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Organoethynylxenon(II) Tetrafluoroborates, [RC=CXe][BF₄] – The First Examples of Isolated Alkynylxenonium Salts: Preparation and Multi-NMR Characterisation

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The perfluorinated organoethynylxenon(II) salts, $[RC=CXe][BF_4]$ $[R = CF_3, C_3F_7, (CF_3)_2CF, cis-, trans-CF_3CF=CF, C_6F_5]$, were prepared by the reaction of XeF₂ with the corresponding perfluoroorganoethynyldifluoroboranes, $RC=CBF_2$, in 1,1,1,3,3-pentafluoropropane (PFP) or CH_2Cl_2 at -60 to -40 °C and isolated in 30–98 % yield. Similarly, the non-fluorinated organoethynylxenon(II) salts $[C_4H_9C=CXe][BF_4]$ and $[(CH_3)_3CC=CXe][BF_4]$ were obtained in 20 to 40 % yield. All [RC=CXe][BF₄] salts are soluble in anhydrous HF (aHF) and the salts with R = C_4H_9 or R = (CH₃)₃C display sufficient solubility in the weakly coordinating solvents CH₂Cl₂ and PFP. The xenonium salts [RC=CXe][BF₄] were unambiguously characterised by their ¹H-, ¹¹B-, ¹³C-, ¹⁹F-, and ¹²⁹Xe NMR spectra in solution. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

The preparative chemistry of organoxenon compounds was established in 1989 with the synthesis of pentafluorophenylxenon(II) salts, $[C_6F_5Xe][Y]$, obtained by the reaction of XeF₂ with $(C_6F_5)_3B$.^[1,2] In the subsequent years xenonium salts, [RXe][Y], with different types of organo groups in the cation (R = substituted phenyl, polyfluorocycloalk-1-enyl) as well as arylxenon(II) molecules ArXeX (X = F, Cl, O₂CC₆F₅, CN, C₆F₅) and the first example of a Xe(IV)–C compound, $[C_6F_5XeF_2][BF_4]$, were investigated. The achievements made in the first decade of xenon–carbon chemistry are compiled in some reviews published in 1999– 2002.^[3] In the following years reactivities of arylxenon(II) salts,^[4,5] of diarylxenon ArXeAr',^[6] and the preparation and reactivity of a series of acyclic polyfluoroalk-1-enylxenon(II) salts [RCF=CR'Xe][BF₄]^[7–9] were reported. In 2004 Naumann et al. observed RC=CXeF molecules (R = Me, Bu, Ph) in the fluoride-catalysed reaction of XeF₂ and Me₃SiC=CR. The authors reported a significant decomposition of RC=CXeF in solution above -60 °C.^[10]

In 1992, Zhdankin et al. published a short communication on the salt [*t*BuC=CXe][BF₄] obtained by the reaction of Li[*t*BuC=CBF₃] with BF₃ and XeF₂ in CH₂Cl₂ (Scheme 1).^[11] This salt, which could not be isolated because of its decomposition at -30 °C, was characterised by ¹H-, ¹¹B-, ¹³C-, and ¹²⁹Xe NMR spectroscopy at -40 °C, by IR spectroscopy at 0 °C, and by the alkynylation of PPh₃ to [*t*BuC=CPPh₃][BF₄] at -78 °C.

In the analogous reactions of XeF₂ with alkynylsilanes, RC=CSiMe₃ (R = Et, Pr, *t*Bu, and Me₃Si), and BF₃·OEt₂ in CD₂Cl₂ at -45 °C, the authors reported no multi-NMR spectroscopic data of the desired products, the xenonium salts. Each reaction solution was only characterised by a

$$tBuC \equiv CLi \xrightarrow{\text{BF}_3 (excess), CH_2Cl_2} Li[tBuC \equiv CBF_3] \xrightarrow{\text{XeF}_2, CH_2Cl_2} [tBuC \equiv CXe][BF_4]$$

Scheme 1.

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singlet in the ¹²⁹Xe NMR spectrum. No ¹²⁹Xe resonances were found in the spectra of the reaction solutions for R =H, Me, Ph, CF₃, 4-CH₃C₆H₄SO₂, (*i*Pr)₃Si, PhMe₂Si.^[11]

We published a preliminarily report of the first isolation of an alkynylxenon(II) salt in 2003 when we succeeded in preparing trifluoropropynylxenon(II) tetrafluoroborate $[CF_3C=CXe][BF_4]$.^[12] We employed the previously developed approach to polyfluorinated arylxenon(II) and alk-1enylxenon(II) salts: the reaction of xenon difluoride with

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polyfluoroorganoboron difluoride in the appropriate solvent.^[3b] This preparative method allowed for the isolation of the new salt as a pure product and opened the possibility of extensive and unambiguous characterisation. Subsequently, we extended this preparative method to a representative series of alkynylxenon(II) salts, $[RC=CXe][BF_4]$, where R represents any alkyl chain, a perfluoroalkyl group, a perfluoroalk-1-enyl group or a perfluoroaryl group.

