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Distinct reactivities of *cis*- and *trans*-$R_FCF{=}CFBF_2$ towards XeF_2 and the first synthesis of a [*trans*-$R_FCF{=}CFXe]^+$ salt

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The competitive reaction of $C_4F_9CF{=}CFBF_2$ (*cis*:*trans* = 1.2:1) with XeF_2 demonstrated for the first time a remarkably lower reaction rate of the *trans* isomer with respect to the *cis* isomer in the xenodeborylation reaction (formation of the $[C_4F_9CF{=}CFXe]^+$ cation with a *cis*:*trans* ratio of 2.5 to 4:1) and allowed us to develop reaction conditions for the syntheses of [*trans*-$C_4F_9CF{=}CFXe]^+$ salts.

We have developed a widely applicable method to synthesise organoxenonium(II) salts [RXe][Y]. Using the reaction of XeF_2 with (organo)difluoroboranes RBF_2, we were able to prepare a representative series of organoxenonium salts with R = aryl, alkenyl and alkynyl groups following Scheme 1.[1–4]

$$XeF_2 + RBF_2 \xrightarrow{\text{i}} [RXe][BF_4]$$

Scheme 1 *Conditions*: i, CH_2Cl_2, 1,1,1,3,3-pentafluoropropane (PFP), or SO_2FCl, –65 to –30 °C.

However, the reactivity of alk-1-enyldifluoroboranes $XCF{=}CFBF_2$ towards XeF_2 diverged from the pattern described in Scheme 1. When X was F, *cis*-C_nF_{2n+1} (n = 1, 2) and *trans*-H, the corresponding alkenylxenon(II) salts were formed. In case of X = *trans*-C_nF_{2n+1} (n = 1, 4), the perfluoroalkenyldifluoroborane starting compound was slowly consumed, but no organoxenonium salts were detected among the reaction products.[2] This was surprising because the *trans* configuration was realised in the structurally related perfluorocyclohexa-1,4-dien-1-ylxenonium and perfluorocyclohex-1-enylxenonium salts, which were obtained by the oxidative fluorine addition to $[C_6F_5Xe][Y]$ as relatively stable compounds.[5] Furthermore, the closely related reaction of *trans*-$CF_3CF{=}CFBF_2$ with other hypervalent F–E–F moieties such as in 4-$FC_6H_4IF_2$ yielded smoothly the corresponding iodonium salt [(4-FC_6H_4)(*trans*-$CF_3CF{=}CF$)I][BF_4].[6] We have assumed that the formation of [*trans*-$XCF{=}CFXe][Y]$ from *trans*-$XCF{=}CFBF_2$ and XeF_2 is sterically hindered when X represents a bulky substituent (perfluoroalkyl group). In such cases, competitive side-processes (oxidative fluorination *etc.*) became predominant.[2]

The relative rate of xenodeborylation [the formal replacement of the difluoroboryl group by xenon(+)] of *cis*- and *trans*-perfluoroalk-1-enyldifluoroboranes can be estimated by reacting an equimolar mixture of both isomers with XeF_2. For this competitive reaction, we prepared a solution of $C_4F_9CF{=}CFBF_2$ (*cis*:*trans* = 1.2:1) (**1**) in CH_2Cl_2,† and treated it with a solution of xenon difluoride in 1,1,1,3,3-pentafluoropropane (PFP) at –35 to –40 °C. After 1 h, the mixture of *cis*-perfluorohex-1-enylxenon(II) (*cis*-**2**) and *trans*-perfluorohex-1-enylxenon(II) (*trans*-**2**) salts (molar ratio of 4:1) was precipitated, and a white solid was isolated. The opposite order of mixing the reagents, the addition of **1** to XeF_2 in PFP, gave a mixture of *cis*-**2** and *trans*-**2** in the molar ratio 2.5:1‡ (Scheme 2). The way how the ratio of isomers in the product depends on the order of mixing shows that, in case of a local excess of the borane starting material, *trans*-$C_4F_9CF{=}CFBF_2$ is faster consumed in a by-reaction competing with xenodeborylation than the *cis* isomer.

† A solution of *cis*-**1** and *trans*-**1** was prepared in a quantitative yield by bubbling BF_3 (in an excess) into a cold (–45 °C) stirred suspension of K[$C_4F_9CF{=}CFBF_3$] (*cis*:*trans* = 1.3:1)[8] in CH_2Cl_2 or PFP and subsequent decantation of the mother liquor from insoluble K[BF_4]. The NMR spectra of *trans*-**1** coincided with the reported one.[2,9]

cis-**1**: ^{11}B NMR (PFP, 0 °C) δ: 19.3 (br. s). ^{19}F NMR (PFP, 0 °C) δ: –79.9 [tt, 3F, F(6), $^3J_{F(6)–F(5)}$ 2 Hz, $^4J_{F(6)–F(4)}$ 10 Hz], –82.3 (s, 2F, BF_2), –115.0 [m, 2F, F(3)], –122.2 [m, 2F, F(4)], –122.4 [m, F, F(2)], –124.8 [m, 2F, F(5)], –145.1 [m, 1F, F(1)].

