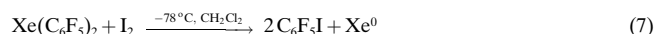


The symmetric C-Xe-C molecule **2** as well as the asymmetric molecules **1** and **3** are soluble in polar, weak-coordinating solvents, such as CH₂Cl₂. When dissolved in basic, strongly coordinating MeCN compound **1** shows no heterolysis to the [C₆F₅Xe]⁺ and F[−] ions. Compounds **1–3** are unstable at room temperature and even at −78 °C their CH₂Cl₂ solutions decompose within a few weeks. The products of decomposition point to homolytic breakage of bonds followed by radical recombinations and radical attacks on the solvent.

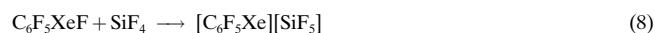
Both electronegative aryl groups in **2** show a relatively high anionic character. In the superacidic solvent aHF (anhydrous HF) one of the aryl groups can be quantitatively split off through electrophilic attack forming equimolar amounts of [C₆F₅Xe]⁺ and C₆F₅H [Eq. (6)]:



In the presence of I₂ compound **2** behaves as an arylating agent [Eq. (7)]:



The reactions of **3** with I₂ or HF proceed in a more complex manner because of the inequivalent C–Xe bonds. The reaction of the C₆F₅ group in **3** was monitored by ¹⁹F NMR spectroscopy and the products C₆F₅I, C₆F₅H, and C₆F₅CN (5:3:1) or [C₆F₅Xe]⁺, C₆F₅H, and C₆F₅CN (4:1:3) were detected. As a result of its good fluoride donor ability **1** reacts even with weak Lewis acids such as SiF₄ or C₆F₅BF₂ [Eqs. (8), (9)]:



The constitution of **1–3** was confirmed by heteronuclear NMR spectroscopy (¹⁹F, ¹²⁹Xe, ¹³C, ¹⁵N; Table 1) in CH₂Cl₂ solutions. The coupling constants were determined in some cases by ¹⁹F- or ¹²⁹Xe-decoupling experiments. The ¹²⁹Xe NMR spectrum of **1** shows the large ¹J_{Xe,F} (doublet, 4014 Hz) and the smaller ³J_{Xe,o-F} coupling (triplet, 82 Hz) that confirm unambiguously the constitution of **1**. In the ¹²⁹Xe NMR spectrum of **2** the resonance signal at δ = −4152 (the lowest frequency of a Xe^{II} species!) appears as a not fully resolved multiplet. The accompanying o-F signal at δ = −133.05 shows ¹²⁹Xe satellites of appropriate intensity. The ³J_{F,Xe} coupling is determined (by using selective m-F decoupling) to be 43 Hz. The ¹²⁹Xe NMR spectrum of C₆F₅XeCN shows a triplet (³J_{Xe,F} = 86 Hz) at δ = −3883.2. In the labeled compound C₆F₅Xe¹³CN (Figure 1) an additional doublet (¹J_{Xe,C} = 1060 Hz) is observed. In the labeled compound C₆F₅XeC¹⁵N the ¹²⁹Xe NMR resonance signal (¹⁹F decoupled) appears as a doublet (²J_{Xe,N} = 21 Hz).

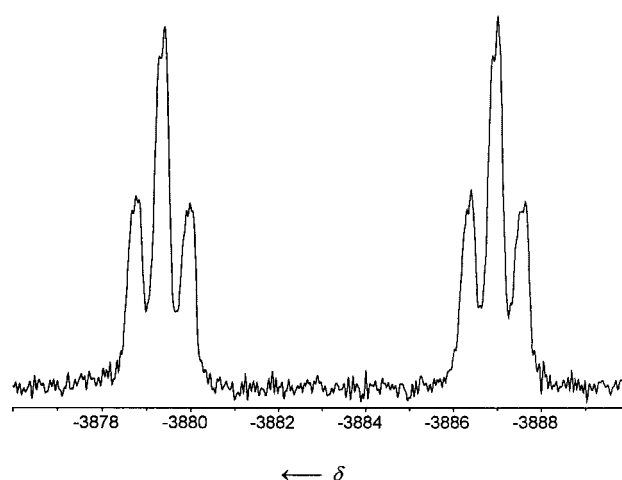


Figure 1. ¹²⁹Xe NMR spectrum of C₆F₅Xe¹³CN in CD₂Cl₂ at −78 °C.

