

# Reviews

## Preparation and Reactivity of Compounds Containing a Carbon–Xenon Bond

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The chemistry of carbon–xenon compounds is one of the newest in the field of organo-element chemistry. The specific character of carbon–xenon chemistry can be ascribed to the fact that in all Xe<sup>II</sup> and Xe<sup>IV</sup> compounds hypervalent bonds—symmetrical or asymmetrical—with a high partial positive charge on Xe are present. Different from the class of high-oxidation-state organometallic derivatives of d metals, C–Xe compounds have low coordination numbers and, additionally, contain three or two lone electron pairs. It is the intent of this review to present the still limited number of synthetic approaches to C–Xe compounds and to organize their presently known reactivities into categories. It is hoped that C–Xe compounds can be introduced in the future as precursors in synthetic organic and organo-element chemistry.

### I. Introduction

This review covers the preparative chemistry of the organic compounds of xenon(II) and -(IV). Consequently, C–Xe chemistry in the gas phase<sup>1</sup> and in the matrix<sup>2</sup> is excluded, as well as the formation of C–Xe species by radiochemical methods<sup>3</sup> ( $\beta^-$  decay of C–<sup>131</sup>I compounds).

When in 1962 the paradigm of the inertness of noble gases had been overcome by the discovery of the first Xe(II) compound by Bartlett,<sup>4</sup> an intensive research in noble-gas chemistry was initiated. A result of this activity was the early discovery of the binary xenon fluorides XeF<sub>2</sub>, XeF<sub>4</sub>, and XeF<sub>6</sub>, which are directly accessible by reactions of the elements. On the basis of reactions of these fluorides, bonds of xenon to oxygen, nitrogen and xenon were unambiguously realized.<sup>5–7</sup> The first compounds containing a C–Xe<sup>II</sup> bond were reported in 1989.<sup>8,9</sup> Since then a wide variety of orga-

noxenon(II) derivatives containing a relatively wide range of organic substituents have been prepared. In 2000 the first C–Xe<sup>IV</sup> compound was reported.<sup>10</sup>

An early review in 1993<sup>11</sup> dealt only with the beginnings of C–Xe chemistry, and the 1993 review of Zhdankin<sup>12</sup> focused comprehensively on the numerous attempts to realize carbon–xenon bonds. Thus, it is useful to review the new developments in this active area at the present time.

**Properties of XeF<sub>2</sub> and XeF<sub>4</sub> and the Related Cations [XeF]<sup>+</sup> and [XeF<sub>3</sub>]<sup>+</sup> with Relevance for the Formation of C–Xe Bonds.** The bond between xenon and the fluorine atoms in XeF<sub>2</sub> and XeF<sub>4</sub> is best described in terms of MO theory:<sup>13</sup> e.g., for XeF<sub>2</sub> as a 3c–4e bond. This triad usually is described as a hypervalent bond.<sup>14</sup> Typical characteristics of such hypervalent bond triads are the strongly polar Xe–F bond with a weak covalent component (formal bond order 0.5) and a distinctly electrostatic component. Overall, XeF<sub>2</sub>

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and XeF<sub>4</sub> have no permanent dipole moment. Despite the high opposite partial charges on Xe and F, there is no intermolecular interaction in crystalline XeF<sub>2</sub><sup>15</sup> (shortest intermolecular distance Xe...F = 3.42 Å) and there are only very weak ones in crystalline XeF<sub>4</sub><sup>16</sup> (>3.22 Å; the sum of van der Waals radii of Xe and F is 3.47 Å).<sup>17</sup>

Xenon difluoride shows no tendency to form stable adducts with nucleophiles, even with the fluoride anion. The absence of <sup>18</sup>[F]–<sup>19</sup>[F] fluorine exchange under neutral or basic conditions in the system (Xe<sup>19</sup>F<sub>2</sub> + <sup>18</sup>[F]<sup>–</sup>)<sup>18</sup> is in agreement with the property of XeF<sub>2</sub> of forming no adducts.

