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Bis(pentafluorophenylxenonium) tetrafluoroterephthalate, *p*-$C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5$, a hypervalent compound with two xenon–carbon bonds

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Dedicated to Professor Henry Selig on the occasion of his receipt of the 2009 ACS Award for Creative Work in Fluorine Chemistry.

A B S T R A C T

Bis(pentafluorophenylxenonium) tetrafluoroterephthalate (**1**) was obtained by metathesis reactions of pentafluorophenylxenonium and tetrafluoroterephthalate salts. The availability of suitable solvents for the metatheses hampered the optimization of the reaction. The new xenon–carbon compound with two polar Xe–O bonds was characterized by NMR spectroscopy in solution and by Raman spectroscopy in the solid state. From $(CF_3)_2CHOH$/MeCN solutions single crystals were obtained with four alcohol molecules attached to **1** by hydrogen bridges. The thermal properties of the intrinsically unstable title compound are reported.

1. Introduction

At present, three prototypes for Xe–C compounds – the major number are arylxenon compounds – can be distinguished by their bonding: arylxenonium salts [ArXe][Y] with weakly coordinating anions $[Y]^-(Ar{=}C_6F_5$ or $C_6H_{5-n}F_n$; $Y = BF_4$, $BF_{4-n}(C_6F_5)_n$, $B(CN)_4$, $B(CF_3)_4$, $B(OTeF_5)_4$, $AsF_6)$ [1–5], diaryl xenon molecules Ar_2Xe or ArXeAr' [2,3,6–8], and finally arylxenon compounds ArXeZ (Z = CN [3,6,8,12], Cl [1–3,9,11], F [1–3,6,8,12], $C_6F_5CO_2$ [3,10], Br [11]) with asymmetrical 3c–4e (hypervalent) C–Xe–Z bonds. In both salts $[(C_6F_5Xe)_2Cl][AsF_6]$ [1–3,9] and $[(C_6F_5Xe)_2F][BF_4]$ [3,6], two electrophilic $[C_6F_5Xe]^+$ cations are bridged by a monoatomic, singly charged anion. The present study is focused on the bifunctional coordinating tetrafluoroterephthalate anion $[p\text{-}(O_2C)_2C_6F_4]^{2-}$, which in the presence of two electrophilic $[C_6F_5Xe]^+$ cations forms the neutral title compound, *p*-$C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5$ (**1**).

2. Results and discussion

The methodology applied for the synthesis of $C_6F_5XeO(O)CC_6F_5$ – the reaction of $[C_6F_5Xe][AsF_6]$ with $Cs[O_2CC_6F_5]$ in water [3,10] – failed in the case of a 2:1 reaction with bifunctional $Cs_2[p\text{-}(O_2C)_2C_6F_4]$. An insoluble product resulted already from the interaction of one $[C_6F_5Xe]^+$ cation with one tetrafluoroterephthalate anion and was very unstable. Even at 0 °C it decomposed rapidly despite attempts to rapidly isolate it. Alternative reaction conditions were therefore investigated.

2.1. Alternative procedures for the synthesis of 1 by metatheses

We have chosen three types of solvents (strongly coordinating MeCN, weakly coordinating CH_2Cl_2, and the proton-donor solvent, CF_3CH_2OH) which allowed all reactions to be carried out at −40 °C and below. In MeCN, we used $[C_6F_5Xe][BF_4]$ and $[N(^nBu)_4]_2[p\text{-}(O_2C)_2C_6F_4]$ as soluble starting materials (Eq. (1)).

$$2[C_6F_5Xe][BF_4] + [N(^nBu)_4]_2[p\text{–}(O_2C)_2C_6F_4] \xrightarrow[-40\,^\circ C]{MeCN} p\text{–}C_6F_5XeO(O)CC_6\underset{\mathbf{1}}{F_4}C(O)OXeC_6F_5 \cdot 2MeCN\downarrow + 2[N(^nBu)_4][BF_4] \qquad (1)$$

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In the 2:1 reaction at −40 °C, product **1** precipitated and the co-product $[N(^nBu)_4][BF_4]$ remained in solution. Product **1** contained 2 MeCN, presumably co-crystallized. But MeCN could not be removed over a period of more than 50 h under vacuum despite warming to 0 °C. At 20 °C, the decomposition of **1** occurred parallel to the removal of MeCN. The decomposition is discussed later. When the precipitate of the 2:1 reaction product in MeCN, **1**·2 MeCN, was repeatedly washed with CH_2Cl_2 while vigorously stirring (−78 °C), **1** could be isolated free of MeCN.

In order to start the synthesis in the absence of coordinating solvents, e.g., in polar CH_2Cl_2 $[C_6F_5Xe]^+$ salts with weakly coordinating anions having a sphere of fluoroorganic ligands like $[B(CF_3)_4]^-$ or $[B(C_6F_5)_4]^-$ [4,5] were required. When a cold solution of $[N(^nBu)_4]_2[p\text{-}(O_2C)_2C_6F_4]$ in CH_2Cl_2 (−78 °C) was added to a cold suspension of poorly soluble $[C_6F_5Xe][B(CF_3)_4]$, **1** was formed as an insoluble product. After repeated washings at low temperature and drying, pure **1** could be isolated free of solvent (Eq. (2)).

$$2[C_6F_5Xe][B(CF_3)_4] + [N(^nBu)_4]_2[p\text{–}(O_2C)_2C_6F_4] \xrightarrow[-78\,^\circ C]{CH_2Cl_2} \underset{\mathbf{1}}{p\text{–}C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5} \downarrow + 2[N(^nBu)_4][B(CF_3)_4] \quad (2)$$

The analogous reaction with the $[C_6F_5Xe][B(C_6F_5)_4]$ salt at −78 °C suffered from the handicap that one MeCN molecule is coordinated to the cation of $[C_6F_5Xe][B(C_6F_5)_4]$ [4,5]. MeCN could be removed from the product after the reaction of $[N(^nBu)_4]_2[p\text{-}(O_2C)_2C_6F_4]$ with $[C_6F_5Xe{\cdot}NCMe][B(C_6F_5)_4]$ by extensive washing with CH_2Cl_2.

