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Synthesis, NMR spectroscopic characterisation and reactions of 2,6-difluorophenylxenon fluoride, 2,6-F₂C₆H₃XeF

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Dedicated to Professor Boris Žemva

Abstract

 $[2,6-F_2C_6H_3Xe][BF_4]$ is quantitatively transferred into 2,6- $F_2C_6H_3XeF$ in reactions with $[NMe_4]F$. The latter has been isolated as a colourless solid which is stable in dichloromethane solution at room temperature for approximately 1 h. 2,6- $F_2C_6H_3XeF$ readily reacts with Me₃SiX (X = Cl, Br, CN, NCO, OCOCF₃, OSO₂CF₃, C₆F₅, 2,6- $F_2C_6H_3$) to give compounds of general compositions 2,6- $F_2C_6H_3XeX$ which were identified by multinuclear NMR experiments. Evidence was found for C₆H₅Xe(2,6- $F_2C_6H_3$) as a product of the reaction with C₆H₅SiF₃. (© 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Two reviews on the synthesis and reactions of organoxenon derivatives have been recently published [1,2]. While ligand exchange reactions with less or low co-ordinating anions have been a major part of investigations [3–7], attempts to prepare hypervalent [10-Xe-2] remained of lower success [8–12].

The first examples of organoxenon compounds with two Xe–C bonds were those of $Xe(C_6F_5)_2$ [8–10] and $Xe(C_6F_5)CN$ [9]. In a recent publication [12] Frohn and Theißen proved the existence of 2,4,6-F₃C₆H₂XeC₆F₅ and $Xe(2,4,6-F_3C_6H_2)_2$ by ¹⁹F and ¹²⁹Xe NMR spectroscopic means and supported their results by theoretical calculations.

From all organoxenon compounds synthesised so far, those bearing a 2,6- $F_2C_6H_3$ moiety and a low co-ordinating anion

exhibited to be those of highest thermal stability, e.g. $[2,6-F_2C_6H_3Xe][N(SO_2F)_2]$ ($T_{dec} = 155$ °C) [6]. With this knowledge, we decided to investigate possibilities to obtain further derivatives with the 2,6-F_2C_6H_3Xe unit starting from 2,6-F_2C_6H_3XeF and different silanes.

2. Results and discussion

2.1. Synthesis and characterisation of 2,6difluorophenylxenon fluoride, 2,6-F₂C₆H₃XeF

The sparingly soluble nature of $[NMe_4][BF_4]$ in common organic solvents makes $[NMe_4]F$ to a versatile tool for ligand exchange reactions with arylxenon tetrafluoroborates (Eq. (1)):

$$\begin{bmatrix} \mathsf{F} \\ \mathsf{F} \end{bmatrix} [\mathsf{BF}_4] + [\mathsf{NMe}_4]\mathsf{F} \xrightarrow{\mathsf{CH}_2\mathsf{Cl}_2} \xrightarrow{\mathsf{F}} \mathsf{Xe}-\mathsf{F} + [\mathsf{NMe}_4][\mathsf{BF}_4] \quad (1)$$

The reaction proceeds selectively at -78 °C in CH₂Cl₂ giving 2,6-F₂C₆H₃XeF in nearly quantitative yield. The colourless solid decomposes completely at ambient temperature within a period of 30 min (dry Ar-atmosphere). In CH₂Cl₂ solution a

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half-life time of approximately 1 h can be estimated. The decomposition proceeds with exclusive formation of 1,2,3-trifluorobenzene as the only fluorine containing product (Eq. (2)):



 $2,6-F_2C_6H_3XeF$ reacts with H_2O to give 1,3-difluorobenzene probably in a manner as outlined for different arylxenon



The reaction of 2,6- $F_2C_6H_3XeF$ and C_6F_5I implies oxidation to give an iodine(III) intermediate which decomposes in reactions with the solvent mainly into 1,3-difluoro-2-iodobenzene, pentafluorobenzene and 1,3-difluorobenzene (Eq. (4)). No ¹⁹F NMR spectroscopic evidence is found for consecutive reactions of the fluorine atom in these reactions:



compounds [13]. At room temperature reactions with elemental mercury, $Hg(2,6-F_2C_6H_3)F$ (Eq. (3)) is presumably formed and identified in comparison with known data of related compounds [14]:

All in all, 2,6- $F_2C_6H_3XeF$ shows the expected reaction behaviour as a strong oxidizing reagent.