Results and Discussion

The addition of XeF_2 to the solution of either trifluoropropynyldifluoroborane (1a) or heptafluoropent-1-ynyldifluoroborane (2a) in PFP^[13] at -40 to -55 °C was accompanied by the precipitation of trifluoropropynylxenon(II) tetrafluoroborate (1b) or heptafluoropent-1-ynylxenon(II) tetrafluoroborate (2b), respectively. Both salts are insoluble in PFP and form white solids. After decantation of the mother liquors and removal of the residual volatiles in vacuo, alkynylxenon salts 1b and 2b were isolated in 60–90% yield (Scheme 2).

$$C_nF_{2n+1}C \equiv CBF_2 + XeF_2 \xrightarrow{PFP \text{ or } CH_2Cl_2} [C_nF_{2n+1}C \equiv CXe][BF_4]$$
1a, 2a

$$-40 \text{ to } -55 \text{ °C} \qquad \textbf{1b, 2b}$$
1a, 1b (n = 1), **2a, 2b** (n = 3)

Scheme 2.

In a similar way, the reaction of heptafluoro-3-methylbut-1-ynyldifluoroborane (**3a**) with XeF_2 gave heptafluoro-3-methylbut-1-ynylxenon(II) tetrafluoroborate (**3b**) in 82% yield (Scheme 3).

	PFP	
$(CF_3)_2CFC \equiv CBF_2 + XeF_2$	\longrightarrow	[(CF ₃) ₂ CFC≡CXe][BF ₄]
3a	-45 °C	3b

Scheme 3.

The replacement of the perfluorinated alkyl group at C-2 of boranes 1a, 2a, and 3a by the pentafluoropropenyl or pentafluorophenyl group did not affect the course of the reaction. Both pentafluoropent-3-en-1-ynyldifluoroboranes (*cis*-4a) and (*trans*-4a) and pentafluorophenylethynyldifluoroborane (5a) were successfully converted into pentafluoropent-3-en-1-ynylxenon(II) tetrafluoroborates (*cis*-4b) and (*trans*-4b) and pentafluorophenylethynylxenon(II) tetrafluoroborate (5b), respectively. No addition of fluorine to the double bond in the perfluorinated propenyl or phenyl moiety of 4a or 5a occurred. The ratio *cis*-4b/*trans*-4b = 1:2 was equal to that in the parent boranes 4a (Scheme 4).

To complete the investigations of xenon difluoride with alkynyldifluoroboranes, we studied the reaction of XeF_2 with boranes that contained a hydrocarbon alkynyl chain. XeF_2 was treated with hex-1-ynyldifluoroborane (**6a**) and 3,3-dimethylbut-1-ynyldifluoroborane (**7a**) under the conditions mentioned above and formed hex-1-ynylxenon(II) tetrafluoroborate (**6b**) and 3,3-dimethylbut-1-ynylxenon(II)

	PFP	
$CF_3CF=CFC\equiv CBF_2 + XeF_2$	\longrightarrow	[CF ₃ CF=CFC≡CXe][BF ₄]
cis-4a and trans-4a	−55 °C	cis-4b and trans-4b
	PFP or CH ₂ Cl	2
$C_6F_5C \equiv CBF_2 + XeF_2$		$\rightarrow \qquad [C_6F_5C\equiv CXe][BF_4]$
5a	-60 °C	5h

Scheme 4.

tetrafluoroborate (7b), respectively (Scheme 5). Surprisingly, these salts are significantly soluble in PFP even below -40 °C. Salt **6b** is more soluble than salt **7b**. Thus, under comparable reaction conditions in PFP at -50 °C, **6b** remained in solution whereas half of isomer **7b** precipitated. When borane **6a** reacted with XeF₂ in CH₂Cl₂ at -65 °C solely a solution of **6b** was obtained.

	PFP (-50 °C) or CH ₂ Cl ₂ (-65 °C)	
$RC \equiv CBF_2 + XeF_2$	\longrightarrow	[RC≡CXe][BF₄]
6a, 7a		6b, 7b
6a , 6b ($\mathbf{R} = \mathbf{C}_4 \mathbf{H}_9$) 7a	, 7b $[R = (CH_3)_3C]$	

Scheme 5.

In contrast to the reaction of alk-1-enyldifluoroboranes, RCF=CFBF₂, with XeF₂,^[7] neither the alk-1-enyltrifluoroborate anions, [RCF=CFBF₃]⁻, nor their fluorination products, [XBF₃]⁻ (X = RCF=CF, RCF₂CF₂), were observed.

The results demonstrate the easy xenodeborylation (replacement of the three-coordinate boron atom by xenon) of both non-fluorinated organoethynyldifluoroboranes and perfluoroorganoethynyldifluoroboranes, $RC \equiv CBF_2$, in reactions with xenon difluoride. Significant differences between the present reactions and the previously studied reactions of XeF₂ with alk-1-enyldifluoroboranes are their insensitivity to the type of R group attached to C-2 of the multiple C–C bond. It is worth mentioning that in the reactions of hydrocarbon alk-1-enyldifluoroboranes with XeF₂ no xenonium salts were obtained. Thus under the same reaction conditions as those of alkynyldifluoroboranes, *cis*-and *trans*-hex-1-enyldifluoroboranes, C₄H₉CH=CHBF₂, only gave complex mixtures but no hexenylxenon compounds.^[7]