1 could also be obtained from the 2:1 reaction of $[C_6F_5Xe][BF_4]$ and $Cs_2[p\text{-}(O_2C)_2C_6F_4]$ in CF_3CH_2OH at −40 °C (Eq. (3))

$$2[C_6F_5Xe][BF_4] + Cs_2[p-(O_2C)_2C_6F_4] \xrightarrow[\sim -40\,^\circ C]{CF_3CH_2OH} \underset{1}{p - C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5} + 2Cs[BF_4]\downarrow \quad (3)$$

This approach, however, has disadvantages. The insoluble co-product, $Cs[BF_4]$, is micro-crystalline and transparent. Thus, its separation from the mother liquor could not be easily followed visually and was very time consuming. After 5 h at <−35 °C, ≥34% of **1** was decomposed. Only one type of C_6F_5 and C_6F_4 groups was present in the product besides C_6F_5H (38% related to C_6F_4). The ratio was C_6F_5:C_6F_4 = 1.66 instead of 2.0 (for **1**) and the presence of C_6F_5H are in agreement with a mixture of **1** (major) and $p\text{-}C_6F_5XeO(O)CC_6F_4CO_2H$ (minor). The presence of $p\text{-}(HO_2C)_2C_6F_4$ can be excluded based on the ^{19}F NMR spectrum.

2.2. Thermal stability: neat and in solution

The neat compound, **1**·2 MeCN, is less stable than base-free **1**, but both are intrinsically unstable. When **1**·2 MeCN was handled for less than 30 min at 20 °C, no change could be detected by NMR spectroscopy after dissolution. After 2 weeks at 20 °C, the total decomposition led in a clean reaction (elimination of Xe^0) to the diester, $p\text{-}(C_6F_5O(O)C)_2C_6F_4$. The absence of C_6F_5H is indicative of the absence of MeCN in the coordination sphere of Xe^{II} [4] in **1**·2 MeCN. The decomposition of solid **1**·2 MeCN was characterized by an exothermic process at 89 °C (DSC, T_{onset}). In base-free **1**, T_{onset} of the exothermic process increased to 118 °C. One sample of **1** was stored inside the glove box and the stability was checked periodically at 20 °C by Raman spectroscopy after 1 d, 6 d, and 10 d. In the latter case, only small amounts of **1** had not decomposed.

The DSC measurements of **1** and **1**·2 MeCN featured an endothermic process at 145 and 141 °C, respectively, which followed the decomposition and can be attributed to the melting point of the diester, $p\text{-}(C_6F_5O(O)C)_2C_6F_4$, the primary decomposition product of **1**. This effect was confirmed for an isolated sample of the diester.

We have found two types of solvents suitable for **1**: basic nitriles like MeCN (poor solubility) and acidic alcohols like CF_3CH_2OH (mp −44 °C) or $(CF_3)_2CHOH$ (mp −4 °C) (satisfactory solubilities). The thermal stability of **1** in both alcohol solutions is lower than in MeCN solution. Thus, at −40 °C the decomposition of **1** in CF_3CH_2OH resulted in 20% C_6F_5H after 20 min whereas in more acidic $(CF_3)_2CHOH$ after 20 min at 0 °C, only 6% C_6F_5H was detected (^{19}F NMR). The addition of MeCN to $(CF_3)_2CHOH$ (1:1, vol) lowered the melting point significantly (mp −86 °C) and provided an acceptable stability and solubility of **1**. After 21 h at −30 °C, only 3% C_6F_5H had been formed. MeCN solutions of **1** showed no decomposition at −20 °C after 4 h but were decomposed completely after 5.5 h at 20 °C. The complex mixture showed three main products derived from the tetrafluoroterephthalate unit: $p\text{-}(C_6F_5O(O)C)_2C_6F_4$ (24%), $p\text{-}C_6F_5O(O)CC_6F_4CO_2H$ (43%), and $p\text{-}(HO_2C)_2C_6F_4$ (30%). 30% of the C_6F_5 groups (C_6F_5Xe unit) were not found in the products. This may be caused by diffusion of volatile C_6F_5H (only 79% observed) through the trap material.

2.3. NMR and Raman spectroscopic characterizations of 1 and 1·2 MeCN

The solubility of **1** in MeCN is very poor. Therefore, the ^{13}C and ^{129}Xe NMR data were only measured in a $(CF_3)_2CHOH$/MeCN-mixture (1:1, vol). Table 1 allows a comparison of the C_6F_5Xe unit in **1** with the ionic species $[C_6F_5Xe][BF_4]$ in the same solvent mixture at the same temperature and of the tetrafluoroterephthalate group in related compounds. The shieldings of the *m*- and *p*-F resonances (C_6F_5Xe unit) in **1** are indicative for a strong arylxenonium tetrafluoroterephthalate interaction which can be described as an asymmetric 3c–4e C–X–O bond with significant polarity for the Xe–O part. In addition to the Xe–O covalency, the low frequency shift of *o*-F in **1** is caused by the proximity of the "keto" oxygen of the carboxylate group to Xe^{II}. The covalent contribution in the Xe–O bond is supported by the large $^3J(^{19}F, ^{129}Xe)$ coupling of 81 Hz which is 11 Hz larger than in $[C_6F_5Xe][BF_4]$ and has a magnitude that is similar in C_6F_5XeF (82 Hz) where the covalency of Xe–F was proven by a $^1J(^{19}F, ^{129}Xe)$ coupling of 4014 Hz [6]. The ^{129}Xe NMR resonance of **1** appears to low frequency (−3857 ppm) to that of $[C_6F_5Xe][BF_4]$ (−3825 ppm). C^1 in **1** (89.2 ppm, $^1J(^{13}C, ^{129}Xe) = 168$ Hz) shows a resonance at higher frequency than in $[C_6F_5Xe][BF_4]$ (84.8 ppm, $^1J(^{13}C, ^{129}Xe) = 132$ Hz) and C_6F_5XeF (in CH_2Cl_2 at −78 °C: 86.4 ppm, $^1J(^{13}C, ^{129}Xe) = 111$ Hz) but at lower frequency relative to $(C_6F_5)_2Xe$ (in $(CD_3)_2CO$ at −60 °C: 123.2 ppm, $^1J(^{13}C, ^{129}Xe) = 315$ Hz); the latter having a symmetrical 3c–4e bond. The influence of the less usual solvents CF_3CH_2OH and $(CF_3)_2CHOH$ on the shift values of the C_6F_5Xe unit in **1** differs from that of the cation in the $[C_6F_5Xe][BF_4]$ salt (Table 1). In the latter case, the *m*-F and *p*-F resonances appear deshielded and are comparable to those in aHF solutions [4].