NMR data of $2,6-F_2C_6H_3XeF$ are summarized in Table 1. All ¹⁹F and ¹²⁹Xe NMR values are in close

Table 1

Compilation of NMR data of 2,6-difluorophenylxenon compounds (δ in ppm; J in Hz)

Compound	$\delta(^{13}C)$	${}^{1}J({}^{129}Xe, {}^{13}C)$	δ(C-2,6)	δ(C-3,5)	δ(C-4)	$\delta(^{19}\text{F})$	${}^{3}J({}^{129}\text{Xe}, {}^{19}\text{F})$	$\delta(^{129}\text{Xe})$	Solvent	<i>T</i> (°C)
$[2,6-F_2C_6H_3Xe][BF_4]^a$	88.8	99	156.8	115.2	137.8	-99.6	52	-2115	CD ₃ CN	-30
$[2,6-F_2C_6H_3Xe]OSO_2CF_3^{b,c}$	89.4	106	157.5	115.5	138.4	-100.1	54	-2125	CD ₃ CN	+21
$(2,6-F_2C_6H_3)XeF$	90.0	168	159.0	113.4	134.8	-100.6	70 ^d	-2018	CD_2Cl_2	-70
$(2,6-F_2C_6H_3)$ XeCl ^e	104.1	205	159.5	116.3	137.4	-103.6	79	-2250	CH_2Cl_2	-70
$(2,6-F_2C_6H_3)$ XeBr ^f	103.7	261	157.3	114.2	134.9	-104.4	87	-2348	CD_2Cl_2	-80
$(2,6-F_2C_6H_3)$ XeOCOCF ₃ ^g	91.6	154	157.0	112.3	137.3	-101.4	68	-2145	CH ₂ Cl ₂	-50
$(2,6-F_2C_6H_3)$ XeCN ^h	96.3	150	162.7	111.2	130.7	-102.6	80	-2359	CH ₂ Cl ₂	-70
$(2,6-F_2C_6H_3)$ XeNCO ⁱ	96.0	150 ^j	157.3	114.2	134.9	-102.3	68	-2109	CH ₂ Cl ₂	-80
$(2,6-F_2C_6H_3)XeC_6F_5^k$	125.4	105	160.2^{1}	112.2	131.6	-105.3	74	-2312	CD_2Cl_2	k
$(2,6-F_2C_6H_3)XeC_6F_5^{k}$	126.5	530	143.8 ^m	136.5	140.1	-129.5	43		CD_2Cl_2	k
$Xe(C_6F_5)2^n$	123.2	320	143.4	136.7	141.1	-130.8	45	-2376	$(CD_3)_2CO$	-58
$(2,6-F_2C_6H_3)_2Xe$						-102.3	35	-2268	CH ₂ Cl ₂	-70
$C_6H_5Xe(2,6-F_2C_6H_3)$						-102.6	Broad	-2234	CH_2Cl_2	-80

^a Taken from Ref. [22].

^b Taken from Ref. [5].

^c $\delta(OSO_2CF_3)$: -78.5 ppm (¹⁹F); 121.3 ppm (¹³C), ¹J(¹⁹F, ¹³C) = 319 Hz.

^d $\delta(\text{Xe}^{19}\text{F})$: -8.4 ppm; ¹ $J(^{129}\text{Xe}, ^{19}\text{F}) = 3673 \text{ Hz}.$

^e The sample was contaminated by minor amounts of (CH₃)₃SiCl and (CH₃)₃SiF.

^f The sample contained minor amounts of (CH₃)₃SiBr and (CH₃)₃SiF.

- ^g δ(CF₃): 116.9 ppm; δ(CO₂): 159.7 ppm.
- ^h δ (CN): 127.4 ppm, broad. The sample was contaminated by minor amounts of (CH₃)₃SiF.

