MHz). The chemical shifts  $\delta$ (F) were referred to internal C<sub>6</sub>F<sub>6</sub> and related to CFCl<sub>3</sub> [ $\delta$ (F) (C<sub>6</sub>F<sub>6</sub>) = -162.9 ppm)],  $\delta$ (<sup>129</sup>Xe) to external XeF<sub>2</sub>/aHF and to XeOF<sub>4</sub> (neat, 24 °C) (given in braces { $\delta$ (<sub>XeOF4</sub>)}). The molecular formulas of the iodoalkenes **8** and **9** and of the bromoalkenes **10** and **11** were determined from the high resolution mass spectra of their mixtures using a Finnigan MAT 8200 mass spectrometer.

Anhydrous HF (aHF) was dried electrolytically (stainless steel cell, Ni electrodes). All experiments were performed in FEP tubes under a dry Ar-atmosphere.

### Fluorination of arylxenon(II) salts 1a, b

A. Xenon difluoride (52 mg, 0.31 mmol) was added in three portions to the solution of **1b** (65 mg, 0.18 mmol) in aHF (0.2 ml) at -15 °C. After each addition the reaction mixture was warmed to room temperature and maintained until the gas evolution stopped. The molar ratio of **2** : **4** : **5** : **7** was 6.6 : 2.0 : 1.0 : 0.5 (<sup>19</sup>F NMR) besides traces of **6**. A further amount of XeF<sub>2</sub> was added (a total of 74 mg, 0.44 mmol) and the reaction mixture was maintained at room temperature for 1.5 h. Compounds **5b** and **6b** were obtained in 2 : 1 molar ratio (<sup>19</sup>F NMR). This solution which contains small amounts of XeF<sub>2</sub> was kept at room temperature for 1 week without any changes. Hexafluorobenzene was added in excess at -20 °C to remove the residual XeF<sub>2</sub>. After warming to room temperature the volatile compounds were removed in a vacuum to give 68 mg of salts **5b** and **6b** (yields 58 and 28 %, respectively).

B. The reaction of **1a** (130 mg, 0.28 mmol) with  $XeF_2(232 mg, 1.37 mmol)$  in aHF (0.3 ml) was performed in a similar manner. The solution of **5a** and **6a** (60 and 30 % yields, respectively, based on **1a**) (<sup>19</sup>F NMR) was kept at room temperature for further 2 days without changes.

**2a**: <sup>19</sup>F NMR (aHF, -15 °C): -93.0 (F-3,3), -98.0 (F-6,6), -147.7 (F-4), -148.9 (F-5) ppm.

**2b**: <sup>19</sup>F NMR (aHF, -40 °C): -94.6 (F-3,3), -99.6 (F-6,6), -149.6 (F-5) ppm (the resonance of F-4 overlaps with the resonance of the [BF<sub>4</sub>]<sup>-</sup> anion at -148.1 ppm); J/ Hz: (3,4) 20, (3,5) 9.7, (5,6) 21.5. <sup>1</sup>H NMR (aHF, -40 °C): 8.31 ppm (m). <sup>129</sup>Xe NMR (aHF, -40 °C): -2208 ppm { $\delta_{(XeOF4)} = -3772 \text{ ppm}$ }, d, <sup>3</sup>J(Xe, H-2) *ca*. 15 Hz.

**5a**: <sup>19</sup>F NMR (SO<sub>2</sub>, -50 °C): -101.7 (F-3,3), -106.9 (F-6,6), -129.7 and -134.2 (F-4,4,5,5) ppm. <sup>19</sup>F NMR (aHF, -15 °C): -99.1 (F-3,3), -104.7 (F-6,6), -127.3 and -132.0 (F-4,4,5,5) ppm. <sup>19</sup>F NMR (CH<sub>3</sub>CN, -25 °C): -101.9 (F-3,3), -107.1 (F-6,6), -129.6 and -133.2 (F-4,4,5,5) ppm. <sup>1</sup>H NMR (SO<sub>2</sub>, -50 °C): 7.63 ppm.

