DOI: 10.1002/ejic.200600366

Organoethynylxenon(II) Tetrafluoroborates, [RC≡CXe][BF_4] – The First Examples of Isolated Alkynylxenonium Salts: Preparation and Multi-NMR Characterisation

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Keywords: Alkynes / Boranes / Xenon / NMR spectroscopy

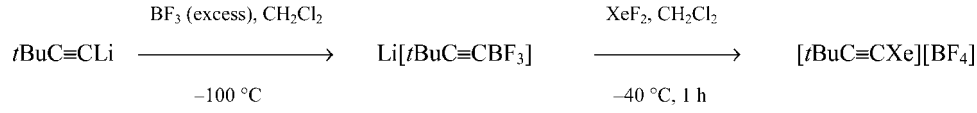
The perfluorinated organoethynylxenon(II) salts, [RC≡CXe][BF_4] [R = CF_3, C_3F_7, $(CF_3)_2CF$, *cis*-, *trans*-CF_3CF=CF, C_6F_5], were prepared by the reaction of XeF_2 with the corresponding perfluoroorganoethynyldifluoroboranes, RC≡CBF_2, in 1,1,1,3,3-pentafluoropropane (PFP) or CH_2Cl_2 at –60 to –40 °C and isolated in 30–98 % yield. Similarly, the non-fluorinated organoethynylxenon(II) salts [C_4H_9C≡CXe][BF_4] and [$(CH_3)_3$CC≡CXe][BF_4] were obtained in 20 to 40 % yield. All [RC≡CXe][BF_4] salts are soluble in anhydrous HF (aHF) and the salts with R = C_4H_9 or R = $(CH_3)_3$C display sufficient solubility in the weakly coordinating solvents CH_2Cl_2 and PFP. The xenonium salts [RC≡CXe][BF_4] were unambiguously characterised by their ^{1}H-, ^{11}B-, ^{13}C-, ^{19}F-, and ^{129}Xe NMR spectra in solution.

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 XeF_2 with $(C_6F_5)_3$B.[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, $O_2CC_6F_5$, CN, C_6F_5) 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][BF_4][7–9] were reported. In 2004 Naumann et al. observed RC≡CXeF molecules (R = Me, Bu, Ph) in the fluoride-catalysed reaction of XeF_2 and Me_3SiC≡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][BF_4] obtained by the reaction of Li[*t*BuC≡CBF_3] with BF_3 and XeF_2 in CH_2Cl_2 (Scheme 1).[11] This salt, which could not be isolated because of its decomposition at –30 °C, was characterised by ^{1}H-, ^{11}B-, ^{13}C-, and ^{129}Xe NMR spectroscopy at –40 °C, by IR spectroscopy at 0 °C, and by the alkynylation of PPh_3 to [*t*BuC≡CPPh_3][BF_4] at –78 °C.

In the analogous reactions of XeF_2 with alkynylsilanes, RC≡$CSiMe_3$ (R = Et, Pr, *t*Bu, and Me_3Si), and BF_3·OEt_2 in CD_2Cl_2 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 singlet in the ^{129}Xe NMR spectrum. No ^{129}Xe resonances were found in the spectra of the reaction solutions for R = H, Me, Ph, CF_3, 4-$CH_3C_6H_4SO_2$, $(i$Pr$)_3$Si, $PhMe_2$Si.[11]



Scheme 1.

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-1-enylxenon(II) salts: the reaction of xenon difluoride with

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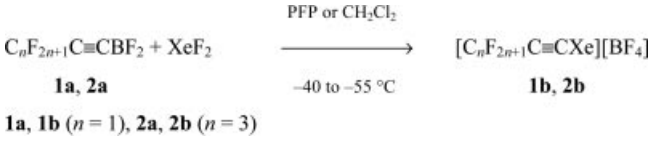
polyfluoroorganoboron difluoride in the appropriate solvent.[3b] This preparative method allowed for the isolation of the new salt as a pure product and opened the possibility of extensive and unambiguous characterisation. Subsequently, we extended this preparative method to a representative series of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

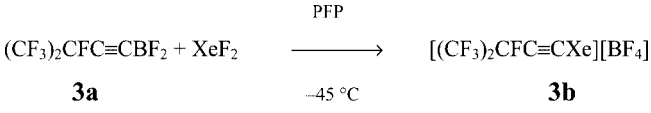
Results and Discussion

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).