ⁱ δ(NCO): 131.3 ppm.

^j Coupling is estimated, $\tau_{1/2} \approx 60$ Hz.

^k The sample was impured by traces of $(CH_3)_3SiC_6F_5$ and $(CH_3)_3SiF$. Data are collected from several ¹³C NMR experiments run at 193 and 203 K. 2D-¹³C, ¹⁹F HMBC NMR spectra were optimised for both *ortho*-fluorine resonances with the assumption of a ² $J(^{19}F^{-13}C)$ coupling of 30 Hz. As a consequence of digital resolution, shifts exhibit errors of up to ± 0.1 ppm, couplings of up to ± 5 Hz.

 1 $^{2}J(^{129}\text{Xe}-^{13}\text{C})$: 29 Hz.

 ${}^{m}{}^{2}J({}^{129}Xe-{}^{13}C):$ not observed.

ⁿ Taken from Ref. [8]; ${}^{2}J({}^{129}Xe, {}^{13}C) = 148$ Hz.

agreement with those reported for the related 2,4,6- $F_3C_6H_2XeF$ [12].

2.2. Ligand exchange reactions of $2,6-F_2C_6H_3XeF$ and Me_3SiX (X = Cl, Br, CN, NCO, OCOCF₃, OSO₂CF₃)

All reactions of 2,6- $F_2C_6H_3XeF$ and Me₃SiX proceed more or less indiscriminately with formation of the corresponding substitution products and Me₃SiF as the leaving moiety (Eq. (5)):



The selectivity of these reactions is best demonstrated with the formation of 2,6- $F_2C_6H_3XeBr$, a compound which has been expected to be unstable but now representing the first xenon bromine compound. In contrast, reactions with Me₃SiI exclusively gave 1-I-2,6- $F_2C_6H_3$, Me₃SiF and elemental xenon (Eq. (6)):



Chemical shifts and coupling constants (Table 1) in the series 2,6- $F_2C_6H_3XeF$, 2,6- $F_2C_6H_3XeC1$ and 2,6- $F_2C_6H_3XeBr$ indicate increasing hypervalent character within the kernels C-Xe-Hal (Hal = F, Cl, Br) expressed by an increase of the absolute value of the ${}^{1}J({}^{129}Xe, {}^{13}C)$ coupling constants together with a significant highfield shift of the ${}^{129}Xe$ NMR signal. All these findings are supported by quantum-chemical calculations [15] and are in agreement with data published elsewhere [12].

Reactions of 2,6- $F_2C_6H_3XeF$ and Me_3SiCN , respectively Me_3SiNCO , arise the compounds 2,6- $F_2C_6H_3XeCN$ and 2,6-

These findings are also in agreement with solid state structures of $[2,6-F_2C_6H_3Xe]OSO_2CF_3$ [17] and $C_6F_5XeO-COC_6F_5$ [18] indicating a significantly higher ionic character for triflates than for perfluorocarboxylates. Differences are best demonstrated comparing the ${}^{1}J({}^{129}Xe, {}^{13}C)$ NMR couplings and the ${}^{129}Xe$ NMR shifts (Table 1). The differences of the nature of xenon perfluoroalkanesulfonates and perfluorocarboxylates have already been discussed earlier [19].

(5)

+ Me₃SiF

2.3. Syntheses of diarylxenon derivatives, $2,6-F_2C_6H_3XeAr$ ($Ar = C_6F_5$, $2,6-F_2C_6H_3$, C_6H_5)

As recently described, bis(pentafluorophenyl)xenon, $Xe(C_6F_5)_2$, can either be generated via the reaction of XeF_2 and $Me_3SiC_6F_5$ in the presence of catalytic quantities of

$$e + Me_3SiF$$
 (6)

[NMe₄]F [8,10] or the reaction of C_6F_5XeF and $Cd(C_6F_5)_2$ [9]. Cadmium reagents were also employed in the syntheses of 2,4,6-F₃C₆H₂XeC₆F₅ and Xe(2,4,6-F₃C₆H₂)₂ [12].