The novel alkynylxenon(II) compounds **1b**–**5b** were isolated as white solids at low temperatures (<-40 °C). When warmed from -40 °C the solutions took on a brown colouration, and at 20 °C the conversion into dark liquids took place within a few minutes (**4b**, **5b**) or a few hours (**1b**–**3b**). Salts **1b**–**5b** are very soluble in aHF and insoluble in PFP and CH₂Cl₂. A characteristic property of solutions of **1b**– **5b** in aHF is their longer lifetime at room temperature than that of the salts themselves in the solid state. In detail, no decomposition of perfluoroalkynylxenon tetrafluoroborates **1b**–**3b** was detected in aHF solutions within 20–24 h. The salts **4b** and **5b**, which contain the unsaturated perfluoro groups R = CF₃CF=CF and R = C₆F₅, respectively, at C– 2, decomposed much faster than **1b**–**3b**. Salt **5b** totally decomposed in aHF at –40 °C within 1 h, whereas the total decomposition of **4b** in aHF at 22–24 °C took ca. 4 h. The complete decomposition of pure solids **4b** and **5b** at 20 °C led to the formation of brown materials, insoluble in aHF, which consisted of non-volatile complex mixtures (¹⁹F NMR).

Hex-1-ynylxenon(II) tetrafluoroborate **6b** and its isomer **7b** were isolated as brownish powders (probably contaminated with impurities) which were easily liquefied above $-40 \,^{\circ}\text{C}$ (cf.^[11]). Solutions or suspensions of these salts in either PFP or CH₂Cl₂ decomposed in a manner similar to that of the salts in the solid state. Surprisingly, solutions of **6b** and **7b** in aHF are stable at 22–25 °C for more than 12 h. After 22 h, 38% of **6b** and 80% of **7b** still remained unchanged. Finally the complete decomposition led to tar.

Salts 1b-7b were unambiguously characterised by multi-NMR spectroscopy. The ¹⁹F NMR spectra of fluoroorganoethynylxenon(II) tetrafluoroborates 1b-5b in aHF displayed signals for the fluoroorgano groups and for the $[BF_4]^-$ anion (at approximately $\delta = -148$ ppm) with the expected integrations. Long-range couplings $J_{^{19}\text{E}^{129}\text{Xe}}$ were observed in the spectra of both isomers of $[CF_3CF=CFC=CXe][BF_4]$. The signal for F-4 at $\delta =$ -128.2 ppm (*cis*-**4b**) and F-3 at $\delta = -149.3$ ppm (*trans*-**4b**) displayed ¹²⁹Xe satellites (${}^{5}J_{\text{F-4,Xe}} = 17 \text{ Hz}$ and ${}^{4}J_{\text{F-3,Xe}} = 6 \text{ Hz}$, respectively) in accordance with the natural abundance of the ¹²⁹Xe isotope of 26%. The assignment of the coupling ${}^{4}J_{\text{F-3,Xe}} = 8 \text{ Hz}$ in the ${}^{19}\text{F}$ NMR spectrum of $[(CF_3)_2 CFC \equiv CXe][BF_4]$ was confirmed in a ¹⁹F{¹⁹F(CF_3)} homodecoupling NMR experiment. In the ¹⁹F NMR spectrum of salts with unbranched perfluoroalkyl R groups, as in **1b** (signal for the CF₃ group at $\delta = -52.5$ ppm, $\tau_{1/2} =$ 1.5 Hz) or **2b** $[^{19}F{^{19}F(CF_3)}]$ spectrum of the CF₃CF₂CF₂ group] such couplings were not observed. For comparison, in the case of *cis*-perfluoroalk-1-envlxenonium salts, larger ${}^{4}J_{\text{F-3.Xe}}$ couplings are known. In the spectra of $[cis-YCF_2CF=CFXe][BF_4], {}^4J_{F-3,Xe} = 40 \text{ Hz} (Y = F) \text{ and}$ ${}^{4}J_{\text{F-3,Xe}} = 56 \text{ Hz} (\text{Y} = \text{CF}_3) \text{ were measured}.^{[7]}$

The ¹²⁹Xe NMR signals of salts [RC=CXe][BF₄] **1b–5b** in aHF at –60 °C are singlets located between δ = –3600 and –3662 ppm (Table 1). The influence of the type of the perfluorinated R group in [RC=CXe]⁺ on the ¹²⁹Xe NMR chemical shifts is demonstrated by the remarkably high-frequency shift (deshielding) of the xenon atom parallel to the replacement of fluorine atoms in [CF₃C=CXe]⁺ by perfluoroalkyl groups: δ (¹²⁹Xe) = –3636 ppm (R_F=CF₃) < –3609 ppm (R_F=CF₃CF₂CF₂) < –3600 ppm [R_F = (CF₃)₂CF]. Furthermore, there is yet a very small but still experimentally detectable distinction in the ¹²⁹Xe NMR chemical shifts caused by configurational distinctions at C-4 as shown in the case of the isomeric cations [*cis*-CF₃CF=CFC=CXe]⁺ (δ = –3613.2 ppm) and [*trans*-CF₃CF=CFC=CXe]⁺ (δ = –3613.4 ppm).

Solutions of the salts $[C_4H_9C=CXe][BF_4]$ and $[(CH_3)_3-CC=CXe][BF_4]$ in aHF (-60 °C) displayed the most shielded xenon nuclei in the series of alkynylxenonium salts with ¹²⁹Xe resonances at $\delta = -3775$ ppm and $\delta = -3781$ ppm, respectively (Table 1).