In contrast to XeF<sub>2</sub>, the molecules XeF<sub>4</sub> and XeF<sub>6</sub>, with a higher partial charge on Xe, form fluoride ion adducts.<sup>19,20</sup> XeF<sub>2</sub> interacts readily with Lewis acids as a consequence of the relatively high negative partial charge of the fluorine atoms. Depending on the strength of the Lewis acid, the solid-state structures of such adducts show that the Xe–F distance involving the interacting F atom becomes longer (mainly an electrostatic Xe...F interaction) but without complete separation, whereas the second Xe–F bond becomes shorter and more covalent (2c–2e bond). The [FXe]<sup>+</sup> cation as the extreme case is a strong oxidizing agent (EA = 10.6,<sup>21</sup> 10.9 eV<sup>22</sup>) and is not compatible with organic nucleophiles. The electronegativity of Xe<sup>II</sup> in XeF<sub>2</sub> is 2.4 and increases to 2.5 in [FXe]<sup>+</sup> (calculated by the correlation of Allred and Rochow). The increase in electronegativity is accompanied by the change of Mulliken charges on F from –0.666 to –0.284 and on Xe from 1.331 to 1.284 for the transition from XeF<sub>2</sub> to [FXe]<sup>+</sup> (ab initio calculations: RHF, LANL2DZ).<sup>23</sup> A similar tendency was calculated for the change from XeF<sub>4</sub> (Xe, 2.494; F, –0.623) to [XeF<sub>3</sub>]<sup>+</sup> (Xe, 2.283; 2 F<sub>ax</sub>, –0.500; F<sub>eq</sub>, –0.286).<sup>24</sup> The comparison of the fluoride donor ability shows that XeF<sub>2</sub> is a better fluoride donor than XeF<sub>4</sub>. The higher effective charge on Xe<sup>IV</sup> makes the fluoride abstraction more difficult.

## II. Current Preparative Methods of C–Xe<sup>II</sup> Bond Formation

**Attempted Formation of Carbon–Xenon Compounds.** In 1979 Lagow<sup>25</sup> claimed to have synthesized Xe(CF<sub>3</sub>)<sub>2</sub> by reacting XeF<sub>2</sub> with CF<sub>3</sub> radicals. The waxy

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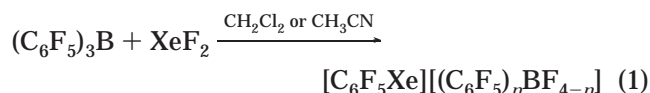
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product with a half-life of ~30 min at room temperature and ~2 weeks at –192 °C and a “vapor pressure significantly larger (?) than that of XeF<sub>2</sub>” was not unambiguously characterized or reproduced successfully. Schmeisser et al. tried to add CF<sub>3</sub> radicals to Xe<sup>0</sup> in analogy to the direct synthesis of XeF<sub>2</sub> by addition of fluorine atoms to Xe<sup>0</sup>, but without success.<sup>26</sup> The successful introduction of O and N groups into the Xe<sup>II</sup> moiety by metathesis stimulated different groups to examine metathetical methods for carbon–xenon(II) bond formation. By direct analogy with the introduction of oxygen- and nitrogen-containing groups Seppelt and coworkers<sup>27</sup> reacted the CH acid [FSO<sub>2</sub>]<sub>3</sub>CH with XeF<sub>2</sub> but observed only the formation of [FS(O)<sub>2</sub>]<sub>3</sub>CF. A similar result was obtained in the reactions of K[CH<sub>3</sub>–(NO<sub>2</sub>)<sub>2</sub>C] with XeF<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>.<sup>28</sup>

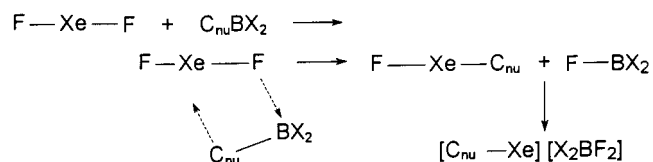
**Organoxenonium(II) Salts by Substitution of Boron in Organoboranes (Xenodeborylation).** In the case of the nucleophilic introduction of organic groups into XeF<sub>2</sub> it is necessary to overcome the low electrophilicity of the Xe center in XeF<sub>2</sub>. Additionally, the lack of a permanent dipole moment in XeF<sub>2</sub> explains its low reactivity. One solution to overcome these problems is the use of organic group transfer reagents with a Lewis acidic center, which polarizes the hypervalent F–Xe–F bond and increases the electrophilicity of the xenon atom. However, the degree of polarization should be not too high, because too strong a polarization favors the oxidation ability of [FXe]<sup>+</sup>. The first examination of this concept was carried out using an appropriate triarylborane as the source of the organic group. Tris(pentafluorophenyl)borane was found to react with xenon difluoride with formation of arylxenonium fluoroborates<sup>8,9,29</sup> (eq 1).



$$n = 3, \text{CH}_3\text{CN};^8 \quad n = 1, \text{CH}_2\text{Cl}_2;^9 \quad n = 2, \text{CH}_2\text{Cl}_2^{29}$$

The attempted use of pentafluorophenyl-containing Lewis acids having central atoms other than boron with a tetrahedral or trigonal-bipyramidal configuration was not successful.