Scheme 2.

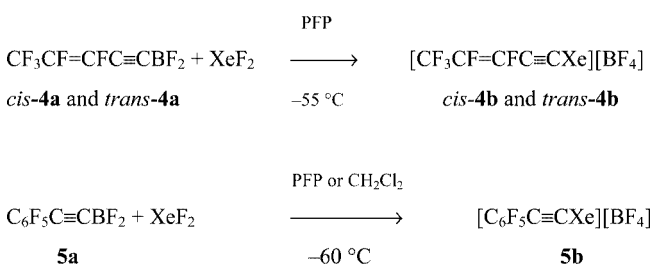
In a similar way, the reaction of heptafluoro-3-methylbut-1-ynyldifluoroborane (**3a**) with XeF_2 gave heptafluoro-3-methylbut-1-ynylxenon(II) tetrafluoroborate (**3b**) in 82% yield (Scheme 3).



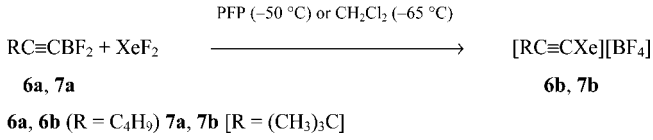
Scheme 3.

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) 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 XeF_2 in CH_2Cl_2 at –65 °C solely a solution of **6b** was obtained.



Scheme 4.



Scheme 5.

In contrast to the reaction of alk-1-enyldifluoroboranes, $RCF{=}CFBF_2$, with XeF_2,[7] neither the alk-1-enyltrifluoroborate anions, $[RCF{=}CFBF_3]^-$, nor their fluorination products, $[XBF_3]^-$ (X = RCF=CF, RCF_2CF_2), 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 XeF_2 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 XeF_2 no xenonium salts were obtained. Thus under the same reaction conditions as those of alkynyldifluoroboranes, *cis*- and *trans*-hex-1-enyldifluoroboranes, $C_4H_9CH{=}CHBF_2$, 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 CH_2Cl_2. 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 = $CF_3CF{=}CF$ and R = C_6F_5, 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 (^{19}F 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 °C (cf.[11]). Solutions or suspensions of these salts in either PFP or CH_2Cl_2 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 ^{19}F NMR spectra of fluoroorganoethynylxenon(II) tetrafluoroborates **1b**–**5b** in aHF displayed signals for the fluoroorgano groups and for the $[BF_4]^-$ anion (at approximately δ = –148 ppm) with the expected integrations. Long-range couplings $J_{^{19}F,^{129}Xe}$ were observed in the spectra of both isomers of $[CF_3CF{=}CFC{\equiv}CXe][BF_4]$. The signal for F-4 at δ = –128.2 ppm (*cis*-**4b**) and F-3 at δ = –149.3 ppm (*trans*-**4b**) displayed ^{129}Xe satellites ($^5J_{F\text{-}4,Xe}$ = 17 Hz and $^4J_{F\text{-}3,Xe}$ = 6 Hz, respectively) in accordance with the natural abundance of the ^{129}Xe isotope of 26%. The assignment of the coupling $^4J_{F\text{-}3,Xe}$ = 8 Hz in the ^{19}F NMR spectrum of $[(CF_3)_2CFC{\equiv}CXe][BF_4]$ was confirmed in a $^{19}F\{^{19}F(CF_3)\}$ homodecoupling NMR experiment. In the ^{19}F NMR spectrum of salts with unbranched perfluoroalkyl R groups, as in **1b** (signal for the CF_3 group at δ = –52.5 ppm, $\tau_{1/2}$ = 1.5 Hz) or **2b** [$^{19}F\{^{19}F(CF_3)\}$ spectrum of the $CF_3CF_2CF_2$ group] such couplings were not observed. For comparison, in the case of *cis*-perfluoroalk-1-enylxenonium salts, larger $^4J_{F\text{-}3,Xe}$ couplings are known. In the spectra of [*cis*-$YCF_2CF{=}CFXe][BF_4]$, $^4J_{F\text{-}3,Xe}$ = 40 Hz (Y = F) and $^4J_{F\text{-}3,Xe}$ = 56 Hz (Y = CF_3) were measured.[7]

