Trifluorovinylxenon(II) tetrafluoroborate

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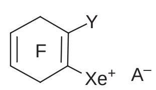
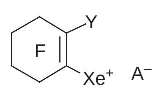
The first acyclic alkenylxenon(II) compound, trifluorovinylxenon(II) tetrafluoroborate, was prepared from XeF_2 and trifluorovinylboron difluoride and characterized by ^{13}C, ^{19}F and ^{129}Xe NMR spectroscopy.

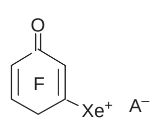
In 1993 we reported the first preparation of the cyclic alkenylxenon(II) compounds, (heptafluorocyclohexa-1,4-dien-1-yl)xenon(II) **1** and (nonafluorocyclohexen-1-yl)xenon(II) **2** hexafluoroarsenates by stepwise fluorine addition to $[C_6F_5Xe]^+[AsF_6]^-$ using XeF_2 in anhydrous HF (aHF).[1] Later (2-H-hexafluorocyclohexa-1,4-dien-1-yl)xenon(II) **3** and (2-H-octafluorocyclohexen-1-yl)xenon(II) **4** tetrafluoroborates[2] 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_2 and stoichiometric amounts of H_2O 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.[3]



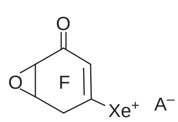
1 Y = F, A^- = $[AsF_6]^-$
3 Y = H, A^- = $[BF_4]^-$



2 Y = F, A^- = $[AsF_6]^-$
4 Y = H, A^- = $[BF_4]^-$



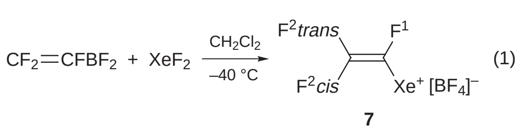
5 A^- = $[AsF_6]^-$



6 A^- = $[AsF_6]^-$

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_2 with polyfluoroalkenylboron difluorides. When XeF_2 was reacted with trifluorovinylboron difluoride at −40 °C in CH_2Cl_2 the first acyclic alkenylxenon(II) salt, trifluorovinylxenon(II) tetrafluoroborate **7**,† was obtained in very good yield [eqn. (1)].



(1)

7

Salt **7** is a white solid which decomposes above *ca*. 0 °C. It is insoluble in CH_2Cl_2 but dissolves well in anhydrous HF (aHF), MeCN and EtCN. Its solution in aHF is stable at room temperature for some hours (monitored by ^{19}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 ^{19}F NMR spectrum[4] of the vinylxenon salt **7** in aHF (−30 °C) consists of resonances at δ −81.91 (F-2 *trans*) [^2J(F-2 *trans*)-(F-2 *cis*) 42 Hz, ^3J(F-2 *trans*)–(F-1) 105 Hz], −100.13 (F-2 *cis*) [^3J(F-2 *cis*)–(F-1) 126 Hz], −126.36 (F-1), −148.22 ($[BF_4]^-$, br) and HF at δ −190.83. All resonances of fluorine atoms bonded to carbon have ^{129}Xe satellites corresponding to the natural abundance of ^{129}Xe (I = 1/2) of 26.4%: ^3J(F-2 *cis*)-(^{129}Xe) 30 Hz, ^3J(F-2 *trans*)–(^{129}Xe) 146 Hz and ^2J(F-1)–(^{129}Xe) 248 Hz.

Resonances[4] of the carbon atoms C-1 and C-2 in the ^{19}F-decoupled ^{13}C NMR spectrum of **7** were located at δ 100.60 and 148.77, respectively and both displayed ^{129}Xe satellites: ^1J(C-1)–(^{129}Xe) 131 Hz and ^2J(C-2)–(^{129}Xe) 18 Hz. For comparison, the resonance of the carbon atom C-1 in the ^{13}C NMR spectrum of (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenate **2** in aHF (−10 °C) occurs at δ 96.28 and ^1J(C-1)–(^{129}Xe) is 114 Hz.[1]