The ¹³C NMR spectra of [RC=CXe][BF₄] are of particular interest because they should allow a direct and unambiguous proof of the C-Xe bond in alkynylxenon(II) salts. To our surprise, the resonances C-1 are located at unusually low frequencies between 8 and -24 ppm. The shielding of C-1 in aHF solutions of alkynylxenon(II) salts bearing either hydrocarbon or perfluoroalkyl groups increases in the same order as the shielding of the xenon atom, e.g. from $R = (CF_3)_2 CF$ to $R = (CH_3)_3 C$ (Table 1). Salts 4b and 5b with unsaturated perfluoro R groups attached to C-2 possess the most deshielded C-1, which is probably the result of a π -electron interaction of the CF₃CF=CF group or the C_6F_5 group with the C=C triple bond. The ¹³C NMR spectra for C-1 of the cations $[RC=CXe]^+$ contains satellites from the ${}^{13}C{}^{-129}Xe$ coupling, which increases from ca. ${}^{1}J_{C}$ $_{1,Xe}$ = 265 Hz [R = C₄H₉, (CH₃)₃C] to $^{1}J_{C-1,Xe}$ = 308 Hz (R = C_6F_5) to approximately ${}^1J_{C-1,Xe}$ = 345 Hz (R = perfluoroalkyl). An opposite course of couplings is found for ${}^{2}J_{C-2,Xe}$. In addition, it is worth mentioning that the chemi-

Table 1. ¹²⁹Xe and selected ¹³C NMR spectroscopic data for [RC=CXe][BF₄].

R	Solvent	<i>T</i> [°C]	$\delta(Xe)$ [ppm]	δ (C-1) [ppm]	${}^{1}J_{\text{C-1,Xe}}$ [Hz]	δ(C-2) [ppm]	${}^{2}J_{\text{C-2,Xe}}$ [Hz]
(CH ₃) ₃ C	aHF	-60	-3781	-23.7	267	107.0	76
$(CH_3)_3C$	PFP	-60	-3773				
$(CH_3)_3C$	CH_2Cl_2	-40	-3719	-15.7	[a]	105.7	[a]
$(CH_3)_3C^{[11]}$	CDCl ₃	-40	-3631	26.9	120	105.2	79
C_4H_9	aHF	-30	-3783	-24.0	264	101.6	69
		-60	-3775				
C ₄ H ₉	PFP	-60	-3762	-21.2	279	99.3	73
C_4H_9	CH_2Cl_2	-60	-3698	-16.7	288	98.7	75
C_6F_5	aHF	-60	-3662	0.6	308	81.0	62
CF ₃	aHF	-60	-3636	-5.2	343	81.2	69
cis-CF ₃ CF=CF	aHF	-60	-3613.2	6.9	[a]	79.8	64
trans-CF ₃ CF=CF	aHF	-60	-3613.4	7.9	332	79.8	64
C_3F_7	aHF	-20	-3619	-0.7	349	80.9	70
$(CF_3)_2CF$	aHF	-20	-3610	-0.5	343	80.4	68
			(-3601) ^[b]				

[a] The coupling ¹³C–¹²⁹Xe was not observed because of the low intensity of the parent signal. [b] Extrapolated to -60 °C from the equation: $\Delta \delta^{(129}$ Xe)/ $\Delta T = -0.22$ ppm K⁻¹.^[20]

cal shift values for C-2 in the above series show an opposite trend to that of C-1 and diminish from $\delta = 107$ ppm to approximately $\delta = 80$ ppm.

In contrast to 1b–5b, the salts $[C_4H_9C\equiv CXe][BF_4]$ and $[(CH_3)_3CC \equiv CXe][BF_4]$ are soluble in weakly coordinating solvents such as CH₂Cl₂ and PFP and do not decompose in these solutions below -60 °C over the course of several weeks. The ¹²⁹Xe resonances of **6b** and **7b** in PFP are similar to those in aHF but are slightly shifted by (9-13 ppm) to higher frequencies. In contrast, the NMR spectra of **6b** and **7b** in CH₂Cl₂ display significant distinctions relative to those in aHF. Thus, in CH₂Cl₂ the ¹²⁹Xe NMR spectra show signals that are shifted by 67 ppm (7b) and 77 ppm (6b) to higher frequencies. In the ¹³C NMR spectra of both salts, the resonance for C-1 is even shifted by 8 ppm into the same direction, whereas the resonance for C-2 moves by 2 ppm in the opposite direction. The position of the resonance for the [BF₄]⁻ anion in the ¹⁹F NMR spectra of **6b** and **7b** is shifted to $\delta = -144 \pm 1$ ppm in CH₂Cl₂ and to δ = -140 ± 1 ppm in PFP. For comparison, solutions of [Bu₄N][BF₄] in aHF (-20 °C), CH₂Cl₂ (24 °C) and PFP (-10 °C) display the ¹⁹F NMR signal at δ = -148.3, -151.8 and -148.4 ppm, respectively. The deshielding of the signal for the anion in the ¹⁹F NMR spectra of the solutions of salts **6b** and **7b** in CH₂Cl₂ and PFP is attributed to a significant cation-anion interaction (borderline description as contact or tight ion pair). This is in contrast to their behaviour in aHF solutions where the salts exist as solvent-shared ion pairs. The solvation of $[BF_4]$ in aHF can be described as the protonation of the fluorine terminus by the superacid aHF or by the formation of a hydrogen bridge between $[BF_4]^-$ and the fluorine atom of the HF molecule. Recently the related phenomena have been reported for solutions of (aryl)(pentafluorophenyl)iodonium tetrafluoroborates^[14] and (pentafluorophenyl)(perfluoroalkenyl)iodonium tetrafluoroborates^[15] in CH₂Cl₂ and aHF.