**5b**: <sup>19</sup>F NMR (aHF, -40 °C): -100.5 (F-3,3), -105.8 (F-6,6), -128.3 and -132.7 (F-4,4,5,5) ppm. <sup>1</sup>H NMR (aHF, -40 °C): 8.46 ppm (m).<sup>129</sup>Xe NMR (aHF, -40 °C): -2150 ppm, d, <sup>3</sup>J(Xe, H-2) *ca.* 15 Hz; { $\delta_{(XeOF4)} = -3714$  ppm}.

#### Reactions with NaX (X = Br, I).

A. The solution of **5a** and **6a** (2 :1, molar) (60 mg) in MeCN (0.2 ml) was treated with NaI (120 mg) at -30 °C (immediate Xe evolution and I<sub>2</sub> formation). The reaction mixture was warmed to room temperature, the mother liquor was decanted and the iodopolyfluorocyclohexenes **8** and **9** (1.8 : 1, molar) were obtained in quantitative yield ( $^{19}$ F NMR). **8**: <sup>19</sup>F NMR (CH<sub>3</sub>CN): -101.9 (F-6,6), -107.6 (F-3,3), -131.5 and -133.8 (F-4,4,5,5) ppm. MS: found:  $M^+$ : 351.9005; calculated (C<sub>6</sub>HF<sub>8</sub>I):  $M^+$ : 351.8995.

**9**: <sup>19</sup>F NMR (CH<sub>3</sub>CN): -98.1 (F-2), -100.4 (F-6,6), -117.3 (F-3,3), -131.1 and -133.1 (F-4,4,5,5) ppm (*cf.* [9]). MS: found:  $M^+$  369.8909; calculated (C<sub>6</sub>F<sub>9</sub>I):  $M^+$  369.8901.

B. Similarly, bromopolyfluorocyclohexenes 10 and 11 (2 : 1, molar) were obtained in quantitative yield ( $^{19}$ F NMR) from 5a and 6a (2 :1, molar) (99 mg) and NaBr (165 mg) in MeCN (0.5 ml).

**10**: <sup>19</sup>F NMR (CH<sub>3</sub>CN): -107.2 and -107.7 (F-3,3,6,6), -131.8 and -133.7 (F-4,4,5,5) ppm.

**11**: <sup>19</sup>F NMR (CH<sub>3</sub>CN): -106.3 (F-6,6), -111.5 (F-2), -117.4 (F-3,3), -130.3 and -132.8 (F-4,4,5,5) ppm (*cf.* [10]).

C. A solution of **5b** and **6b** (2 : 1, molar) (68 mg) in aHF (0.2 ml) was treated with NaBr (100 mg) at -35 °C and warmed to room temperature. After 15 min the reaction mixture was extracted with  $CH_2Cl_2$  (0.1 ml). The <sup>19</sup>F NMR spectrum showed the quantitative conversion of both compounds **5b** and **6b** into the bromocyclohexenes **10** and **11** (2 : 1, molar).

**10**:  ${}^{19}$ F NMR (CH<sub>2</sub>Cl<sub>2</sub>): -108.5 and -109.5 (F-3,3,6,6), -133.2 and -135.3 (F-4,4,5,5) ppm.  ${}^{1}$ H NMR (CH<sub>2</sub>Cl<sub>2</sub>): 6.40 ppm (m). MS: found: M<sup>+-</sup> 303.9126; calculated (C<sub>6</sub>HBrF<sub>8</sub>): M<sup>+-</sup> 303.9134.

**11**: <sup>19</sup>F NMR (CH<sub>2</sub>Cl<sub>2</sub>): -108.0 (F-6,6), -112.6 (F-2), -118.8 (F-3,3), -133.2 and -134.6 (F-4,4,5,5) ppm (*cf.* [10]) MS: found:  $M^+$  321.9042; calculated (C<sub>6</sub>BrF<sub>9</sub>):  $M^+$  321.9040.

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