In our investigations, we chose the silane route. Considerably, reactions of 2,6-F₂C₆H₃XeF and Me₃SiAr (Ar = C₆F₅, 2,6-F₂C₆H₃) proceeded selectively in the presence of catalytic amounts of [NMe₄]F to give the corresponding diarylxenon compounds Xe(2,6-F₂C₆H₃)₂ and 2,6-F₂C₆H₃XeC₆F₅ (Eq. (7)). Unfortunately, none of the derivatives was obtained free of impurities by the starting materials:



 $F_2C_6H_3XeNCO$ as most probable. In the case of the cyanide, results match well with those given for C_6F_5XeCN [9], while those obtained for 2,6- $F_2C_6H_3XeNCO$ to our knowledge appear to be unique so far.

Great differences in thermal stability as well as NMR spectroscopic data of the products resulting from exchange reactions with Me₃SiOSO₂CF₃ and Me₃SiOCOCF₃ gave materials of more ionic [5,16,17], [2,6-F₂C₆H₃Xe]OSO₂CF₃, or covalent character, 2,6-F₂C₆H₃XeOCOCF₃, with respect to the xenon–oxygen bond [17,18] (Scheme 1).

Due to differences in the polarity of the silicon–aryl bonds of the starting materials Me₃SiAr, longer reaction times and higher temperatures were necessary for the 2,6-F₂C₆H₃ group transfer (24 h/–30 °C (2,6-F₂C₆H₃) versus 1 h/ -78 °C (C₆F₅)). The formation of the reactive silicate intermediate appeared to be the rate determining step. It has to be noted that formation of polyphenyls as described for the decay of intermediately formed silicates [20] can be excluded in reactions with Me₃SiC₆F₅ under the chosen conditions.



Scheme 1. Suggested bond structures for $[2,6-F_2C_6H_3Xe]OSO_2CF_3$ and $2,6-F_2C_6H_3XeOCOCF_3$.

2.6-F₂C₆H₃XeC₆F₅ was isolated as a pale vellow solid in nearly quantitative yield with a decomposition point of approximately -20 °C. NMR spectra and chemical behaviour make 2,6-F₂C₆H₃XeC₆F₅ unambiguous (Table 1). ¹⁹F NMR chemical shifts were detected in the region of those reported for $Xe(C_6F_5)_2$ [8–10] and $Xe(2,4,6-F_3C_6H_2)_2$ [12], significantly shifted from those of salt-like fluorophenvlxenon derivatives (e.g. [6,12,16,17]). The same can be applied in a somewhat less significant manner with respect to 2.6-difluorophenvlxenon compounds. The ¹²⁹Xe NMR chemical shift (-2312 ppm) matches well that of reported under comparable conditions [8– 10,12]. While all shift values (¹⁹F, ¹²⁹Xe, ¹³C) were found in the expected regions, the ${}^{1}J(Xe, C)$ couplings are outstanding. The absolute values of 105 Hz (${}^{1}J(Xe, C)$ to 2,6-F₂C₆H₃) and of 530 Hz (${}^{1}J(Xe, C)$ to C₆F₅) impressively differ from each other. The sum of coupling constants - under the hypothesis of the same relative sign - is nearly identical for both, 2,6- $F_2C_6H_3XeC_6F_5$ (635 Hz) and $Xe(C_6F_5)_2$ (640 Hz [8] or 630 Hz [9]), therefore, a strongly polarized 3c-4e bond must be assumed for the compound, $2,6-F_2C_6H_3XeC_6F_5$ (Scheme 2).