Finally, we have to mention that some of the NMR spectroscopic data of salt **7b** presented here differ (see Table 1) from those reported for the product solution obtained in accordance with Scheme 1.^[11]

Experimental Section

The NMR spectra were recorded with an AVANCE 300 Bruker spectrometer. The chemical shifts are referenced to TMS (¹H, ¹³C), BF₃·OEt₂/CDCl₃ (15% v/v) (¹¹B), CCl₃F (¹⁹F) [with C₆F₆ as a secondary reference, $\delta = -162.9$ ppm], and XeOF₄ (¹²⁹Xe) [with XeF₂ as a secondary reference, XeF₂/MeCN/24 °C (c \rightarrow 0), $\delta = -1813.28$ ppm].^[16] The multiplicities of the ¹³C- and ¹⁹F NMR signals caused by couplings with the ¹²⁹Xe nucleus (satellites) are denoted by (*). The composition of the reaction mixtures and the yields of the products were determined by NMR spectroscopy by using the internal quantitative standard 1,1,2-trichlorotrifluoroe-thane.

1,1,1,3,3-Pentafluoropropane (Honeywell), 1,1,2-trichlorotrifluoroethane (Merck) were used as supplied. Dichloromethane (Fluka) was purified and dried by standard procedures.^[17] Anhydrous hydrogen fluoride was stored over CoF₃. Solutions of organoethynyldifluoroboranes **1a–7a** were prepared from the corresponding potassium organoethynyltrifluoroborate salts.^[18] All manipulations with organoethynyldifluoroboranes, organoethynylxenon(II) salts and anhydrous HF were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment under an atmosphere of dry argon.

Trifluoropropynylxenon(II) Tetrafluoroborate, $[CF_3C=CXe][BF_4]$, (1b): A solution of $CF_3C=CBF_2$ (0.45 mmol) in PFP (1.5 mL) was cooled to -47 °C, and xenon difluoride (83 mg, 0.49 mmol) was added in one portion. Within a few minutes, a white suspension was formed which was stirred at -45 °C for an additional 1.5 h before all volatiles were removed in vacuo at -45 °C to give 1b (82 mg, 59%). Similarly, salt 1b (123 mg, 57%) was prepared in CH₂Cl₂ (4.8 mL) at -55 °C from CF₃C=CBF₂ (0.80 mmol) and xenon difluoride (120 mg, 0.71 mmol).

1b: ¹¹B NMR (96.29 MHz, aHF, -20 °C): $\delta = -2.4$ (s, $[BF_4]^-$) ppm. ¹³C{¹⁹F} NMR (75.46 MHz, aHF, -20 °C): $\delta = 112.2$ (C-3), 80.5 (d*, ²*J*_{C,Xe} = 69 Hz, C-2), -5.2 (d*, ¹*J*_{C,Xe} = 345 Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, aHF, -20 °C): $\delta = -52.5$ (s, 3 F, C*F*₃), -148.0 (s, 4 F, $[BF_4]^-$) ppm.

Heptafluoropent-1-ynylxenon(II) Tetrafluoroborate, $[C_3F_7C \equiv CXe]$ -[**B**F₄], (2b): A solution of $C_3F_7C \equiv CBF_2$ (0.66 mmol) in PFP (1.5 mL) was cooled to -40 °C, and xenon difluoride (99 mg, 0.58 mmol) was added in one portion. The resulting white suspension was stirred at -40 °C for 2 h before the volatiles were removed in vacuo (0.13 hPa) at -40 °C to give 2b (237 mg, 98%).

2b: ¹¹B NMR (96.29 MHz, aHF, -20 °C): $\delta = -1.3$ (s, $[BF_4]^{-}$) ppm. ¹³C{¹⁹F} NMR (75.46 MHz, aHF, -20 °C): $\delta = 117.5$ (C-5), 107.9 and 106.9 (C-3 and C-4), 80.9 (d*, ² $J_{C,Xe} = 70$ Hz, C-2), -0.7 (d*, ¹ $J_{C,Xe} = 349$ Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, aHF, -20 °C): $\delta = -78.6$ (t, ⁴ $J_{F,F} = 9$ Hz, 3 F, F-5), -101.1 (t, ³ $J_{F,F} = 3$ Hz, q, ⁴ $J_{F,F} = 9$ Hz, 2 F, F-3), -124.2 (t, ³ $J_{F,F} = 3$ Hz, 2 F, F-4), -147.2 (s, 4 F, [BF₄]⁻) ppm.