It is worth mentioning that all ^{19}F NMR resonances of **1** in MeCN solution at −40 °C are shifted to low frequencies relative to those in $(CF_3)_2CHOH$ solutions. This tendency may be explained by a strong interaction between the tetrafluoroterephthalate group and C_6F_5Xe moiety under basic conditions. The presence of $(CF_3)_2CHOH$ lowers the nucleophilicity of the carboxylate groups in **1**. In accordance with this assumption, the $^3J(^{19}F, ^{129}Xe)$ coupling constant in **1** increases in MeCN solution to 85 Hz and the C_6F_4 resonance of the tetrafluoroterephthalate anion becomes deshielded when changing from MeCN to CF_3CH_2OH solutions (see also the solvent influence on $[N(^nBu)_4]$ and Cs salts, Table 1)

In the Raman spectrum of **1**, the most intense vibration at 180 cm^{-1} is tentatively assigned to the Xe–C stretching mode. For

Table 1
^{19}F NMR spectral data for p-$(C_6F_5XeO(O)C)_2C_6F_4$ (**1**) and related compounds (δ in ppm, J in Hz).

Compound	Solvent	T (°C)	C_6F_5 fragment					2,3,5,6-C_6F_4 fragment	
			o-F	$^3J(^{19}F, ^{129}Xe)$	p-F	$^3J(^{19}F, ^{19}F)$	m-F	$F^{2,6}$	$F^{3,5}$
p-$(C_6F_5XeO(O)C)_2C_6F_4$	CH_3CN	−40	−128.7	85	−146.3	20	−156.6	−142.4[a]	
p-$(C_6F_5XeO(O)C)_2C_6F_4$	$(CF_3)_2CHOH/CH_3CN$[b]	−30	−127.9	81	−145.1	19	−155.8	−141.3[a]	
p-$(C_6F_5XeO(O)C)_2C_6F_4$	CF_3CH_2OH	−40	−127.2	78	−143.1	18	−154.4	−140.7	
p-$(C_6F_5XeO(O)C)_2C_6F_4$	$(CF_3)_2CHOH$	0	−128.2	77	−142.8	18	−154.0	−140.4	
$[C_6F_5Xe][BF_4]$	CH_3CN	−40	−125.5	68	−142.3	20; 5[c]	−155.1		
$[C_6F_5Xe][BF_4]$	$(CF_3)_2CHOH/CH_3CN$[b]	−30	−125.7	70	−142.3	20; 5[c]	−154.7		
$[C_6F_5Xe][BF_4]$	CF_3CH_2OH	−30	−124.8	63	−139.6	19	−152.6		
$[C_6F_5Xe][BF_4]$	$(CF_3)_2CHOH$	0	−124.6	61	−137.6	18; 6[c]	−151.0		
p-$(C_6F_5O(O)C)_2C_6F_4$	CH_3CN	−40	−152.0		−156.8	21	−161.8	−135.0	
p-$(C_6F_5O(O)C)_2C_6F_4$	$(CF_3)_2CHOH/CH_3CN$[b]	−40	−152.0		−156.6	21	−161.9	−134.7	
p-$C_6F_5O(O)CC_6F_4CO_2H$	CH_3CN	−40	−152.2		−157.0	21	−161.9	−135.8	−138.9
p-$C_6F_5O(O)CC_6F_4CO_2H$	$(CF_3)_2CHOH/CH_3CN$[b]	−40	−152.1		−157.1	21	−162.2	−135.7	−140.6
p-$((CF_3)_2HCO(O)C)_2C_6F_4$[d]	CH_3CN	24						−135.6	
p-$((CF_3)_2HCO(O)C)_2C_6F_4$[e]	$(CF_3)_2CHOH/CH_3CN$[b]	−40						−135.4	
p-$(HO_2C)_2C_6F_4$	CH_3CN	−40						−138.9	
$Cs_2[p$-$(O_2C)_2C_6F_4]$	CF_3CH_2OH	−40						−141.4	
$[N(n$-$C_4H_9)_4]_2[p$-$(O_2C)_2C_6F_4]$	CH_3CN	−40						−145.7[f]	
$[N(n$-$C_4H_9)_4]_2[p$-$(O_2C)_2C_6F_4]$	$(CF_3)_2CHOH$	0						−140.4	

[a] $\Delta\nu_{1/2}$ = 5 Hz.
[b] Mixture: 1:1 vol.
[c] $^4J(^{19}F, ^{19}F)$.
[d] $\delta(CF_3) = -72.2$ ppm.
[e] $\delta(CF_3) = -72.4$ ppm.
[f] $\Delta\nu_{1/2}$ = 2 Hz.

comparison, in $[C_6F_5Xe][BF_4]$ with a stronger C–Xe bond, this vibration was found at 205 cm^{-1} [5]. When comparing **1** with **1**·2 MeCN, no significant shift of this vibration (181 cm^{-1}) was noticed. The vibrational frequencies of **1**·2 MeCN at 2253, 2946, and 3005 are assigned to C≡N and C–H stretches, respectively.