Table 1. NMR spectroscopic characterization of compounds **1–3**[a].

¹⁹ F NMR		δ(o-F)	δ(p-F)	δ(m-F)	δ(Xe-F)	³ J _{p-F}	³ J _{F,Xe}	⁴ J _{F,Xe-F}	¹ J _{F,Xe}
RXeF	1	−129.35	−146.87	−156.49	−3.50 ^[b]	20	81 ^[c]	19 ^[c]	4010
RXeR	2	−133.05	−154.14	−159.04		21	43 ^[c]		
RXeCN	3	−131.54	−147.50	−156.39		21	87		
¹³ C[¹⁹ F] NMR		δC(1)	δC(2,6)	δC(3,5)	δC(4)	¹ J _{C,Xe}	² J _{C(1),o-F}	² J _{C,Xe-F}	³ J _{C,Xe-F}
RXeF	1	86.35	143.90	137.14	143.09	111 ^[d]	28	115 ^[d]	ca. 6 ^[c]
RXeR	2	122.59	143.01	136.31	140.64				
RXeCN	3 ^[e]	103.07	143.11	137.10	142.82	66			
¹²⁹ Xe		Xe				³ J _{Xe,F}	¹ J _{Xe,F}		
RXeF	1	−3789.2				82	4014		
RXeR	2	−4152 ^[f]							
RXeCN	3	−3883.2				86			
selected δ and J-values of the labeled compound 3 :									
¹³ C		δCN				¹ J _{CN,Xe}	² J _{CN,C(1)}		
RXe ¹³ CN		125.68				1060	142		
¹⁵ N		δCN				² J _{N,Xe}			
RXeC ¹⁵ N		123.7				22			

[a] R = C₆F₅. The NMR measurements proceeded in FEP sample tube liners (FEP = tetrafluoromethylene hexafluoropropylene copolymer) in CD₂Cl₂ at −78 °C with a Bruker AVANCE-DRX-500 spectrometer. The absolute values of the coupling constants J in Hz. The ¹⁹F, ¹²⁹Xe, ¹³C, and ¹⁵N chemical shift values are relative to the standards C₆F₆ (δ(CCl₃F) = −162.9 ppm), XeOF₄ (24 °C), TMS, and CD₃NO₂ (24 °C), respectively, at the corresponding measurement temperature. [b] s, br, τ_{1/2} becomes smaller after addition of F[−] ions.^[11] [c] From ¹⁹F-decoupling experiments. [d] From insensitive nuclei enhancement by polarization transfer (INEPT) experiments. [e] δ(CN) = 125.22. [f] m, τ_{1/2} ≈ 150 Hz.

Table 2. Calculated (Gaussian 94, RHF, LANL2DZ) geometric parameters and charges (Mulliken) of C_6F_5Xe-Z molecules^[a].

C_6F_5Xe-Z	Molecule	Sym.	Selected geometric parameters ^[b]			Selected Mulliken charges			
			C(1)-Xe	Xe-Z	C(2)-C(1)-C(6)	Xe	C_6F_5	C(1)	Z
C_6F_5Xe-F	1	C_s	2.20	2.13	117.7	1.148	-0.415	-1.001	-0.733
$C_6F_5Xe-C_6F_5$	2	C_1	2.34	2.34	117.4	0.980	-0.490	-0.687	-0.490
C_6F_5Xe-CN	3	C_s	2.24	2.38	118.1	0.967	-0.403	-0.853	-0.564 ^[c]
for comparison see ref [12]									
$C_6F_5Xe \cdots F-AsF_5$		$\approx C_s$	2.12	2.56	121.3	1.083	-0.134	-1.032	-0.948
$[C_6F_5Xe]^+$		C_s	2.16	—	122.7	0.886	0.114	-0.870	—
$FXeF$		$D_{\infty h}$	—	2.03	—	1.306	—	—	-0.653

[a] Z = second ligand bound to Xe^{II} ; [b] in [Å] or [°], respectively; [c] Mulliken charges of C in the CN ligand: -0.466.