The ¹³C, ¹⁹F HMBC NMR spectrum clearly shows that 2,6- $F_2C_6H_3XeC_6F_5$ is a discrete molecule rather than a mixture of symmetric diarylxenon compounds. The ¹⁹F signals of the 2,6- $F_2C_6H_3$ group correlate to the resonances of the quarternary carbon atoms of both, the 2,6- $F_2C_6H_3$ group and the C_6F_5 group. Additionally, ¹⁹F signals of the *ortho*-fluorine atoms of the pentafluorophenyl ring show crosspeaks to the quarternary carbon atoms. These correlations prove unambiguously that both aromatic rings are bonded to the same xenon atom. Since the spectrum is recorded without ¹³C decoupling the two crosspeaks owing to the larger ${}^{2}J(C, F)$ coupling can be distinguished from the two crosspeaks of the ${}^{4}J(C, F)$ couplings by their larger splitting along the fluorine axis. As a consequence, the resonances of the quarternary carbon atoms can be assigned definitely. Furthermore, this spectrum allows to identify all carbon signals of 2,6-F₂C₆H₃XeC₆F₅.

All attempts to find at least NMR spectroscopic evidence for $C_6H_5Xe(2,6-F_2C_6H_3)$ from reactions of $2,6-F_2C_6H_3XeF$ and $Me_3SiC_6H_5$ remained unsuccessful. This aim was achieved using $C_6H_5SiF_3$ as an arylating reagent in fluoride mediated reactions (Eq. (8)):



Scheme 2. Suggested bond structure for (2,6-F₂C₆H₃)XeC₆F₅.

 $C_6H_5Xe(2,6-F_2C_6H_3)$ was identified by ¹⁹F and ¹²⁹Xe NMR spectroscopic means in comparison with related data [8–10,12].

The characteristic multiplet of the 2,6-F₂C₆H₃ group occurred 2 ppm deshielded from that of the starting material, 2,6-F₂C₆H₃XeF (-102.6 versus -100.6 ppm); additionally, the ¹²⁹Xe NMR signal was shifted upfield by 216 ppm into the region of values reported for other diarylxenon derivatives (-2234 versus -2018 ppm) clearly indicating the formation of C₆H₅Xe(2,6-F₂C₆H₃).

Similar changes were observed for $Xe(2,6-F_2C_6H_3)_2$ (Table 1). A close look onto the ${}^3J({}^{129}Xe, {}^{19}F)$ coupling constant (35 Hz) in comparison with reported values [8–10,12] exhibits that it could be interesting to determine the relative sign of the coupling constants for a better understanding of the nature of the 3c–4e-bonds in those molecules.

Unfortunately, all three diarylxenon derivatives were found to be too instable to be further investigated by diffraction methods.

3. Experimental

3.1. General remarks

All chemicals were obtained from commercial providers and used as received. XeF₂ [21], [2,6-F₂C₆H₃Xe][BF₄] [22], Me₃Si(2,6-F₂C₆H₃) [23] and Me₃SiC₆F₅ [24] were prepared according to literature procedures. [NMe₄]F was prepared from [NMe₄][BF₄] and carefully dried KF in methanol.

Solvents were purified by standard methods [25]. Schlenk (argon-atmosphere) and vacuum techniques were used throughout all preparative procedures. NMR spectra were recorded on Bruker spectrometers: DRX 500 (19 F, 470.8 MHz; 129 Xe, 138.3 MHz; 13 C, 125.8 MHz), AMX 300 (1 H, 300.1 MHz; 19 F, 282.4 MHz; 129 Xe, 83.3 MHz; 13 C, 75.5 MHz) and AC 200 (1 H, 200.1 MHz; 19 F, 188.3 MHz; 13 C, 50.3 MHz). Positive shifts denote signals occurring downfield from the external standards 1 M XeF₂ in CH₃CN (129 Xe), CCl₃F (19 F) and Me₄Si (1 H, 13 C).



3.2. Synthesis of 2,6-difluorophenylxenon fluoride

 CD_2Cl_2 (15 mL) was condensed onto 0.45 g (1.36 mmol) [2,6-F₂C₆H₃Xe][BF₄] and 0.13 g (1.40 mmol) [NMe₄]F at -100 °C. The temperature was raised to -78 °C and the suspension stirred for 2 h. During this period, [NMe₄][BF₄] quantitatively precipitated and was removed by filtration at -78 °C. 2,6-F₂C₆H₃XeF was analysed by NMR spectroscopy (cf. Table 1). The pure compound was obtained after distilling off all volatile material at -40 °C. 2,6-F₂C₆H₃XeF was obtained as a colourless solid in nearly quantitative yield (0.35 g, 1.33 mmol, 98%).