Heptafluoro-3-methylbut-1-ynylxenon(II) Tetrafluoroborate, $[(CF_3)_2-CFC \equiv CXe][BF_4]$, (3b): A solution of $(CF_3)_2CFC \equiv CBF_2$ (0.73 mmol) in PFP (2 mL) was cooled to -45 °C before solid xenon difluoride (128 mg, 0.75 mmol) was added in one portion. Within a few minutes, a white suspension was formed which was stirred at -40 °C for an additional 1.5 h. The mother liquor was decanted, and the residue was washed with cold (-40 °C) PFP (1 mL). After drying in vacuo (0.13 hPa) at -40 °C, salt 3b (207 mg, 69%) was obtained. The mother liquor contained borane 3a (0.16 mmol) along with traces of $(CF_3)_2CFC \equiv CH$ and unknown products (¹⁹F NMR).

3b: ¹¹B NMR (96.29 MHz, aHF, -20 °C): $\delta = -1.3$ (s, $[BF_4]^-$) ppm. ¹³C{¹⁹F} NMR (75.46 MHz, aHF, -20 °C): $\delta = 118.8$ (*C*F₃), 85.9 (C-3), 80.4 (d*, ²*J*_{C,Xe} = 68 Hz, C-2), -0.5 (d*, ¹*J*_{C,Xe} = 343 Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, aHF, -20 °C): $\delta = -74.0$ (d, ³*J*_{F,F} = 10 Hz, 6 F, *CF*₃), -170.9 (³*J*_{F,F} = 10 Hz, d*, ⁴*J*_{F,Xe} = 8 Hz, septet, 1 F, F-3), -147.6 (s, 4 F, $[BF_4]^-$) ppm.

Pentafluoropent-3-en-1-ynylxenon(II) Tetrafluoroborate, [CF₃-CF=CFC=CXe][BF₄], (4b): A solution of CF₃CF=CFC=CBF₂ (0.50 mmol) (*cisltrans* = 1:2) in PFP (2 mL) was cooled to $-55 \,^{\circ}$ C, and solid xenon difluoride (84 mg, 0.50 mmol) was added in one portion. Within a few minutes, a white suspension was formed which was stirred at $-55 \,^{\circ}$ C for an additional 1 h. After centrifugation at $-78 \,^{\circ}$ C, the mother liquor was decanted at $-60 \,^{\circ}$ C, the residue was washed with cold ($-60 \,^{\circ}$ C) PFP (2 mL) and dried in vacuo at $-55 \,^{\circ}$ C to give 4b (130 mg, 70%).

cis-4b: ¹¹B NMR (96.29 MHz, aHF, -20 °C): $\delta = -1.3$ (s, [*B*F₄]⁻) ppm. ¹³C{¹⁹F} NMR (75.46 MHz, aHF, -60 °C): $\delta = 150.3$ and

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135.1 (C-3 and C-4), 119.5 (C-5), 79.8 (d*, ${}^{2}J_{C,Xe} = 64$ Hz, C-2), 6.9 (C-1) (the signal was too low in intensity to detect ${}^{1}J_{C,Xe}$) ppm. ¹⁹F NMR (282.40 MHz, aHF, -60 °C): $\delta = -68.1$ (d, ${}^{3}J_{F,F} = 12$ Hz, d, ${}^{4}J_{F,F} = 6$ Hz, 3 F, F-5), -128.2 (d, q, ${}^{3}J_{F,F} = 12$ Hz, d*, ${}^{5}J_{F,Xe} = 17$ Hz, 1 F, F-4), -134.4 (d, ${}^{3}J_{F,F} = 3$ Hz, q, ${}^{4}J_{F,F} = 6$ Hz, 1 F, F-3), -147.5 (s, 4 F, [BF₄]⁻) ppm.

trans-4b: ¹¹B NMR (96.29 MHz, aHF, -20 °C): $\delta = -1.3$ (s, $[BF_4]^-$) ppm. ¹³C{¹⁹F} NMR (75.46 MHz, aHF, -60 °C): $\delta = 148.0$ and 133.2 (C-3 and C-4), 116.3 (C-5), 79.8 (d*, ${}^{2}J_{C,Xe} = 64$ Hz, C-2), 7.9 (d*, ${}^{1}J_{C,Xe} = 332$ Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, aHF, -60 °C): $\delta = -67.9$ (d, ${}^{3}J_{F,F} = 7$ Hz, d, ${}^{4}J_{F,F} = 18$ Hz, 3 F, F-5), -150.0 (d, ${}^{3}J_{F,F} = 139$ Hz, q, ${}^{3}J_{F,F} = 7$ Hz, 1 F, F-4), -149.3 (d, ${}^{3}J_{F,F} = 139$ Hz, q, ${}^{4}J_{F,F} = 18$ Hz, 1 F, F-3), -147.5 (s, 4 F, [BF₄]⁻) ppm.

Pentafluorophenylethynylxenon(II) Tetrafluoroborate, $[C_6F_5C\equiv CXe]-[BF_4]$, (5b)

A: A solution of $C_6F_5C \equiv CBF_2$ (0.34 mmol) in PFP (0.9 mL) was cooled to -55 °C, and xenon difluoride (50 mg, 0.29 mmol) was added in one portion. The resulting suspension was stirred at -50 to -55 °C for 1 h. After centrifugation at -78 °C the brown mother liquor was decanted at -45 °C. The residue was dried in vacuo (0.13 hPa) at -45 °C, and pale brownish **5b** was obtained (37 mg, 31%). The dissolution in aHF at -40 °C was accompanied by decomposition of **5b**. Total decomposition occurred within 30–50 min (¹⁹F and ¹²⁹Xe NMR).