2.4. The molecular structure of 1·4 $(CF_3)_2CHOH$

Single crystals of **1**·4 $(CF_3)_2CHOH$ were obtained from a $(CF_3)_2CHOH$/MeCN (2:1, vol) solution of **1** at −70 °C. **1**·4 $(CF_3)_2CHOH$ crystallizes in the space group $P2_1/c$ with four molecules in the unit cell (Table 2). Fig. 1 shows the important molecular parameters and the interaction between **1** and the acidic solvent molecules. The typical structural features of **1**·4 $(CF_3)_2CHOH$ are briefly compared with that of $C_6F_5XeO(O)CC_6F_5$ (no acidic alcohol was present in the crystal) [10]. Xe^{II} has a nearly linear environment (C–Xe–O: 175.0(3)°, average) in **1**·4 $(CF_3)_2CHOH$ compared with 178.1(1)° in $C_6F_5XeO(O)CC_6F_5$. The C–Xe distance in **1**·4 $(CF_3)_2CHOH$ is 2.103(4) Å (average) and should be compared with that in $C_6F_5XeO(O)CC_6F_5$ (2.122(4) Å) and that in the $[C_6F_5Xe]^+$ cation of $[C_6F_5Xe][AsF_6]$ (2.083(5) Å, average) [12]. The Xe–O distances behave opposite and were measured to be 2.503(6) Å (average) in **1**·4 $(CF_3)_2CHOH$ compared to 2.367(3) Å in $C_6F_5XeO(O)CC_6F_5$ and 2.687(9) Å in the salt $[2,6$-$C_6H_3F_2Xe][OS(O)_2CF_3]$ [13]. A special feature of **1**·4 $(CF_3)_2CHOH$ are the four contacts via hydrogen bridges of the alcohols to both types of carboxylate oxygen atoms, the “keto” and the “ester” oxygen atoms with O···O distances of 2.608(6) to 2.650(6) Å, respectively. The different distances do not correlate with both types of oxygen atoms (*vide supra*). The hydrogen bridges lower the nucleophilicities of the oxygen atoms bonded to Xe^{II} and are responsible for the differences in the molecular structures between **1**·4 $(CF_3)_2CHOH$ and $C_6F_5XeO(O)CC_6F_5$. Also, the deshielding of the C_6F_5Xe unit in the ^{19}F NMR spectra of **1** in alcohol solutions can be explained by a weaker Xe–O interaction caused by hydrogen bridges. Their influence is supported by a comparison of both types of carbon-oxygen bonds. In the carboxylate group, the C═O bonds are 1.232 and 1.228(6) and the C–O bonds 1.273 and 1.268(6) Å, respectively. These parameters are related to 1.220(3) and 1.271(4) Å in $C_6F_5XeO(O)CC_6F_5$. The dihedral angles between the carboxylate groups are 15° (average) and the dihedral angles between the C_6F_4 planes are 42° and 58° (average). The two alcohol molecules coordinated to each carboxylate group did not lie exactly in the CO_2 plane, but were positioned slightly above and below of this plane.

Table 2
Crystallographic and refinement data for p-$(C_6F_5XeO(O)C)_2C_6F_4$ (**1**)·4 $(CF_3)_2CHOH$.

Compound	p-$(C_6F_5XeO(O)C)_2C_6F_4$·4 $(CF_3)_2CHOH$
Empirical formula	$C_{20}F_{14}O_4Xe_2$·4 $C_3H_2F_6O$
Crystal size	0.26 mm × 0.21 mm × 0.08 mm
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 16.0126(8) Å b = 14.7397(8) Å c = 21.2081(11) Å β = 112.171(2)°
Volume	4635.5(4) $Å^3$
Z (molecules/unit cell)	4
Density (calculated)	2.156 g cm^{-3}
Temperature	183 ± 2 K
Radiation	Mo K_α (λ = 0.71073 Å)
F(0 0 0)	2856
Theta range for data collection	1.04–30.51°
Final R indices	R_1 = 0.0390, wR_2 = 0.0945

2.5. Attempts to use 1 as a $[C_6F_5Xe]^+$ source in a metathesis reaction

The borderline bonding situation (covalent Xe–O bond with significant polarity) in **1** prompted us to investigate the substitution of the $[p$-$(O_2C)_2C_6F_4]^{2-}$anion by two weakly coordinating singly charged anions in order to displace the C_6F_5Xe unit as cation from **1** (Eq. (4)). Thus we combined a solution of $Cs[B(C_6F_5)_4]$ in MeCN with a suspension of partially soluble **1** in MeCN.

$$p\text{–}C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5 + 2Cs[B(C_6F_5)_4] \overset{\text{MeCN}}{-/\rightarrow} 2[C_6F_5Xe][B(C_6F_5)_4] + Cs_2[p\text{–}(O_2C)_2C_6F_4]\downarrow \quad (4)$$

The desired co-product, $Cs_2[p$-$(O_2C)_2C_6F_4]$, is insoluble in MeCN at 20 °C. This fact was expected to be a driving force for the

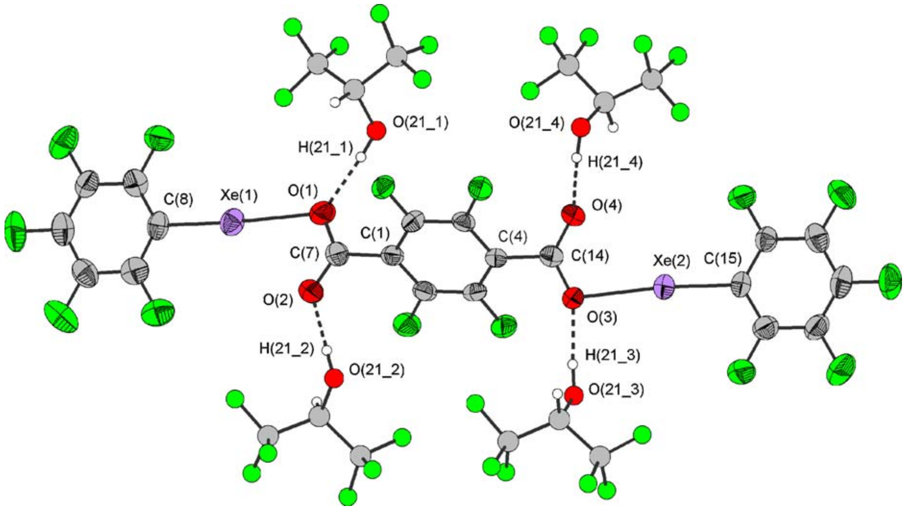

Fig. 1. Molecular structure of p-$(C_6F_5XeO(O)C)_2C_6F_4$ (**1**)·4 $(CF_3)_2CHOH$.
Selected distances (Å) and angles (°): Xe(1)–C(8) 2.101(4), Xe(2)–C(15) 2.105(5), Xe(1)–O(1) 2.495(3), Xe(2)–O(3) 2.511(4), Xe(1)- -O(2) 3.156(5), Xe(2)- -O(4) 3.120(5), O(1)–C(7) 1.273(6), O(2)–C(7) 1.232(6), O(3)–C(14) 1.268(6), O(4)–C(14) 1.228(6), O(1)···O(21_1) 2.622(6), O(2)···O(21_2) 2.649(6), O(3)···O(21_3) 2.650(6), O(4)···O(21_4) 2.608(6), C(8)–Xe(1)–O(1) 174.7(2), C(15)–Xe(2)–O(3) 175.4(2).

metathesis reaction. At −40 °C (1 h) as well as at 20 °C (5 min), no metathesis proceeded. A longer reaction time at 20 °C (18 h) was accompanied by decomposition of **1**. Thus, **1** is not a source of $[C_6F_5Xe]^+$ under basic conditions.