The ^{129}Xe NMR spectrum[4] of compound **7** in aHF (−30 °C) displays a doublet of doublets of doublets at δ −3636.1($\Delta\nu_{1/2}$ = 13 Hz) [^2J(^{129}Xe)–(F-1) 248 Hz, ^3J(^{129}Xe)–(F-2 *cis*) 30 Hz, ^3J(^{129}Xe)–(F-2 *trans*) 146 Hz] (Fig. 1). This deshielding of the xenon atom in **7** is remarkable when compared to δ(^{129}Xe) values of the (polyfluorocycloalken-1-yl)xenon(II) compounds **1**–**6** (δ −3912.3, −3858.4, −3771.8, −3714.0, −3916.2 and −3900.3, respectively)[1–3] 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 ^2J(^{129}Xe)–(F-1), which is the largest of the the known coupling constants in organoxenon compounds.

The ^{19}F NMR spectrum of a solution of **7** in EtCN at −40 °C consists of resonances at δ −84.97 (F-2 *trans*) [^2J(F-2 *trans*)–(F-2 *cis*) 46 Hz, ^3J(F-2 *trans*)–(F-1) 90 Hz], −103.36 (F-2 *cis*) [^3J(F-2 *cis*)–(F-1) 124 Hz], −137.81 (F-1) and −149.59 ($[BF_4]^-$) [^3J(F-2 *cis*)–(^{129}Xe) 29 Hz, ^3J(F-2 *trans*)–(^{129}Xe) 139 Hz, ^2J(F-1)–(^{129}Xe) 191 Hz]. The ^{129}Xe NMR signal was located at δ −3510.6 [^2J(^{129}Xe)–(F-1) 197 Hz, ^3J(^{129}Xe)–(F-2

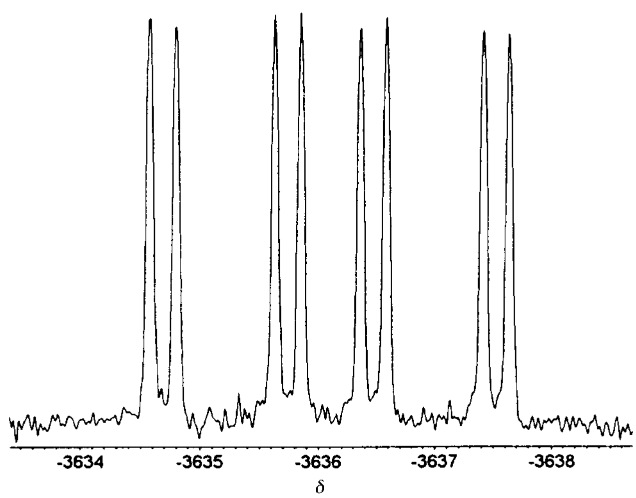
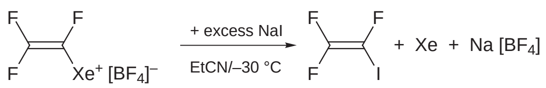


Fig. 1 ^{129}Xe NMR resonance of **7** (aHF, −30 °C, 5 mm glass tube with FEP inliner, measured on a Bruker DRX 500 spectrometer at 138.34 MHz; shift values relative to neat $XeOF_4$ at 24 °C.

cis) 27 Hz, $^3J(^{129}Xe)$–(F-2 *trans*) 136 Hz]. Cooling to −70 °C led to shielding of the fluorine atom F-1 and a decrease of ^2J(F-1)–(^{129}Xe) to 188 Hz resulting from a favoured cation–anion interaction over the cation–EtCN interaction:[5] δ −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*) [^3J(F-2 *cis*)–(F-1) 123 Hz], −138.27 (F-1) and −150.31 ($[BF_4]^-$) [^3J(F-2 *cis*)–(^{129}Xe) 28 Hz, ^3J(F-2 *trans*)–(^{129}Xe) 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^0 when a solution of **7** in EtCN was treated with NaI in excess at ≤−30 °C [eqn. (2)] (*cf*. ref. 6).



(2)

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

† *Synthesis of trifluorovinylxenon*(II) *tetrafluoroborate* **7**: a solution of XeF_2 (1.83 mmol) in CH_2Cl_2 (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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4 The NMR shift values are relative to CCl_3F (^{19}F), TMS (^{13}C) and $XeOF_4$ (^{129}Xe).
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