The ^{129}Xe NMR signals of salts $[RC{\equiv}CXe][BF_4]$ **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 $[RC{\equiv}CXe]^+$ on the ^{129}Xe NMR chemical shifts is demonstrated by the remarkably high-frequency shift (deshielding) of the xenon atom parallel to the replacement of fluorine atoms in $[CF_3C{\equiv}CXe]^+$ by perfluoroalkyl groups: $\delta(^{129}Xe)$ = –3636 ppm ($R_F{=}CF_3$) < –3609 ppm ($R_F{=}CF_3CF_2CF_2$) < –3600 ppm [R_F = $(CF_3)_2CF$]. Furthermore, there is yet a very small but still experimentally detectable distinction in the ^{129}Xe NMR chemical shifts caused by configurational distinctions at C-4 as shown in the case of the isomeric cations [*cis*-$CF_3CF{=}CFC{\equiv}CXe]^+$ (δ = –3613.2 ppm) and [*trans*-$CF_3CF{=}CFC{\equiv}CXe]^+$ (δ = –3613.4 ppm).

Solutions of the salts $[C_4H_9C{\equiv}CXe][BF_4]$ and $[(CH_3)_3CC{\equiv}CXe][BF_4]$ in aHF (–60 °C) displayed the most shielded xenon nuclei in the series of alkynylxenonium salts with ^{129}Xe resonances at δ = –3775 ppm and δ = –3781 ppm, respectively (Table 1).

The ^{13}C NMR spectra of $[RC{\equiv}CXe][BF_4]$ 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 = $(CF_3)_2CF$ to R = $(CH_3)_3C$ (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 $CF_3CF{=}CF$ group or the C_6F_5 group with the C≡C triple bond. The ^{13}C NMR spectra for C-1 of the cations $[RC{\equiv}CXe]^+$ contains satellites from the ^{13}C–^{129}Xe coupling, which increases from ca. $^1J_{C\text{-}1,Xe}$ = 265 Hz [R = C_4H_9, $(CH_3)_3C$] to $^1J_{C\text{-}1,Xe}$ = 308 Hz (R = C_6F_5) to approximately $^1J_{C\text{-}1,Xe}$ = 345 Hz (R = perfluoroalkyl). An opposite course of couplings is found for $^2J_{C\text{-}2,Xe}$. In addition, it is worth mentioning that the chemi-

Table 1. ^{129}Xe and selected ^{13}C NMR spectroscopic data for $[RC{\equiv}CXe][BF_4]$.