‡ A cold (5 °C) solution of XeF_2 (160 mg, 0.95 mmol) in PFP (1.5 ml) was added to a cold (–40 °C) stirred solution of *cis*-**1** (0.33 mmol) and *trans*-**1** (0.27 mmol) in CH_2Cl_2 (1.5 ml). A white suspension was formed and stirred at –35 °C for 1 h, the mother liquor was decanted, the solid residue was washed with cold (–30 °C) PFP (1.5 ml) and dried in a vacuum at –25 °C for 30 min to give a white solid mixture of **2** (55 mg) (*cis*:*trans* = 4:1) ($[BF_4]^-$:$[C_6F_{13}BF_3]^-$ = 1:3). The mother liquor contained *cis*-$C_4F_9CF{=}CFH$ (0.03 mmol), *trans*-$C_4F_9CF{=}CFH$ (0.08 mmol), $C_6F_{13}BF_2$ (0.08 mmol), C_6F_{14} (0.11 mmol), CH_2FCl and CHF_2Cl (^{19}F NMR). Similarly, **2** (144 mg) (*cis*:*trans* = 2.5:1) ($[BF_4]^-$:$[C_6F_{13}BF_3]^-$ = = 2:1) was obtained by the addition of *cis*-**1** (0.31 mmol) and *trans*-**1** (0.26 mmol) in PFP (2 ml) to XeF_2 (113 mg, 0.66 mmol) in PFP (1 ml). Salts *trans*-**2** ($[BF_4]^-$:$[C_6F_{13}BF_3]^-$ = 15:85) (110 mg) were obtained by the addition of *trans*-**1** (0.77 mmol) in PFP (2.5 ml) to XeF_2 (135 mg, 0.79 mmol) in PFP (2 ml) at –40 °C and working up after stirring for 4 h (88% conversion of *trans*-**1**; the yields of $C_6F_{13}BF_2$ and C_6F_{14} were 0.08 and 0.20 mmol, respectively).

2: ^{19}F NMR (aHF, –20 °C) δ: –71.8 [dd*, 1F, F(1), $^3J_{F(1)–F(2)}$ 72 Hz, $^2J_{F(1)–Xe}$ 146 Hz], 79.4 [t, 3F, F(6), $^4J_{F(6)–F(4)}$ 10 Hz], –112.6 [tdd*, 2F, F(3), $^4J_{F(3)–F(5)}$ 13 Hz, $^3J_{F(3)–F(2)}$ 13 Hz, $^4J_{F(3)–Xe}$ 53 Hz], –117.7 [dd*, 1F, F(2), $^3J_{F(2)–F(1)}$ 72 Hz, $^3J_{F(2)–Xe}$ 180 Hz], –120.6 [m, 2F, F(4)], –124.2 [m, 2F, F(5)] (*cis*-**2**); –79.5 [t, 3F, F(6), $^4J_{F(6)–F(4)}$ 10 Hz], –86.9 [tdd*, 1F, F(1), $^4J_{F(1)–F(3)}$ 25 Hz, $^3J_{F(1)–F(2)}$ 123 Hz, $^2J_{F(1)–Xe}$ 161 Hz], –114.6 [ddt, 2F, F(3), $^4J_{F(3)–F(1)}$ 25 Hz, $^3J_{F(3)–F(2)}$ 12 Hz, $^4J_{F(3)–F(5)}$ 12 Hz], –121.4 [m, 2F, F(4)], –124.4 [m, 2F, F(5)], –133.1 [d, 1F, F(2), $^3J_{F(2)–F(1)}$ 123 Hz] (*trans*-**2**); –79.6 [t, 3F, F(6), $^4J_{F(6)–F(4)}$ 10 Hz], –120.1 (m, CF_2), –120.9 (m, CF_2), –121.6 (m, CF_2), –124.4 [m, 2F, F(5)], –132.2 [m, 2F, F(1)], –147.7 (br. s, BF_3) ([$C_6F_{13}BF_3]^-$), 147.7 (br. s) ([$BF_4]^-$). ^{129}Xe NMR (aHF, –20 °C) δ: –3413 (ddt, $^2J_{Xe–F(1)}$ 148 Hz, $^3J_{Xe–F(2)}$ 183 Hz, $^4J_{Xe–F(3)}$ 55 Hz) (*cis*-**2**); –3495 (dd, $^2J_{Xe–F(1)}$ 162 Hz, $^3J_{Xe–F(2)}$ 50 Hz) (*trans*-**2**). ^{11}B NMR (aHF, –20 °C) δ: –0.6 (br. s, [$C_6F_{13}BF_3]^-$), –2.2 (s, [$BF_4]^-$).

