Trifluoropropynylxenon(II) tetrafluoroborate [CF₃C≡CXe] [BF₄] – isolation of an alkynylxenon(II) compound for the first time

Hermann-Josef Frohn*[a] and Vadim V. Bardin[b]

[a] *Institute of Chemistry, Inorganic Chemistry, University Duisburg – Essen, Lotharstr. 1, D-47048 Duisburg, Germany*

[b] *N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, Acad. Lavrentjev Ave., 9, 630090 Novosibirsk, Russia*

The salt [CF₃C≡CXe] [BF₄] was prepared as neat compound by the reaction of the hitherto unknown alkynyldifluoroborane CF₃C≡CBF₂ with XeF₂ in 1,1,1,3,3-pentafluoropropane (PFP) at −45 °C in 59% yield. [CF₃C≡CXe] [BF₄] was unambiguously characterised by multinuclear NMR spectroscopy in anhydrous HF (aHF) solution.

The preparative chemistry of organoxenon compounds started in 1989 with the isolation and structural characterisation of arylxenon(II) salt [ArXe] [Y].[1,2] Later alkenylxenon(II) salts [RXe] [Y] (R = polyfluorocycloalk-1-enyl and trifluorovinyl) were obtained.[3,4] Pentafluorophenyldifluoroxenon(IV) tetrafluoroborate [C₆F₅XeF₂] [BF₄] was the first example of a Xe^{IV}–C compound.[5] Recently the neutral polyfluorophenyl xenon(II) molecules of the type ArXeF, Ar₂Xe, and ArXeAr′ were prepared.[6,7,8] The current research in Xe–C chemistry is compiled in some reviews.[9]

In 1992 Zhdankin *et al.* published a short communication on the detection of the [t-BuC≡CXe] [BF₄] salt obtained by the reaction of Li [t-BuC≡CBF₃] with XeF₂ in CH₂Cl₂ (Scheme 1), but they were not able to isolate this thermally unstable salt (decomposition at −30 °C) in a pure state.[10] They proved the presence of a Xe–C species in the dark oily product by multinuclear NMR spectroscopy at −40 °C, by IR spectrum (at 0 °C) and by alkynylation of PPh₃ to [t-BuC≡CPPh₃] [BF₄] (−78 °C). They established that the preparation of xenonium salts from other starting alkynes analogously to Scheme 1 was unsuccessful, but they were able to monitor the formation of some alkynylxenon(II) tetrafluoroborates by their ¹²⁹Xe resonance (singlet) in the reaction of RC≡CSiMe₃ with XeF₂ and BF₃·OEt₂ in CD₂Cl₂ at −45 °C when R = Et, Pr, t-Bu and Me₃Si. No xenon-containing species were monitored by ¹²⁹Xe NMR when R = H, Me, Ph, **CF₃**, 4-CH₃C₆H₄SO₂, (i-Pr)₃Si, PhMe₂Si.

In 1999 we elaborated a convenient route to arylxenon(II) tetrafluoroborates which consists of the reaction of aryldifluoroborane with xenon difluoride in CH₂Cl₂ at −40 to −30 °C.[11] This route was successfully applied to the preparation of the trifluoroethenylxenon(II) salt[3] and a series of 2-X-1,2-difluoroethenylxenon(II)[12] and 1-X-2,2-difluoroethenylxenon(II) salts, all these were isolated as neat salts.[13] This synthetic method allowed the isolation of the new salts in a pure form and the possibility of characterising them unambiguously. Pursuing our systematic efforts in the field of organoxenon chemistry, we decided to extend this procedure also to the synthesis of alkynylxenon(II) salts in order to demonstrate the common character of the methodical approach. Therefore we investigated the reaction of trifluoropropynyldifluoroborane 1 with xenon difluoride. A neat alkynylxenon(II) salt could be isolated in a satisfactory to good yield for the first time.

A typical procedure will be described as follows. Solid XeF₂ (83 mg, 0.49 mmol) was added in one portion to a cold (−47 °C)

solution of CF₃C≡CBF₂[14] (0.45 mmol) in 1,1,1,3,3-pentafluoropropane (PFP) (1.5 ml). After 10 minutes a white precipitate was formed. The reaction mixture was stirred at −45 °C for 1.5 h before the volatile components were removed under vacuum at −45 °C to give trifluoropropynylxenon(II) tetrafluoroborate **2** (82 mg, 59%) (Scheme 2).