R	Solvent	T [°C]	δ(Xe) [ppm]	δ(C-1) [ppm]	$^1J_{C\text{-}1,Xe}$ [Hz]	δ(C-2) [ppm]	$^2J_{C\text{-}2,Xe}$ [Hz]
$(CH_3)_3C$	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_4H_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-$CF_3CF{=}CF$	aHF	–60	–3613.2	6.9	[a]	79.8	64
trans-$CF_3CF{=}CF$	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 ^{13}C–^{129}Xe 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 δ = 107 ppm to approximately δ = 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 CH_2Cl_2 and PFP and do not decompose in these solutions below –60 °C over the course of several weeks. The ^{129}Xe 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 CH_2Cl_2 display significant distinctions relative to those in aHF. Thus, in CH_2Cl_2 the ^{129}Xe NMR spectra show signals that are shifted by 67 ppm (**7b**) and 77 ppm (**6b**) to higher frequencies. In the ^{13}C 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 $[BF_4]^-$ anion in the ^{19}F NMR spectra of **6b** and **7b** is shifted to $\delta = -144 \pm 1$ ppm in CH_2Cl_2 and to $\delta = -140 \pm 1$ ppm in PFP. For comparison, solutions of $[Bu_4N][BF_4]$ in aHF (–20 °C), CH_2Cl_2 (24 °C) and PFP (–10 °C) display the ^{19}F NMR signal at δ = –148.3, –151.8 and –148.4 ppm, respectively. The deshielding of the signal for the anion in the ^{19}F NMR spectra of the solutions of salts **6b** and **7b** in CH_2Cl_2 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 CH_2Cl_2 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 (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2/CDCl_3$ (15% v/v) (^{11}B), CCl_3F (^{19}F) [with C_6F_6 as a secondary reference, δ = –162.9 ppm], and $XeOF_4$ (^{129}Xe) [with XeF_2 as a secondary reference, XeF_2/MeCN/24 °C (c→0), δ = –1813.28 ppm].[16] The multiplicities of the ^{13}C- and ^{19}F NMR signals caused by couplings with the ^{129}Xe 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-trichlorotrifluoroethane.

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 CoF_3. 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, $[CF_3C{\equiv}CXe][BF_4]$, (1b): A solution of $CF_3C{\equiv}CBF_2$ (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 CH_2Cl_2 (4.8 mL) at –55 °C from $CF_3C{\equiv}CBF_2$ (0.80 mmol) and xenon difluoride (120 mg, 0.71 mmol).

1b: ^{11}B NMR (96.29 MHz, aHF, –20 °C): δ = –2.4 (s, $[BF_4]^-$) ppm. ^{13}C{^{19}F} NMR (75.46 MHz, aHF, –20 °C): δ = 112.2 (C-3), 80.5 (d*, $^2J_{C,Xe}$ = 69 Hz, C-2), –5.2 (d*, $^1J_{C,Xe}$ = 345 Hz, C-1) ppm. ^{19}F NMR (282.40 MHz, aHF, –20 °C): δ = –52.5 (s, 3 F, CF_3), –148.0 (s, 4 F, $[BF_4]^-$) ppm.

Heptafluoropent-1-ynylxenon(II) Tetrafluoroborate, $[C_3F_7C{\equiv}CXe][BF_4]$, (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: ^{11}B NMR (96.29 MHz, aHF, –20 °C): δ = –1.3 (s, $[BF_4]^-$) ppm. ^{13}C{^{19}F} NMR (75.46 MHz, aHF, –20 °C): δ = 117.5 (C-5), 107.9 and 106.9 (C-3 and C-4), 80.9 (d*, $^2J_{C,Xe}$ = 70 Hz, C-2), –0.7 (d*, $^1J_{C,Xe}$ = 349 Hz, C-1) ppm. ^{19}F NMR (282.40 MHz, aHF, –20 °C): δ = –78.6 (t, $^4J_{F,F}$ = 9 Hz, 3 F, F-5), –101.1 (t, $^3J_{F,F}$ = 3 Hz, q, $^4J_{F,F}$ = 9 Hz, 2 F, F-3), –124.2 (t, $^3J_{F,F}$ = 3 Hz, 2 F, F-4), –147.2 (s, 4 F, $[BF_4]^-$) ppm.

Heptafluoro-3-methylbut-1-ynylxenon(II) Tetrafluoroborate, $[(CF_3)_2CFC{\equiv}CXe][BF_4]$, (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 (^{19}F NMR).