3.3. Reactions of 2,6-difluorophenylxenon fluoride with water, mercury and pentafluoroiodobenzene

To solutions of 0.07 g (0.26 mmol) 2,6-F₂C₆H₃XeF in 3 mL CH₂Cl₂ at -50 °C 0.10 g (5.55 mmol) H₂O, 0.10 g (0.50 mmol) Hg, 0.12 g (0.26 mmol) C₆F₅I, respectively, were added. Reaction mixtures were allowed to warm to room temperature over a period of 1 h and analysed by ¹⁹F NMR spectroscopy. With water, exclusive formation of 1,3-F₂C₆F₄ was observed which was complete after 12 h. The reaction with elemental mercury proceeded selectively to give one mercury derivative (δ (¹⁹F) -91.6 ppm; ³*J*(HgF) 489 Hz) which might be assigned to Hg(2,6-F₂C₆H₄ and C₆F₅H were formed.

3.4. Reactions of 2,6-difluorophenylxenon fluoride with trimethylsilicon derivatives, Me_3SiX (X = Cl, Br, CN, NCO, OCOCF₃, OSO₂CF₃)

To solutions of 0.07 g (0.26 mmol) 2,6- $F_2C_6H_3XeF$ in 3 mL CD_2Cl_2 0.28 mmol Me₃SiX were added via a syringe at -78 °C. Immediately after addition of the silicon compound, ¹⁹F NMR spectra were recorded proving the formation of Me₃SiF. Products were analysed by multinuclear NMR spectroscopic means (cf. Table 1).

3.5. Reactions of 2,6-difluorophenylxenon fluoride with trimethylsilicon derivatives, Me_3SiAr ($Ar = C_6F_5$, 2,6- $F_2C_6H_3$, C_6H_5)

3.5.1. Reaction with $Me_3SiC_6F_5$

To a solution of 0.07 g (0.26 mmol) (2,6- $F_2C_6H_3$)XeF in 3 mL CD₂Cl₂, 0.03 g (0.28 mmol) Me₃SiC₆F₅ and a very small quantity of [NMe₄]F were added. The reaction mixture was stirred for 1 h at -78 °C. The completeness of the exchange was monitored by NMR spectroscopic methods.

2,6- $F_2C_6H_3XeC_6F_5$ was isolated as a pale yellow solid in nearly quantitative yield after removal of all volatile material in high vacuum at -40 °C. In the solid state in a dry argon atmosphere, it decomposes at approximately -20 °C. *Caution*! All attempts to manipulate solid 2,6- $F_2C_6H_3XeC_6F_5$ with glass or metal spatula led to direct explosions even at -78 °C or below.

3.5.2. Reaction with $Me_3Si(2,6-F_2C_6H_3)$

The reaction was performed in a similar manner as described for 2,6-F₂C₆H₃XeC₆F₅ with 0.21 g (0.78 mmol) 2,6-F₂C₆H₃XeF, 0.15 g (0.78 mmol) Me₃Si(2,6-F₂C₆H₃) and a catalytic amount of [NMe₄]F. Complete exchange was achieved after 24 h of stirring a CD₂Cl₂ (10 mL) solution at -30 °C. Attempted isolation by condensing off all volatiles at -40 °C led to decomposition of Xe(2,6-F₂C₆H₃)₂ mainly into elemental xenon and 2,2',6,6'-tetrafluorobiphenyl.

3.5.3. Reaction with $C_6H_5SiF_3$

Quantities of 0.25 g (1.54 mmol) $C_6H_5SiF_3$ and 0.28 g (3.00 mmol) [NMe₄]F were stirred in 10 mL CH₂Cl₂ for 1 h at 0 °C. The mixture was cooled to -90 °C and 0.20 g (0.76 mmol) 2,6-F₂C₆H₃XeF were added. After stirring for 20 min at this temperature a white solid had precipitated. The reaction was terminated and the solution investigated by NMR spectroscopic methods. Isolation was not attempted.

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