The significant difference between our procedure and the one described in[10] consists of the use of alkynyldifluoro**borane** as precursor for the alkynylxenon(II) salt instead of lithium alkynyltrifluoro**borate** or alkynyltrimethylsilane in combination with BF₃·OEt₂. In the reaction of CF₃C≡CSiMe₃, XeF₂ and BF₃·OEt₂ in CD₂Cl₂ no organoxenon(II) species could be detected.[10] The successful synthesis of **2** from **1** and XeF₂ in contrast shows the preference of alkynyldifluoroboranes as starting materials over alkynyltrifluoroborates and -trimethylsilanes.
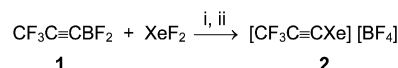
The alkynylxenon(II) salt **2** is a white solid which is stable at 20 °C at least for 2–3 hours. **2** is well soluble in aHF. The solution of **2** in aHF showed remarkable stability. The conversion of **2** into *cis*- and *trans*-CF₃CH=CHF was only approximately 30% after 24 h at 20 °C.

The ¹⁹F NMR spectrum of the propynylxenon(II) salt **2** in aHF (−20 °C) displayed resonances at δ −52.45 (s, CF₃) and −147.72 (s, [BF₄]⁻).[15] Resonances of the carbon atoms C-1, C-2 and C-3 in the ¹⁹F decoupled ¹³C NMR spectrum of **2** were located at δ −5.19, 81.18 and 112.78 ppm, respectively, and displayed ¹²⁹Xe-satellites: ¹J(C-1)–(¹²⁹Xe) 343 Hz and ²J(C-2)–(¹²⁹Xe) 69 Hz (a coupling ³J(C-3)–(¹²⁹Xe) was not observed).[15] These are by far the largest ¹J(¹³C)–(¹²⁹Xe) coupling values observed in Xe–C compounds until now. The ¹²⁹Xe-satellites found for C-1 and C-2 are a proof that the alkynyl fragment was bonded to xenon(II). It is useful to compare the ¹³C NMR data of the new alkynylxenon salt with some related Xe–C salts. The ¹³C resonance of the carbon atom C-1 of (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenate in aHF (−10 °C) occurred at δ 96.28 and ¹J(C-1)–(¹²⁹Xe) was 114 Hz[4] whereas ¹³C signals of [CF₂=CFXe]⁺ were located at δ 100.60 (C-1) and 148.77 ppm (C-2), respectively. Both displayed ¹²⁹Xe-satellites: ¹J(C-1)–(¹²⁹Xe) 131 Hz and ²J(C-2)–(¹²⁹Xe) 18 Hz.[3] Zhdankin *et al.* reported the ¹³C NMR resonances of [t-BuC≡CXe] [BF₄] at δ 21 (C-1) and δ 105 (C-2) and the corresponding spin–spin coupling constants ¹³C–¹²⁹Xe with 120 Hz and 79 Hz, respectively (CDCl₃, −40 °C).[10]

The ¹²⁹Xe NMR signal of compound **2** in aHF (−60 °C) displays a singlet at δ −3636 which was shifted to δ −3645 ($\tau_{1/2}$ = 12 Hz) when the solution was warmed up to −30 °C.[15] These values practically coincide with the ¹²⁹Xe chemical shift of the cation [CF₂=CFXe]⁺ (δ −3636 in aHF at −30 °C[3]). The ¹²⁹Xe chemical shifts of alkynylxenon species reported in[10] were located at δ −1802 to −1887 with respect to XeF₂ (−45 °C).

$$t\text{-BuC≡CLi} \xrightarrow{\ i\ } \text{Li [}t\text{-BuC≡CBF}_3] \xrightarrow{\ ii\ } [t\text{-BuC≡CXe] [BF}_4]$$

Scheme 1 *Reagents and conditions*: i, BF₃ (excess), CH₂Cl₂, −100 °C; ii, XeF₂, CH₂Cl₂, −40 °C, 1 h.

$$\text{CF}_3\text{C≡CBF}_2 + \text{XeF}_2 \xrightarrow{\ i,\ ii\ } [\text{CF}_3\text{C≡CXe] [BF}_4]$$
$$\qquad\qquad\quad\ \mathbf{1}\qquad\qquad\qquad\qquad\qquad\quad\ \mathbf{2}$$

Scheme 2 *Reagents and conditions*: i, 1,1,1,3,3-pentafluoropropane (PFP), −45 °C, 1.5 h; ii, evaporation of volatile substances at −45 °C.

Unfortunately, in ref. 10 neither the solvent nor the temperature used for the reference measurement of xenon difluoride were indicated. This knowledge is important, because of the significant solvent and temperature dependence of the ^{129}Xe chemical shift.[16] A correct direct comparison of our $\delta(^{129}\text{Xe})$ value and those obtained in ref. 10 is therefore not possible.

Notes and references

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