2.6. *Transesterification of p-$(C_6F_5O(O)C)_2C_6F_4$ to p-$((CF_3)_2CHO(O)C)_2C_6F_4$*

The dissolution of p-$(C_6F_5O(O)C)_2C_6F_4$ in a 1:1 mixture of $(CF_3)_2CHOH$/MeCN was accompanied by the complete transformation of p-$(C_6F_5O(O)C)_2C_6F_4$ into p-$((CF_3)_2CHO(O)C)_2C_6F_4$ (Eq. (5)).

$$p\text{–}(C_6F_5O(O)C)_2C_6F_4 \xrightarrow{a} p\text{–}((CF_3)_2CHO(O)C)_2C_6F_4 + 2C_6F_5OH$$

$$a = (CF_3)_2CHOH/MeCN\,(1:1,\ \mathrm{vol}) \qquad (5)$$

The acidic property of the alcohol is responsible for this reaction. Additionally, the transesterification may be supported by the interaction of MeCN with the electrophilic carbonyl centre.

3. Experimental

3.1. *Instrumentation*

The NMR spectra were recorded on a Bruker spectrometer AVANCE 300 (^1H at 300.13 MHz, ^{13}C at 75.46 MHz, ^{19}F at 282.40 MHz, and ^{129}Xe at 83.46 MHz). The chemical shifts are referenced to TMS (^1H, ^{13}C), CCl_3F (^{19}F) [with C_6F_6 as a secondary reference, $\delta = -162.9$ ppm], and $XeOF_4$ (^{129}Xe) [with XeF_2 as a secondary reference, XeF_2/MeCN/24 °C at infinite dilution, $\delta = -1813.28$ ppm] [14]. Raman spectra were measured in FEP or glass capillaries on a Bruker RFS 100/S spectrometer and IR spectra as films between KBr plates on a Nicolet Impact 400 spectrometer. DSC analyses were performed using a Netzsch 204 Phoenix instrument equipped with a CC220 controller; a TASC414/3A microprocessor system, and a personal computer. The solid samples (2–7 mg) were weighed inside a glove box into aluminum pans which were closed by a pierced aluminum lid. The temperature difference between the sample and the empty reference pan with pierced lid was measured choosing a temperature program of 10 K/min. The raw data were processed using the Netzsch Proteus Software Version 4.2.

3.2. *Crystal structure determination*

X-ray diffraction data were collected at 183 ± 2 K using a diffractometer measurement device with a Siemens SMART three-axis goniometer and an APEX II area detector system. Crystal structure solution by Direct Methods and refinement on *F*2 were performed using the Bruker AXS SHELXTL software suite Version 6.12 after data reduction, and empirical absorption correction was performed using the Bruker AXS SAINT program Version 6.0. For crystallographic and refinement details see Table 2.

The structure of **1**·4 $(CF_3)_2CHOH$ was pseudo orthorhombic twinned by the twin law 1 0 0 0 −1 0 − 1 0 −1. Crystal structure data have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Enquiries for data can be directed to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K., CB2 1EZ or (e-mail) deposit@ccdc.cam.ac.uk or fax: +44 0 1223 336033. Any requests sent to the Cambridge Crystallographic Data Centre for this material should quote the full literature citation and the reference number CCDC 735093.

3.3. *Solvents and starting materials*

1,1,1,3,3-pentafluorobutane (PFB) (Solvay Fluor und Derivate GmbH) was dried over molecular sieves (3 Å). CH_3CN (KMF) was refluxed and distilled from $KMnO_4$ and repeatedly refluxed and distilled from P_4O_{10}. CH_2Cl_2 (KMF) was treated in sequence with conc. H_2SO_4, $Na_2CO_{3(aq)}$, and H_2O and finally refluxed and distilled from P_4O_{10} and stored over molecular sieves type 3 Å. CF_3CH_2OH and $(CF_3)_2CHOH$ were distilled and stored over molecular sieves (3 Å). $[C_6F_5Xe][BF_4]$ [15] $[C_6F_5Xe][B(CF_3)_4]$ [4], and $[C_6F_5Xe{\cdot}CH_3CN][B(C_6F_5)_4]$ [4] were prepared using literature protocols. All manipulations with XeF_2 and xenonium salts were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment under an atmosphere of dry argon. The glove box was operated with dry argon ($H_2O < 1$ ppm). $Cs_2[p\text{-}(O_2C)_2C_6F_4]$ and $[N^nBu_4]_2[p\text{-}(O_2C)_2C_6F_4]$ were obtained by neutralization of the corresponding acid in H_2O.

3.3.1. *Analytical data of the ammonium salt*

$[N^nBu_4]_2[p\text{-}(O_2C)_2C_6F_4]$ (ref. [16] reports no experimental or analytical details).

DSC: T_{onset} 158 °C (endothermic effect), T_{onset} at 184 °C (endothermic effect followed by an exothermic). The visual melting point at 160 °C was accompanied by partial decarboxylation: formation of $[2,3,5,6\text{-}C_6HF_4CO_2]^-$, 2,3,5,6-$C_6H_2F_4$, and $N(^nBu)_3$ (^1H, ^{19}F).