3b: ^{11}B NMR (96.29 MHz, aHF, –20 °C): δ = –1.3 (s, $[BF_4]^-$) ppm. ^{13}C{^{19}F} NMR (75.46 MHz, aHF, –20 °C): δ = 118.8 (CF_3), 85.9 (C-3), 80.4 (d*, $^2J_{C,Xe}$ = 68 Hz, C-2), –0.5 (d*, $^1J_{C,Xe}$ = 343 Hz, C-1) ppm. ^{19}F NMR (282.40 MHz, aHF, –20 °C): δ = –74.0 (d, $^3J_{F,F}$ = 10 Hz, 6 F, CF_3), –170.9 ($^3J_{F,F}$ = 10 Hz, d*, $^4J_{F,Xe}$ = 8 Hz, septet, 1 F, F-3), –147.6 (s, 4 F, $[BF_4]^-$) ppm.

Pentafluoropent-3-en-1-ynylxenon(II) Tetrafluoroborate, $[CF_3CF{=}CFC{\equiv}CXe][BF_4]$, (4b): A solution of $CF_3CF{=}CFC{\equiv}CBF_2$ (0.50 mmol) (*cis*/*trans* = 1:2) in PFP (2 mL) was cooled to –55 °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 °C for an additional 1 h. After centrifugation at –78 °C, the mother liquor was decanted at –60 °C, the residue was washed with cold (–60 °C) PFP (2 mL) and dried in vacuo at –55 °C to give **4b** (130 mg, 70%).

***cis*-4b:** ^{11}B NMR (96.29 MHz, aHF, –20 °C): δ = –1.3 (s, $[BF_4]^-$) ppm. ^{13}C{^{19}F} NMR (75.46 MHz, aHF, –60 °C): δ = 150.3 and

135.1 (C-3 and C-4), 119.5 (C-5), 79.8 (d*, $^2J_{C,Xe}$ = 64 Hz, C-2), 6.9 (C-1) (the signal was too low in intensity to detect $^1J_{C,Xe}$) ppm. ^{19}F NMR (282.40 MHz, aHF, –60 °C): δ = –68.1 (d, $^3J_{F,F}$ = 12 Hz, d, $^4J_{F,F}$ = 6 Hz, 3 F, F-5), –128.2 (d, q, $^3J_{F,F}$ = 12 Hz, $^3J_{F,F}$ = 3 Hz, d*, $^5J_{F,Xe}$ = 17 Hz, 1 F, F-4), –134.4 (d, $^3J_{F,F}$ = 3 Hz, q, $^4J_{F,F}$ = 6 Hz, 1 F, F-3), –147.5 (s, 4 F, [BF_4]$^-$) ppm.

***trans*-4b:** ^{11}B NMR (96.29 MHz, aHF, –20 °C): δ = –1.3 (s, [*B*F_4]$^-$) ppm. ^{13}C{^{19}F} NMR (75.46 MHz, aHF, –60 °C): δ = 148.0 and 133.2 (C-3 and C-4), 116.3 (C-5), 79.8 (d*, $^2J_{C,Xe}$ = 64 Hz, C-2), 7.9 (d*, $^1J_{C,Xe}$ = 332 Hz, C-1) ppm. ^{19}F NMR (282.40 MHz, aHF, –60 °C): δ = –67.9 (d, $^3J_{F,F}$ = 7 Hz, d, $^4J_{F,F}$ = 18 Hz, 3 F, F-5), –150.0 (d, $^3J_{F,F}$ = 139 Hz, q, $^3J_{F,F}$ = 7 Hz, 1 F, F-4), –149.3 (d, $^3J_{F,F}$ = 139 Hz, q, $^4J_{F,F}$ = 18 Hz, d*, $^4J_{F,Xe}$ = 6 Hz, 1 F, F-3), –147.5 (s, 4 F, [BF_4]$^-$) 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 (^{19}F and ^{129}Xe NMR).

B: A solution of $C_6F_5C{\equiv}CBF_2$ (0.26 mmol) in CH_2Cl_2 (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%) (^{19}F NMR) was extracted with cold (–65 °C) aHF (0.5 mL).