B: A solution of $C_6F_5C \equiv CBF_2$ (0.26 mmol) in CH₂Cl₂ (1.5 mL) was cooled to -60 °C and xenon difluoride (38 mg, 0.22 mmol) was added in one portion. The white suspension was stirred at -60 °C for 1 h, and subsequently **5b** (0.15 mmol, 68%) (¹⁹F NMR) was extracted with cold (-65 °C) aHF (0.5 mL).

5b: ¹¹B NMR (96.29 MHz, aHF, -60 °C): $\delta = -1.7$ (q, ¹*J*_{B,F} = 11 Hz, [*B*F₄]⁻) ppm. ¹³C{¹⁹F} NMR (75.46 MHz, aHF, -60 °C): $\delta = 149.5$, 145.7, 137.9, 95.2 (C-2,6, C-4, C-3,5, and C-*ipso*, C₆F₅), 81.0 (d*, ²*J*_{C,Xe} = 62 Hz, C-2), 0.6 (d*, ¹*J*_{C,Xe} = 308 Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, aHF, -60 °C): $\delta = -131.7$ (m, 2 F, F-*or*-*tho*), -142.4 (t, ³*J*_{E,F} = 19 Hz, t, ⁴*J*_{E,F} = 6 Hz, 1 F, F-*para*), -159.0 (m, 2 F, F-*meta*), -148.1 (s, 4 F, [B*F*₄]⁻) ppm.

The solution of **5b** in aHF obtained as described under *B* showed no significant decomposition at -60 °C over 13 h (¹⁹F-, ¹²⁹Xe NMR), but when the temperature was raised above -30 °C, **5b** quickly decomposed to give mainly cis-C₆F₅CF=CHF.^[19]

cis-C₆F₅CF²=CHF¹: ¹H NMR (300.13 MHz, CDCl₃, 24 °C): δ = 6.80 (d, ²*J*_{H,F-1} = 71 Hz, d, ³*J*_{H,F-2} = 16 Hz) ppm. ¹⁹F NMR (282.40 MHz, CDCl₃, 24 °C): δ = −135.9 (d, ³*J*_{E,H} = 16 Hz, d, ³*J*_{E,F} = 15 Hz, t, ⁴*J*_{F,F-ortho} = 15 Hz, 1 F, F-2), −138.0 (m, 2 F, F-ortho), −149.1 (d, ²*J*_{E,H} = 71 Hz, d, ³*J*_{E,F} = 15 Hz, t, ⁵*J*_{E,F-ortho} = 5, d, ⁷*J*_{E,F-para} = 3 Hz, 1 F, F-1), −149.8 (t, ³*J*_{E,F} = 21 Hz, 1 F, F-para), −160.4 (m, 2 F, F-meta) ppm.

Hex-1-ynylxenon(II) Tetrafluoroborate, [C₄H₉C=CXe][BF₄], (6b)

A: A solution of $C_4H_9C\equiv CBF_2$ (0.25 mmol) in CH_2Cl_2 (0.6 mL) was cooled to -70 °C and added in one portion to the cold (-70 °C) suspension of xenon difluoride (60 mg, 0.35 mmol) in CH_2Cl_2 (0.2 mL). The dark reaction mixture was stirred at -65 to -70 °C for 1 h. The ¹H- and ¹⁹F NMR spectra showed the quantitative conversion of **6a** into **6b**.

6b: ¹H NMR (300.13 MHz, CH₂Cl₂, -60 °C): $\delta = 2.59$ (t, ³*J*_{H,H} = 7 Hz, 2 H, 3-H), 1.55 (t, ³*J*_{H,H} = 7 Hz, t, ³*J*_{H,H} = 7 Hz, 2 H, 4-H), 1.35 (t, ³*J*_{H,H} = 7 Hz, q, ³*J*_{H,H} = 7 Hz, 2 H, 5-H), 0.87 (t, ³*J*_{H,H} = 7 Hz, 3 H, 6-H) ppm. ¹¹B NMR (96.29 MHz, CH₂Cl₂, -60 °C): $\delta = -1.4$ (s, [*B*F₄]⁻) ppm. ¹³C{¹H} NMR (75.46 MHz, CH₂Cl₂),

-60 °C): δ = 98.7 (d*, ²J_{C,Xe} = 75 Hz, C-2), 28.7, 21.8, 20.5 (C-3, C-4, C-5), 13.4 (C-6), -16.7 (d*, ¹J_{C,Xe} = 288 Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, CH₂Cl₂, -60 °C): δ = -143.0 (s, [BF₄]⁻) ppm.

aHF (0.4 mL) was added to a solution of **6b** in CH_2Cl_2 and stirred at -45 °C for 10 min before the acidic phase was decanted.

6b: ¹H NMR (300.13 MHz, aHF, -30 °C): $\delta = 2.68$ (t, ${}^{3}J_{H,H} = 7$ Hz, 2 H, 3-H), 1.66 (t, ${}^{3}J_{H,H} = 7$ Hz, t, ${}^{3}J_{H,H} = 7$ Hz, 2 H, 4-H), 1.46 (t, ${}^{3}J_{H,H} = 7$ Hz, q, ${}^{3}J_{H,H} = 7$ Hz, 2 H, H-5), 0.95 (t, ${}^{3}J_{H,H} = 7$ Hz, 3 H, 6-H) ppm. ¹¹B NMR (96.29 MHz, aHF, -30 °C): $\delta = -1.2$ (s, $[BF_4]^{-}$) ppm. ¹³C{¹H} NMR (75.46 MHz, aHF, -30 °C): $\delta = 101.6$ (d*, ${}^{2}J_{C,Xe} = 69$ Hz, C-2), 29.0, 21.9, 20.1 (C-3, C-4, C-5), 12.0 (C-6), -24.0 (d*, ${}^{1}J_{C,Xe} = 264$ Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, aHF, -30 °C): $\delta = -147.8$ (s, $[BF_4]^{-}$) ppm.