Raman (20 °C): 120 (19), 164 (9), 253 (21), 313 (11), 409 (10), 442 (13), 501 (25), 753 (7), 778 (3), 791 (3), 800 (2), 878 (11), 907 (15), 986 (2), 1010 (3), 1036 (5), 1055 (14), 1112 (4), 1134 (11), 1150 (7), 1279 (3), 1329 (26), 1374 (6), 1452 (30), 1469 (20), 1487 (12), 1643 (28), 2712 (2), 2734 (4), 2749 (3), 2874 (85), 2922 (94), 2937 (100), 2962 (80) cm^{-1}.

^{13}C NMR (MeCN, 24 °C) δ (ppm): 161.1 (s, $\Delta\nu_{1/2}$ = 3 Hz, CO_2), 141.8 (dm, ^1J(C, F = 245 Hz, C_6F_4, $C^{2,3,5,6}$), 121.9 (m, C_6F_4, $C^{1,4}$), 58.5 (tm, $^1J(C^1, H^1)$ = 143 Hz, $^nC_4H_9$, C^1), 23.8 (tm, $^1J(C^2, H^2)$ = 125 Hz, $^nC_4H_9$, C^2), 19.6 (tm, $^1J(C^3, H^3)$ = 124 Hz, $^nC_4H_9$, C^3);

13.3 (qtt, $^1J(C^4, H^4)$ = 125 Hz, $^3J(C^4, H^3)$ = 4 Hz, $^4J(C^4, H^2)$ = 4 Hz, $^nC_4H_9$, C^4).

^{19}F NMR: see Table 1

3.4. Synthesis of *p*-$C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5\cdot 2$ MeCN (**1**·2 MeCN) in MeCN

$[C_6F_5Xe][BF_4]$ (203 mg, 0.528 mmol) and $[N(^nBu)_4]_2[p\text{-}(O_2C)_2C_6F_4]$ (177 mg, 0.245 mmol) were combined in a FEP trap (8 mm i.d.) and cooled to −40 °C. MeCN (1.5 mL,−40 °C) was added under vigorous stirring. In concert with dissolution of the starting materials, precipitation of product **1** resulted. After 2 h, the suspension was centrifuged at −35 °C. The mother liquor was separated, the solid was suspended and stirred in MeCN (0.5 mL,−45 °C), and the solution phase was separated again. This washing procedure was repeated (23 times) till $[N(^nBu)_4]^+$ and $[BF_4]^-$ ions could not be detected in the NMR spectra (^1H, ^{19}F). The purified solid product was dried under vacuum (4×10^{-2} hPa) for 6 h at −35 to −25 °C (151 mg, 0.165 mmol, 67%), transferred into the glove box and divided in portions in FEP tubes (3.5 mm i.d.). This procedure at 20 °C took less than 30 min. All samples were stored at −70 °C. One sample was checked by Raman spectroscopy and showed that MeCN was still present (ν(C–H) 2946, ν(C≡N) 2253 cm^{-1}). This sample was again pumped under vacuum at −35 to −25 °C for 33 h (no decrease in MeCN) and at 0 °C for 20 h (only a small reduction of MeCN). After 15 h of evacuation at 20 °C, MeCN was removed but significant changes in the Raman spectrum indicated partial decomposition. After storage for an additional 3 h at 20 °C, the composition of the sample was checked by ^{19}F NMR spectroscopy in a $(CF_3)_2CHOH$/MeCN mixture (1:1, vol, −40 °C) (**1** (83%), *p*-$C_6F_5O(O)CC_6F_4CO_2H$ (13%), *p*-$(C_6F_5O(O)C)_2C_6F_4$ (4%), C_6F_5H (3%) and five unknown products ($(CF_3)_2CXY$ derived from the solvent (5%)).

Another sample (15 mg, 16 μmol) was used to determine the ratio, **1**:MeCN, by comparison of the integrated intensities with $C_6H_5CF_3$ (5 μL) from the ^1H and ^{19}F NMR spectra in a CF_3CH_2OH (300 μL) solution at −40 °C. The ratio **1**:MeCN was calculated to be 1:1.9. The ideal value for this product is **1**·2 MeCN.

1·2 MeCN: solubility in MeCN at −40 °C: 1.48 μmol/mL

DSC: T_{onset} 89 °C (exothermic dec.), T_{onset} 141 °C (endothermic effect), T_{onset} 173 °C (weakly exothermic effect), T_{onset} 219 °C (endothermic effect).

Raman (−40 °C): 136 (3), 181 (100), 253 (2), 277 (12), 290 (12), 347 (27), 356 (23), 386 (10), 408 (5), 442 (8), 490 (57), 509 (11), 520 (20), 766 (57), 784 (30), 918 (1), 1012 (2), 1080 (4), 1082 (19), 1280 (10), 1333 (2), 1388 (17), 1407 (30), 1617 (34), 1658 (4), 2253 (7), 2946 (10), 3005 (1) cm^{-1}.

^{19}F NMR: see Table 1

3.5. Removal of MeCN from **1**·2 MeCN by extraction with CH_2Cl_2

Freshly prepared **1**·2 MeCN from $[C_6F_5Xe][BF_4]$ (21.9 mg, 56.9 μmol) and $[N(^nBu)_4]_2[p\text{-}(O_2C)_2C_6F_4]$ (18.7 mg, 25.8 μmol) in 500 μL MeCN at −40 °C was washed free of $[N(^nBu)_4][BF_4]$ with MeCN (three times 500 μL,−40 °C). The product was washed seven times at −78 °C with CH_2Cl_2 (500 μL each) with vigorous stirring and finally dried in vacuum (4×10^{-2} hPa, 0 °C for 3 h). Raman and NMR spectra confirmed the absence of MeCN and CH_2Cl_2. Yield of **1**: 10 mg, 12 μmol, 47%. The solubility of **1** showed the following trend: $(CF_3)_2CHOH$ (mp −4 °C) > CF_3CH_2OH > MeCN. Solvent mixtures of $(CF_3)_2CHOH$/MeCN (2:1, mp −83 °C or 1:1, mp −86 °C or 1:2, mp −67 °C) allowed the formation of solutions of **1** having satisfactory solubilities at low temperatures. For physical and spectroscopic data of **1**, see Section 3.6.1.