The results of ab initio calculations for **1–3** show the following sequence of C-Xe distances: **2** > **3** > **1**, thus opposite to the sequence of Mulliken charges of the ligand Z in C_6F_5XeZ (Table 2). The comparison of data for **1** and $C_6F_5Xe \cdots FAsF_5$ ^[12] elucidates clearly the change when going from the asymmetric hypervalent C-Xe-F bond to a significant C-Xe $\cdots$ F contact: the negative charge on Z gets closer to -1 whereas the negative charge of the C_6F_5 group decreases significantly. The high anionic character of the C_6F_5 group in **1–3** agrees with the observed reactivities towards electrophiles and explains the lower-frequency chemical shifts of the p-F atom compared to $[C_6F_5Xe]^+$.

Experimental Section

1: A cold solution of $[NMe_4]F$ (25 mg, 0.27 mmol) in CH_2Cl_2 (1 mL) was added to a suspension of $[C_6F_5Xe][AsF_6]$ (131 mg, 0.27 mmol) in CH_2Cl_2 (1.5 mL) at $-78^\circ C$ in an 8 mm FEP trap. The suspension was stirred over 2 days at $-78^\circ C$ until all the fluoride was consumed. The mother liquor was separated from solid $[NMe_4][AsF_6]$ and the quantity of **1** was determined (^{19}F NMR): 0.19 mmol, 70%. The other reactions were usually performed directly with the cold solutions of **1**. By evaporating CH_2Cl_2 at 10^{-2} hPa/ $\leq -55^\circ C$ and later drying at $\leq -40^\circ C$ **1** was obtained as a colorless solid, which after warming to $20^\circ C$ decomposed totally within 4 h. In CH_2Cl_2 solution noticeable decomposition proceeded above $-30^\circ C$ with the formation of C_6F_5H and traces of C_6F_5Cl .

2: A cold solution of $Cd(C_6F_5)_2$ (17 mg, 0.04 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of **1** (0.08 mmol) in CH_2Cl_2 (1.5 mL) at $-78^\circ C$. After 5 min of stirring CdF_2 precipitated. The reaction was complete (^{19}F NMR) after further 10 min. The mother liquor was collected. In addition to **2** (0.06 mmol, 75%) the solution contained C_6F_5H (4 μ mol) and $(C_6F_5)_2$ (2 μ mol). The isolation of solid **2** was achieved as described for **1**. Solid **2** decomposes completely at room temperature within 1 h and in CH_2Cl_2 solution at $-40^\circ C$ within 9 h [$C_6F_5H:(C_6F_5)_2 = 1:0.1$].

3: A cold solution of Me_3SiCN (14 μ L, 0.10 mmol; or the labeled ^{13}CN and $C^{15}N$ derivatives) in CH_2Cl_2 (0.5 mL) was added to a solution of **1** (0.10 mmol) and CH_2Cl_2 (1.5 mL) at $-78^\circ C$ and stirred. After 5 min the reaction was complete (^{19}F NMR: quantitative reaction) giving a 1:1 mixture of **3** and Me_3SiF . CH_2Cl_2 and Me_3SiF were distilled at $\leq -55^\circ C/10^{-2}$ hPa and the white solid product was dried at $\leq -40^\circ C/10^{-2}$ hPa. The solid spontaneously decomposed during the rapid warming to room temperature. CH_2Cl_2 solutions of **3** decomposed completely at $-40^\circ C$ within 2 h with the formation of C_6F_5CN and C_6F_5H (4:1).

Checking the purity of the cold solid products after dissolution in CH_2Cl_2 at $-78^\circ C$ showed in the case of **1** and **2** degrees of decomposition of up to 10% and for the thermally more sensitive product **3** up to 30%.

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An Enantiospecific Synthesis of the Potent Immunosuppressant FR901483**

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Bond formations induced by phenol oxidations have a rich history in organic chemistry. The influential two-step synthesis of usnic acid by Sir Derek Barton and co-workers^[1] followed a set of simple rules that provided guidelines for rationalizing the course of oxidative phenolic radical couplings occurring in the biogeneses of a number of natural products.^[2] We were

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