5b: ^{11}B NMR (96.29 MHz, aHF, –60 °C): δ = –1.7 (q, $^1J_{B,F}$ = 11 Hz, [*B*F_4]$^-$) ppm. ^{13}C{^{19}F} NMR (75.46 MHz, aHF, –60 °C): δ = 149.5, 145.7, 137.9, 95.2 (C-2,6, C-4, C-3,5, and C-*ipso*, C_6F_5), 81.0 (d*, $^2J_{C,Xe}$ = 62 Hz, C-2), 0.6 (d*, $^1J_{C,Xe}$ = 308 Hz, C-1) ppm. ^{19}F NMR (282.40 MHz, aHF, –60 °C): δ = –131.7 (m, 2 F, F-*ortho*), –142.4 (t, $^3J_{F,F}$ = 19 Hz, t, $^4J_{F,F}$ = 6 Hz, 1 F, F-*para*), –159.0 (m, 2 F, F-*meta*), –148.1 (s, 4 F, [BF_4]$^-$) ppm.

The solution of **5b** in aHF obtained as described under *B* showed no significant decomposition at –60 °C over 13 h (^{19}F-, ^{129}Xe NMR), but when the temperature was raised above –30 °C, **5b** quickly decomposed to give mainly *cis*-$C_6F_5CF{=}CHF$.[19]

***cis*-$C_6F_5CF^2{=}CHF^1$:** ^{1}H NMR (300.13 MHz, $CDCl_3$, 24 °C): δ = 6.80 (d, $^2J_{H,F\text{-}1}$ = 71 Hz, d, $^3J_{H,F\text{-}2}$ = 16 Hz) ppm. ^{19}F NMR (282.40 MHz, $CDCl_3$, 24 °C): δ = –135.9 (d, $^3J_{F,H}$ = 16 Hz, d, $^3J_{F,F}$ = 15 Hz, t, $^4J_{F,F\text{-}ortho}$ = 15 Hz, 1 F, F-2), –138.0 (m, 2 F, F-*ortho*), –149.1 (d, $^2J_{F,H}$ = 71 Hz, d, $^3J_{F,F}$ = 15 Hz, t, $^5J_{F,F\text{-}ortho}$ = 5, d, $^7J_{F,F\text{-}para}$ = 3 Hz, 1 F, F-1), –149.8 (t, $^3J_{F,F}$ = 21 Hz, 1 F, F-*para*), –160.4 (m, 2 F, F-*meta*) ppm.

Hex-1-ynylxenon(II) Tetrafluoroborate, [$C_4H_9C{\equiv}CXe$][BF_4], (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 ^{1}H- and ^{19}F NMR spectra showed the quantitative conversion of **6a** into **6b**.