3.6. Synthesis of *p*-$C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5$ (**1**) in CH_2Cl_2

$[N(^nBu)_4]_2[p\text{-}(O_2C)_2C_6F_4]$ (9.71 mg, 13.5 μmol) in a FEP trap (3.5 mm i.d.) was dissolved in CH_2Cl_2 (300 μL, −78 °C). This cold solution was added to the suspension of $[C_6F_5Xe][B(CF_3)_4]$ (16.6 mg, 28.4 μmol) in CH_2Cl_2 (300 μL, −78 °C) and vigorously mixed. After 45 min, the suspension was centrifuged (−78 °C) and the mother liquor was separated. Solid product **1** was washed nine times with CH_2Cl_2 (500 μL aliquots at −40 °C) and four times with PFB (350 μL aliquots at −30 °C). The last washing still contained a trace amount of $[C_6F_5Xe][B(CF_3)_4]$ (^{19}F NMR). Therefore, washing (four times) with MeCN (250 μL aliquots at −30 °C) with a high solubility for $[C_6F_5Xe][B(CF_3)_4]$ followed. The suspension was centrifuged at −29 °C. The last MeCN washing contained no $[C_6F_5Xe][B(CF_3)_4]$. After repeated treatment with CH_2Cl_2 the solid product was dried in vacuum (4×10^{-2} hPa, ≤−25 °C and 0 °C for 1.5 h at each temperature). The absence of MeCN and other solvents was proven by Raman and NMR spectroscopy.

In a similar procedure, **1** was prepared from $[C_6F_5Xe\cdot NCMe][B(C_6F_5)_4]$ and $[N(^nBu)_4]_2[p\text{-}(O_2C)_2C_6F_4]$.

3.6.1. *p*-$C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5$ (**1**).

DSC: T_{onset} 118 °C (exothermic dec.), T_{onset} 145 °C (endothermic effect).

Raman (20 °C): 138 (2), 180 (100), 226 (2), 278 (11), 292 (5), 347 (29), 383 (5), 410 (6), 440 (5), 488 (50), 503 (6), 606 (1), 720 (3), 732 (9), 764 (29), 782 (30), 1017 (1), 1071 (2), 1083 (9), 1284 (7), 1336 (2), 1371 (2), 1387 (11), 1409 (14), 1625 (15), 1641 (7) cm^{-1}.

^{13}C and $^{13}C\{^{19}F\}$ NMR $(CF_3)_2CHOH/CH_3CN$ (1:1, vol, −30 °C) δ (ppm): 145.4 (dm, $^1J(C^4, F^4)$ = 260 Hz, C^4), 144.0 (dm, $^1J(C^2, F^2; C^6, F^6)$ = 252 Hz, $C^{2,6}$), 139.0 (dm, $^1J(C^3, F^3; C^5, F^5)$ = 258 Hz, $C^{3,5}$), 89.2 (m, $^1J(C^1, {}^{129}Xe)$ = 168 Hz, C^1), 166.0 (s, $\Delta\nu_{1/2}$ = 4 Hz, CO_2), 144.9 (dm, ^1J(C′, F′) = 252 Hz, C_6F_4, $C^{2',3',5',6'}$), 125.8 (m, C_6F_4, $C^{1',4'}$).

^{129}Xe NMR ($(CF_3)_2CHOH/CH_3CN$ (1:1, vol, −30 °C) δ (ppm): −3857 (t, $^3J(Xe\text{–}F^{2,6})$ = 81 Hz).

^{19}F NMR see Table 1.

3.7. Synthesis of *p*-$C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5$ (**1**) in CF_3CH_2OH

Due to the slow dissolution in cold CF_3CH_2OH $[C_6F_5Xe][BF_4]$ (19.8 mg, 51.5 μmol) was dissolved in 500 μL of CF_3CH_2OH at 20 °C within 5 min and cooled to −40 °C before a solution of $Cs_2[(p\text{-}O_2C)_2C_6F_4]$ (13.1 mg, 26.0 μmol) in CF_3CH_2OH (1 mL, −43 °C) was added. The reaction mixture was stirred for 3 h at −35 to −40 °C in a FEP trap (8 mm i.d.). Despite the fact that no precipitation of $Cs[BF_4]$ could be detected in CF_3CH_2OH, the mixture was centrifuged (−35 °C) several times. Hints of small amounts of transparent solid were observed. After 5 h, a sample of the upper one third of volume was taken for ^{19}F NMR analysis and proved the absence of $[BF_4]^-$ in this part. A significant amount of C_6F_5H (38%) besides **1** was found. The fact that the ratio C_6F_5:C_6F_4 of 1.66 deviated from 2.0 implies that pure **1** cannot be differentiated from *p*-$C_6F_5XeO(O)CC_6F_4CO_2H$ in CF_3CH_2OH. Finally, the mother liquor was separated and evaporated at <−20 C,

4×10^{-2} hPa and the solid residue was suspended in MeCN and showed the presence of $[BF_4]^-$ (^{19}F NMR). It should be noted that in all experiments our attempts to separate the very fine particles of $Cs[BF_4]$ failed even with a 50 μm Teflon frit.

3.8. Thermal behavior of **1** *and* **1**·*2 MeCN, neat and in solution*

A sample of **1** (10.0 mg, 12 μmol) in a FEP trap (3.5 mm i.d.) was stored inside a glove box at 20 °C. The progress of the decomposition was followed by Raman spectroscopy (ν(C–Xe) at 180 cm^{-1}). After 1 d, no decomposition was detected. After 10 d, the majority of **1** was decomposed. After storage of a sample of **1**·2 MeCN (8.3 mg, 9.1 μmol) in a FEP trap (3.5 mm i.d.) inside a glove box at 20 °C over 14 d, a solid white decomposition product resulted which was soluble in *n*-pentane. ^{19}F NMR confirmed that p-$(C_6F_5O(O)C)_2C_6F_4$ was formed as the only product in the residue.

