## Trifluorovinylxenon(II) tetrafluoroborate

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## The first acyclic alkenylxenon(II) compound, trifluorovinylxenon(II) tetrafluoroborate, was prepared from XeF<sub>2</sub> and trifluorovinylboron difluoride and characterized by <sup>13</sup>C, <sup>19</sup>F and <sup>129</sup>Xe NMR spectroscopy.

In 1993 we reported the first preparation of the cyclic alkenylxenon(II) compounds, (heptafluorocyclohexa-1,4-dien-1-yl)xenon(II) **1** and (nonafluorocyclohexen-1-yl)xenon(II) **2** hexafluoroarsenates by stepwise fluorine addition to  $[C_6F_5Xe]^+[AsF_6]^-$  using XeF<sub>2</sub> in anhydrous HF (aHF).<sup>1</sup> Later (2-H-hexafluorocyclohexa-1,4-dien-1-yl)xenon(II) **3** and (2-H-octafluorocyclohexen-1-yl)xenon(II) **4** tetrafluoroborates<sup>2</sup> were obtained in a similar manner from (2,3,4,5-tetrafluorophenyl)xenon(II) tetrafluoroborate. Electrophilic oxygenation of  $[C_6F_5Xe]^+[AsF_6]^-$  with XeF<sub>2</sub> and stoichiometric amounts of H<sub>2</sub>O in HF gave (3-oxopentafluorocyclohexa-1,4-dien-1-yl)xenon(II) **5** and (3-oxo-4,5-epoxypentafluorocyclohexen-1-yl)xenon(II) **6** hexafluoroarsenates.<sup>3</sup>



All these synthetic routes to cyclic alkenylxenon(II) salts are based on the functionalization of arylxenon(II) salts and are restricted to the preparation of compounds with cyclohexadienyl- and cyclohexenyl-xenon(II) skeletons.

The topic of this paper is the elaboration of an alternative and new strategy and a more general approach to the synthesis of fluoroalkenylxenon(II) compounds: the reaction of XeF<sub>2</sub> with polyfluoroalkenylboron difluorides. When XeF<sub>2</sub> was reacted with trifluorovinylboron difluoride at -40 °C in CH<sub>2</sub>Cl<sub>2</sub> the first acyclic alkenylxenon(II) salt, trifluorovinylxenon(II) tetrafluoroborate **7**,<sup>†</sup> was obtained in very good yield [eqn. (1)].



Salt 7 is a white solid which decomposes above *ca*. 0 °C. It is insoluble in CH<sub>2</sub>Cl<sub>2</sub> but dissolves well in anhydrous HF (aHF), MeCN and EtCN. Its solution in aHF is stable at room temperature for some hours (monitored by <sup>19</sup>F NMR), whereas in MeCN (basic medium) 7 decomposes slowly above -20 °C and rapidly at room temperature with formation of xenon and some uncharacterized polyfluoroolefins.

The <sup>19</sup>F NMR spectrum<sup>4</sup> of the vinylxenon salt **7** in aHF (-30 °C) consists of resonances at  $\delta$  -81.91 (F-2 *trans*) [<sup>2</sup>J(F-2

*trans*)-(F-2 *cis*) 42 Hz, <sup>3</sup>*J*(F-2 *trans*)–(F-1) 105 Hz], -100.13 (F-2 *cis*) [<sup>3</sup>*J*(F-2 *cis*)–(F-1) 126 Hz], -126.36 (F-1), -148.22 ([BF<sub>4</sub>]<sup>-</sup>, br) and HF at  $\delta$  –190.83. All resonances of fluorine atoms bonded to carbon have <sup>129</sup>Xe satellites corresponding to the natural abundance of <sup>129</sup>Xe (*I* = 1/2) of 26.4%: <sup>3</sup>*J*(F-2 *cis*)-(<sup>129</sup>Xe) 30 Hz, <sup>3</sup>*J*(F-2 *trans*)–(<sup>129</sup>Xe) 146 Hz and <sup>2</sup>*J*(F-1)–(<sup>129</sup>Xe) 248 Hz.

Resonances<sup>4</sup> of the carbon atoms C-1 and C-2 in the <sup>19</sup>Fdecoupled <sup>13</sup>C NMR spectrum of **7** were located at  $\delta$  100.60 and 148.77, respectively and both displayed <sup>129</sup>Xe satellites: <sup>1</sup>*J*(C-1)–(<sup>129</sup>Xe) 131 Hz and <sup>2</sup>*J*(C-2)–(<sup>129</sup>Xe) 18 Hz. For comparison, the resonance of the carbon atom C-1 in the <sup>13</sup>C NMR spectrum of (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenate **2** in aHF (-10 °C) occurs at  $\delta$  96.28 and <sup>1</sup>*J*(C-1)–(<sup>129</sup>Xe) is 114 Hz.<sup>1</sup>