The procedure where a Lewis acid (borane) was added to the fluorobase (XeF_2) allowed to obtain *trans*-perfluoroalk-1-enylxenonium salts for the first time.

The composition of the *cis*/*trans* mixture of **2** was unambiguously proved by multinuclear magnetic resonance spectroscopy[§] and by conversion to corresponding 1-iodoperfluorohex-1-enes using NaI in aHF[7] (Scheme 3).[¶]

$$\underset{\mathbf{1}}{XeF_2 + C_4F_9CF{=}CFBF_2} \xrightarrow{\text{i}} \underset{}{[C_4F_9CF{=}CFXe][BF_4, C_6F_{13}BF_3] + Xe^0 + C_6F_{13}BF_2 + C_6F_{14}}$$

Scheme 2 *Conditions*: i, CH_2Cl_2 or PFP, –35 °C, 1–1.5 h.

$$\underset{\mathbf{2}}{[C_4F_9CF{=}CFXe][BF_4, C_6F_{13}BF_3] + NaI_{(s)}} \xrightarrow{\text{i}} \underset{\mathbf{3}}{C_4F_9CF{=}CFI}$$

Scheme 3 *Conditions*: i, aHF, –60 °C.

This result demonstrated that [*trans*-R_FCF=CFXe][Y] salts are principally accessible to xenodeborylation. Thus, we changed our earlier applied conditions for the reaction of *trans*-**1** with XeF_2[2] and were able to isolate individual salt *trans*-**2**. In case of *trans*-R_FCF=$CFBF_2$, a diminished rate of xenodeborylation is combined with a larger relative contribution of by-reactions, mainly oxidative fluorination reactions with polarised XeF_2.[2] For comparison, both boranes, *cis*- and *trans*-ClCF=$CFBF_2$, with the sterically less demanding substituent Cl underwent xenodeborylation with equal rates.[2] The replacement of the α-fluorine atom in CF_2=$CFBF_2$ by the more bulky CF_3 group did not affect the rate of xenodeborylation.[3]

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§ The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (^{19}F at 282.40 MHz, ^{129}Xe at 83.46 MHz). The chemical shifts were referenced to CCl_3F (^{19}F) [with C_6F_6 as a secondary reference, δ: 162.9] and $XeOF_4$ (^{129}Xe) [with XeF_2 as a secondary reference, XeF_2/MeCN/24 °C ($c \rightarrow 0$), δ: –1813.28]. As a convention, the multiplicities of the ^{19}F NMR signals caused by couplings with the ^{129}Xe nucleus (satellites) are denoted by (*).

¶ Anhydrous NaI (in an excess) was added to a cold (–60 °C) stirred solution of **2** (*cis*:*trans* = 4:1) in aHF (0.7 ml) and caused immediate gas evolution and a pink colouration. The products were extracted with cold (–60 °C) CH_2Cl_2 (0.5 ml). The ^{19}F NMR spectrum showed the quantitative conversion of **2** to $C_4F_9CF{=}CFI$ **3**.

3: ^{19}F NMR (CH_2Cl_2, –20 °C) δ: –81.8 [t, 3F, F(6), $^4J_{F(6)–F(4)}$ 10 Hz], –82.7 [d, 1F, F(1), $^3J_{F(1)–F(2)}$ 7 Hz], –114.8 [td, 2F, F(3), $^4J_{F(3)–F(5)}$ 12 Hz, $^3J_{F(3)–F(2)}$ 12 Hz], –124.4 [m, 2F, F(4)], –127.4 [m, 2F, F(5)], –130.1 [m, 1F, F(2)] (*cis*-**3**); –81.9 [t, 3F, F(6), $^4J_{F(6)–F(4)}$ 9 Hz], –107.4 [ttd, 1F, F(1), $^5J_{F(1)–F(4)}$ 6 Hz, $^4J_{F(1)–F(3)}$ 26 Hz, $^3J_{F(1)–F(2)}$ 150 Hz], –118.0 [m, 2F, F(3)], –125.7 [m, 2F, F(4)], –127.5 [m, 2F, F(5)], –146.2 [d, 1F, F(2), $^3J_{F(2)–F(1)}$ 150 Hz] (*trans*-**3**)[10] (*cis*:*trans* = 4:1).