The thermal stability of **1** in solution was monitored in MeCN, CF_3CH_2OH, $(CF_3)_2CHOH$, and $(CF_3)_2CHOH$/MeCN (1:1, vol). After 5.5 h at 20 °C, the MeCN solution of **1** showed the following composition related to the C_6F_4 fragment: C_6F_5H (79%), $C_6F_5O(O)CC_6F_4CO_2H$ (43%), p-$(HO_2C)_2C_6F_4$ (30%), p-$(C_6F_5O(O)C)_2C_6F_4$ (24%) $[p\text{-}(O_2C)_2C_6F_4]^{2-}$(3%). **1** was partially decomposed in CF_3CH_2OH at −40 °C after 20 min: C_6F_5H (20%). In the $(CF_3)_2CHOH$ solution of **1** after 20 min at 0 °C C_6F_5H (6%) was detected. A satisfactory stability of **1** was found in a $(CF_3)_2CHOH$/MeCN mixture (1:1). After 21 h at −30 °C only 3% of C_6F_5H was formed.

3.8.1. p-$(C_6F_5O(O)C)_2C_6F_4$ [17]

DSC: T_{onset} 141 °C (endothermic melting), T_{onset} 181 °C (weakly exothermic dec.), T_{onset} 250 °C (endothermic boiling).

Raman (20 °C): 147 (4), 156 (3), 253 (5), 274 (11), 280 (10), 313 (12), 330 (5), 379 (55), 394 (37), 402 (43), 440 (53), 476 (21), 506 (70), 571 (100), 636 (4), 662 (5), 715 (3), 769 (2), 779 (3), 828 (11), 950 (5), 1014 (4), 1150 (4), 1158 (3), 1227 (25), 1237 (18), 1412 (56), 1471 (6), 1656 (70), 1769 (48) cm^{-1}.

IR (20 °C): 638 (vw), 667 (vw), 713 (vw), 755 (vw), 772 (vw), 793 (vw), 895 (vw), 984 (s), 996 (s), 1007 (s), 1123 (m), 1149 (m), 1261 (vw), 1314 (m), 1335 (s), 1494 (s), 1520 (vs), 1682 (w), 1767 (s) cm^{-1}.

^{13}C NMR (CH_2Cl_2, 24 °C) δ (ppm): 145.9 (dm, $^1J(C^2, F^2; C^6, F^6) = 266$ Hz, C_6F_5, $C^{2,6}$), 140.8 (dtt, $^1J(C^4, F^4) = 255$ Hz, $^2J(C^4, F^{3,5}) = 14$ Hz, $^3J(C^4, F^{2,6}) = 4$ Hz, C_6F_5, C^4), 138.5 (dm, $^1J(C^3, F^3; C^5, F^5) = 252$ Hz, C_6F_5, $C^{3,5}$), 114.0 (m, C_6F_5, C^1), 155.1 (s, $\Delta\nu_{1/2} = 4$ Hz, CO_2), 141.4 (dm, $^1J(C'\text{-}F') = 253$ Hz, C_6F_4, $C^{2',3',5',6'}$), 124.4 (m, C_6F_4, $C^{1',4'}$).

^{19}F NMR: see Table 1.

3.9. Attempt to use **1** *as a $[C_6F_5Xe]^+$ source in a metathesis reaction*

In a FEP trap (3.5 mm i.d.) a solution (200 μL, −40 °C) of $Cs[B(C_6F_5)_4]$ (30.9 mg, 38.1 μmol) was added to partially soluble **1** (16.0 mg, 19.2 μmol) in MeCN (300 μL, −40 °C). After 1 h and efficient mixing at −40 °C no reaction could be detected. After 5 min at 20 °C 77% of **1** was dissolved but no conversion was observed. After 18 h decomposition of **1** dominated and after 48 h at 20 °C the decomposition of **1** was completed. No $[C_6F_5Xe][B(C_6F_5)_4]$ was detected at any time. The composition of the final solution is related to the sum of C_6F_4 groups: $[B(C_6F_5)_4]^-$ (200%), p-$(C_6F_5O(O)C)_2C_6F_4$ (83%), p-$C_6F_5O(O)CC_6F_4CO_2H$ (12%), p-$(HO_2C)_2C_6F_4$ (5%), C_6F_5H (6%).

3.10. Transesterification of p-$(C_6F_5O(O)C)_2C_6F_4$ into p-$((CF_3)_2CHO(O)C)_2C_6F_4$

A sample of p-$(C_6F_5O(O)C)_2C_6F_4$ (5.0 mg, 8.8 μmol) dissolved in a 1:1 mixture of $(CF_3)_2CHOH$/MeCN (300 μL) showed after 30 min (^{19}F NMR) complete conversion into p-$((CF_3)_2CHO(O)C)_2C_6F_4$ and C_6F_5OH (−163.2 (*o*-F), −166.4 (*m*-F), −173.4 (*p*-F)).

3.10.1. p-$((CF_3)_2CHO)_2C_6F_4$

IR (20 °C): 690 (m), 750 (w), 760 (vw, sh), 799 (vw, br), 859 (w), 906 (m), 930 (s), 995 (s), 1072 (s), 1108 (vs), 1157 (m), 1205 (vs), 1247 (m, sh), 1260 (s), 1282 (s), 1364 (m), 1380 (m), 1487 (s), 1511 (w), 1774 (vs) cm^{-1}.

^{19}F NMR: see Table 1.

4. Conclusions

The nucleophilicity of the tetrafluoroterephthalate anion is high enough to bind two electrophilic $[C_6F_5Xe]^+$ cations forming the molecular compound p-$C_6F_5XeO(O)CC_6F_4C(O)OXeC_6F_5$ (**1**). When the synthesis of **1** was performed in MeCN, two solvent molecules were co-crystallized without coordination to Xe^{II}. Crystals were obtained from $(CF_3)_2CHOH$/MeCN (1:1, vol) solutions that had four $(CF_3)_2CHOH$ molecules bonded by hydrogen bridges to the four oxygen atoms in **1**. Solvent coordination makes the carboxylate groups less nucleophilic, shifting the Xe–O bond polarity towards the ionic side. The polarity of the Xe–O bond in **1** is not itself high enough to allow metathesis of the tetrafluoroterephthalate anion by two weakly coordinating $[B(C_6F_5)_4]^-$anions under basic conditions. **1** is an intrinsically unstable compound and eliminates two Xe^0 when stored at ambient temperature forming the diester, p-$C_6F_5O(O)CC_6F_4C(O)OC_6F_5$. The latter underwent rapid transesterification at 20 °C when dissolved in $(CF_3)_2CHOH$/MeCN.

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