B: A solution of $C_4H_9C \equiv CBF_2$ (0.25 mmol) in PFP (0.7 mL) was cooled to -70 °C and added in one portion to the cold (-70 °C) suspension of xenon difluoride (54 mg, 0.32 mmol) in PFP (0.2 mL). The brown reaction mixture was stirred at -65 °C for 1 h. The NMR spectra of the suspension showed the total conversion of **6a** and the formation of **6b** in >25% yield.

6b: ¹H NMR (300.13 MHz, PFP, -60 °C): δ = 1.58 (m, 2 H, 4-H), 1.42 (m, 2 H, 5-H), 0.91 (t, ${}^{3}J_{\text{H,H}}$ = 7 Hz, 3 H, 6-H) ppm (the signal for 3-H overlapped with the resonance of PFP at 2.6 ppm). ¹¹B NMR (96.29 MHz, PFP, -60 °C): δ = -0.1 (s, [*B*F₄]⁻) ppm. ¹³C {¹H} NMR (75.46 MHz, PFP, -60 °C): δ = 99.3 (d*, ${}^{2}J_{\text{C,Xe}}$ = 73 Hz, C-2), 28.5, 21.4, 19.6 (C-3, C-4, C-5), 12.1 (C-6), -21.2 (d*, ${}^{1}J_{\text{C,Xe}}$ = 279 Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, PFP, -60 °C): δ = -140.7 (s, [*B*F₄]⁻) ppm. No changes were found in a solution of **6b** in CH₂Cl₂ after storage at -70 °C over 5 months. When **6b** was stored as aHF solution at 22 °C the content of **6b** was reduced from 95–100% (after 2 h) to 38% (after 22 h) to 10% (after 46 h).

3,3-Dimethylbut-1-ynylxenon(II) Tetrafluoroborate, [(CH₃)₃-CC=CXe][BF₄], (7b)

A: A cold (-60 °C) solution of $(CH_3)_3CC \equiv CBF_2$ (0.44 mmol) in PFP (1.7 mL) was added in one portion to the cold (-60 °C) stirred suspension of xenon difluoride (69 mg, 0.40 mmol) in PFP (0.1 mL). After 2 h, the reaction mixture was centrifuged at -78 °C and subsequently the brown mother liquor was decanted at -65 °C. The precipitate was dried at -60 °C in vacuo to give **7b** (37 mg, 0.12 mmol). The mother liquor still contained borane **7a** (0.05 mmol) along with product **7b** (0.15 mmol) (¹H-, ¹¹B-, ¹⁹F NMR).

7b: ¹H NMR (300.13 MHz, PFP, -50 °C): $\delta = 1.30$ (s, *CH*₃) ppm. ¹¹B NMR (96.29 MHz, PFP, -50 °C): $\delta = -1.4$ (s, $[BF_4]^-$) ppm. ¹⁹F NMR (282.40 MHz, PFP, -50 °C): $\delta = -138.9$ (s, $[BF_4]^-$) ppm.

7b: ¹H NMR (300.13 MHz, aHF, -60 °C): $\delta = 1.26$ (s, *CH*₃) ppm. ¹¹B NMR (96.29 MHz, aHF, -50 °C): $\delta = -1.2$ (quintet, ¹*J*_{B,F} = 10 Hz, [B*F*₄]⁻) ppm. ¹³C{¹H} NMR (75.46 MHz, aHF, -60 °C): δ = 107.0 (d*, ²*J*_{C,Xe} = 76 Hz, C-2), 30.9 (C-3), 27.6 (*C*H₃), -23.7 (d*, ¹*J*_{C,Xe} = 267 Hz, C-1) ppm. ¹⁹F NMR (282.40 MHz, aHF, -50 °C): $\delta = -148.0$ (s, [B*F*₄]⁻) ppm.

B: When a solution of **7b** in PFP was warmed to 20 °C, it became dark, and a black precipitate was formed within 5–10 min. The decomposition of the colourless solution of **7b** in aHF proceeded slowly at 20 °C and led to a dark colouration. The intensity of the ¹²⁹Xe NMR signal was also reduced to 80% (after 24 h) and then to 11% (after 44 h).

7b: ¹H NMR (300.13 MHz, CH₂Cl₂, -60 °C): δ = 1.28 (s, CH₃) ppm. ¹¹B NMR (96.29 MHz, CH₂Cl₂, -60 °C): δ = -1.4 (s, [*B*F₄]⁻) ppm. ¹³C{¹H} NMR (75.46 MHz, CH₂Cl₂, -40 °C): δ = 105.7 (C-

Supporting Information (see also the footnote on the first page of this article): Multi-NMR spectra of the $[RC=CXe][BF_4]$ salts.

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