6b: ^{1}H NMR (300.13 MHz, CH_2Cl_2, –60 °C): δ = 2.59 (t, $^3J_{H,H}$ = 7 Hz, 2 H, 3-H), 1.55 (t, $^3J_{H,H}$ = 7 Hz, t, $^3J_{H,H}$ = 7 Hz, 2 H, 4-H), 1.35 (t, $^3J_{H,H}$ = 7 Hz, q, $^3J_{H,H}$ = 7 Hz, 2 H, 5-H), 0.87 (t, $^3J_{H,H}$ = 7 Hz, 3 H, 6-H) ppm. ^{11}B NMR (96.29 MHz, CH_2Cl_2, –60 °C): δ = –1.4 (s, [*B*F_4]$^-$) ppm. ^{13}C{^{1}H} NMR (75.46 MHz, CH_2Cl_2, –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. ^{19}F NMR (282.40 MHz, CH_2Cl_2, –60 °C): δ = –143.0 (s, [BF_4]$^-$) 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: ^{1}H NMR (300.13 MHz, aHF, –30 °C): δ = 2.68 (t, $^3J_{H,H}$ = 7 Hz, 2 H, 3-H), 1.66 (t, $^3J_{H,H}$ = 7 Hz, t, $^3J_{H,H}$ = 7 Hz, 2 H, 4-H), 1.46 (t, $^3J_{H,H}$ = 7 Hz, q, $^3J_{H,H}$ = 7 Hz, 2 H, H-5), 0.95 (t, $^3J_{H,H}$ = 7 Hz, 3 H, 6-H) ppm. ^{11}B NMR (96.29 MHz, aHF, –30 °C): δ = –1.2 (s, [*B*F_4]$^-$) ppm. ^{13}C{^{1}H} NMR (75.46 MHz, aHF, –30 °C): δ = 101.6 (d*, $^2J_{C,Xe}$ = 69 Hz, C-2), 29.0, 21.9, 20.1 (C-3, C-4, C-5), 12.0 (C-6), –24.0 (d*, $^1J_{C,Xe}$ = 264 Hz, C-1) ppm. ^{19}F NMR (282.40 MHz, aHF, –30 °C): δ = –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: ^{1}H 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, $^3J_{H,H}$ = 7 Hz, 3 H, 6-H) ppm (the signal for 3-H overlapped with the resonance of PFP at 2.6 ppm). ^{11}B NMR (96.29 MHz, PFP, –60 °C): δ = –0.1 (s, [*B*F_4]$^-$) ppm. ^{13}C{^{1}H} NMR (75.46 MHz, PFP, –60 °C): δ = 99.3 (d*, $^2J_{C,Xe}$ = 73 Hz, C-2), 28.5, 21.4, 19.6 (C-3, C-4, C-5), 12.1 (C-6), –21.2 (d*, $^1J_{C,Xe}$ = 279 Hz, C-1) ppm. ^{19}F NMR (282.40 MHz, PFP, –60 °C): δ = –140.7 (s, [BF_4]$^-$) ppm. No changes were found in a solution of **6b** in CH_2Cl_2 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, [$(CH_3)_3$-$CC{\equiv}CXe$][BF_4], (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) (^{1}H-, ^{11}B-, ^{19}F NMR).

7b: ^{1}H NMR (300.13 MHz, PFP, –50 °C): δ = 1.30 (s, CH_3) ppm. ^{11}B NMR (96.29 MHz, PFP, –50 °C): δ = –1.4 (s, [*B*F_4]$^-$) ppm. ^{19}F NMR (282.40 MHz, PFP, –50 °C): δ = –138.9 (s, [*B*F_4]$^-$) ppm.

7b: ^{1}H NMR (300.13 MHz, aHF, –60 °C): δ = 1.26 (s, CH_3) ppm. ^{11}B NMR (96.29 MHz, aHF, –50 °C): δ = –1.2 (quintet, $^1J_{B,F}$ = 10 Hz, [BF_4]$^-$) ppm. ^{13}C{^{1}H} NMR (75.46 MHz, aHF, –60 °C): δ = 107.0 (d*, $^2J_{C,Xe}$ = 76 Hz, C-2), 30.9 (C-3), 27.6 (*C*H_3), –23.7 (d*, $^1J_{C,Xe}$ = 267 Hz, C-1) ppm. ^{19}F NMR (282.40 MHz, aHF, –50 °C): δ = –148.0 (s, [BF_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 ^{129}Xe NMR signal was also reduced to 80% (after 24 h) and then to 11% (after 44 h).

7b: ^{1}H NMR (300.13 MHz, CH_2Cl_2, –60 °C): δ = 1.28 (s, CH_3) ppm. ^{11}B NMR (96.29 MHz, CH_2Cl_2, –60 °C): δ = –1.4 (s, [*B*F_4]$^-$) ppm. ^{13}C{^{1}H} NMR (75.46 MHz, CH_2Cl_2, –40 °C): δ = 105.7 (C-

2), 30.4 (C-3), 28.9 (CH_3), –15.7 (C-1) ppm. ^{19}F NMR (282.40 MHz, CH_2Cl_2, –60 °C): δ = –144.7 (s, $[BF_4]^-$) ppm.

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

Acknowledgments

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Russian Foundation for Basic Research (Grant 04–03–04002 NNIO_a) and the Fonds der Chemischen Industrie. We thank Honeywell Specialty Chemicals Seelze GmbH for the generous donation of chemicals.

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Received: April 24, 2006
Published Online: August 7, 2006