The <sup>129</sup>Xe NMR spectrum<sup>4</sup> of compound **7** in aHF (-30 °C) displays a doublet of doublets of doublets at  $\delta$  -3636.1( $\Delta v_{1/2}$  = 13 Hz) [<sup>2</sup>*J*(<sup>129</sup>Xe)–(F-1) 248 Hz, <sup>3</sup>*J*(<sup>129</sup>Xe)–(F-2 *cis*) 30 Hz, <sup>3</sup>*J*(<sup>129</sup>Xe)–(F-2 *trans*) 146 Hz] (Fig. 1). This deshielding of the xenon atom in **7** is remarkable when compared to  $\delta$ (<sup>129</sup>Xe) values of the (polyfluorocycloalken-1-yl)xenon(II) compounds **1–6** ( $\delta$  -3912.3, -3858.4, -3771.8, -3714.0, -3916.2 and -3900.3, respectively)<sup>1–3</sup> and is probably the result of a strong 'through-space' electronic interaction of the xenon atom with the geminal fluorine atom F-1. This consideration is also in agreement with the large value of <sup>2</sup>*J*(<sup>129</sup>Xe)–(F-1), which is the largest of the the known coupling constants in organoxenon compounds.

The <sup>19</sup>F NMR spectrum of a solution of **7** in EtCN at -40 °C consists of resonances at  $\delta$  -84.97 (F-2 *trans*) [<sup>2</sup>*J*(F-2 *trans*)-(F-2 *cis*) 46 Hz, <sup>3</sup>*J*(F-2 *trans*)-(F-1) 90 Hz], -103.36 (F-2 *cis*) [<sup>3</sup>*J*(F-2 *cis*)-(F-1) 124 Hz], -137.81 (F-1) and -149.59 ([BF<sub>4</sub>]<sup>-</sup>) [<sup>3</sup>*J*(F-2 *cis*)-(<sup>129</sup>Xe) 29 Hz, <sup>3</sup>*J*(F-2 *trans*)-(<sup>129</sup>Xe) 139 Hz, <sup>2</sup>*J*(F-1)-(<sup>129</sup>Xe) 191 Hz]. The <sup>129</sup>Xe NMR signal was located at  $\delta$  -3510.6 [<sup>2</sup>*J*(<sup>129</sup>Xe)-(F-1) 197 Hz, <sup>3</sup>*J*(<sup>129</sup>Xe)-(F-2)



**Fig. 1**<sup>129</sup>Xe NMR resonance of **7** (aHF, -30 °C, 5 mm glass tube with FEP inliner, measured on a Bruker DRX 500 spectrometer at 138.34 MHz; shift values relative to neat XeOF<sub>4</sub> at 24 °C.

cis) 27 Hz, <sup>3</sup>J(<sup>129</sup>Xe)–(F-2 trans) 136 Hz]. Cooling to -70 °C led to shielding of the fluorine atom F-1 and a decrease of  ${}^{2}J(F-$ 1)-(129Xe) to 188 Hz resulting from a favoured cation-anion interaction over the cation-EtCN interaction:  $\delta - 84.09$  (F-2 trans) [2J(F-2 trans)-(F-2 cis) 46 Hz, 3J(F-2 trans)-(F-1) 88 Hz], -102.62 (F-2 *cis*) [<sup>3</sup>*J*(F-2 *cis*)–(F-1) 123 Hz], -138.27 (F-1) and -150.31 ([BF<sub>4</sub>]<sup>-</sup>) [<sup>3</sup>J(F-2 cis)–(<sup>129</sup>Xe) 28 Hz, <sup>3</sup>J(F-2 trans)-(129Xe) 136 Hz].

Chemical proof of the carbon-xenon bond and of the electrophilic nature of the vinylxenon(II) cation in 7 was obtained by conversion into trifluoroiodoethene with loss of Xe<sup>0</sup> when a solution of 7 in EtCN was treated with NaI in excess at  $\leq -30$  °C [eqn. (2)] (*cf.* ref. 6).

$$\begin{array}{c} F \\ F \\ F \\ \end{array} \begin{array}{c} F \\ Xe^{+} [BF_{4}]^{-} \end{array} \xrightarrow{+ excess Nal} F \\ \hline EtCN/-30 \ ^{\circ}C \\ F \\ \end{array} \begin{array}{c} F \\ F \\ \end{array} \end{array} \begin{array}{c} F \\ F \\ \end{array} \end{array} \begin{array}{c} F \\ F \\ \end{array} \begin{array}{c} F \\ F \\ \end{array} \end{array}$$

In summary, the trifluorovinylxenon cation is of great importance for preparative and theoretical chemistry because it is an unique precursor for the trifluorovinyl radical and cation.

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## Notes and references

<sup>†</sup> Synthesis of trifluorovinylxenon(II) tetrafluoroborate 7: a solution of XeF<sub>2</sub> (1.83 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was cooled to -40 °C and added to a solution of trifluorovinylboron difluoride (1.54 mmol) in dichloromethane (10 ml) at -40 °C under a dry argon atmosphere. After stirring at -40 to -50 °C for 5 h the mother liquor was decanted and the residual product was washed and dried under vacuum to yield compound 7 (1.30 mmol, 85 %)

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