Scheme 1



Scheme 1 illustrates the course of the xenodeborylation reaction: the interaction of boron with one basic fluorine atom of XeF<sub>2</sub> polarizes the xenon–fluorine

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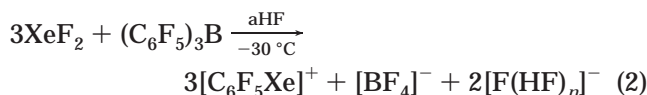
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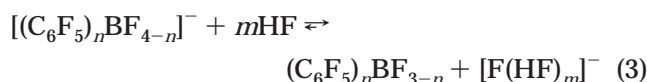
bond, and the hypervalent bond becomes asymmetric. Consequently, the electrophilicity of Xe increases as well as the oxidation potential. On the other side, the interaction of boron with a fluorine bonded to xenon leads to tetracoordination at boron. Simultaneously, the nucleophilicity of the C<sub>6</sub>F<sub>5</sub> group at boron increases. Boranes seem to offer the best geometry for a successful transition state in the fluorine-organyl substitution on XeF<sub>2</sub>.

The oxidation property of XeF<sub>2</sub> itself and of its polarized form in the interaction with boranes limits the choice of appropriate organic groups. The demands of high nucleophilicity and stability to oxidation are best realized by fluorinated aryl groups. The electron-withdrawing fluorine substituents make the C–C σ system electron-poor, whereas the π system becomes enriched by p–p π back-bonding. In organoxenonium cations in which C(1) is part of a π system, Xe increases the π-electron density on C(1) by polarization and this strengthens the C–Xe bond electrostatically.<sup>23</sup> However, in alkylxenonium cations with fluorine atoms bonded at C(1), the C–Xe bond is weakened by repulsion of the highly positive partial charges on C(1) and Xe.

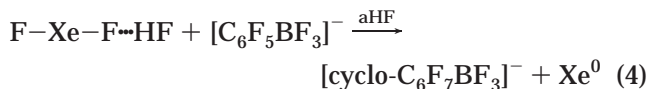
An unusual variant of xenoborylation is the nucleophilic transfer of the C<sub>6</sub>F<sub>5</sub> group in anhydrous HF (aHF).<sup>30</sup> It should be mentioned that XeF<sub>2</sub> is very soluble in aHF (9.88 mol/kg, 30 °C),<sup>31</sup> whereas (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B is practically insoluble even at room temperature and undergoes solvolysis only very slowly (72 h), yielding C<sub>6</sub>F<sub>5</sub>H and [BF<sub>4</sub>]<sup>−</sup>. Xenon difluoride (3 equiv) is consumed within 4 h when reacted with (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B in aHF at ca. −30 °C. The main products are [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> and [BF<sub>4</sub>]<sup>−</sup>. Minor byproducts are [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BF<sub>2</sub>]<sup>−</sup>, [cyclo-C<sub>6</sub>F<sub>7</sub>BF<sub>3</sub>]<sup>−</sup>, and C<sub>6</sub>F<sub>6</sub> (eq 2).



In aHF all C<sub>6</sub>F<sub>5</sub> groups of the borane are transferred to xenon, in contrast to the reaction in CH<sub>2</sub>Cl<sub>2</sub>. Indeed, the fluoroborate anions [(C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>BF<sub>4−n</sub>]<sup>−</sup> cannot transfer C<sub>6</sub>F<sub>5</sub> groups directly to xenon difluoride, but in aHF they undergo abstraction of fluoride by HF (eq 3).

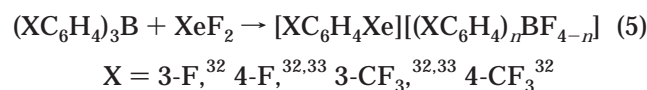


The abstraction of fluoride occurs faster than the oxidation of the aryl group in the fluoroborate anion by the polarized XeF<sub>2</sub> molecule (eq 4).

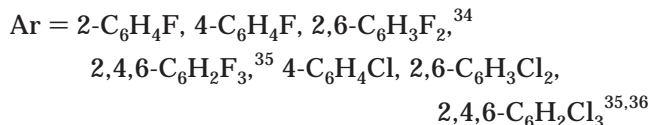
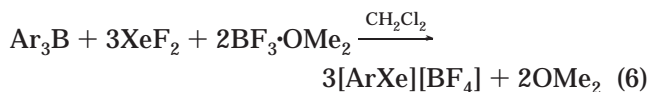


In this interesting modification of xenoborylation the resulting arylxenonium cations are accompanied by a mixture of [BF<sub>4</sub>]<sup>−</sup> and [F(HF)<sub>n</sub>]<sup>−</sup> anions.

The method of xenoborylation could be extended to hydrogen-containing arylxenonium(II) (aryl)fluoroborates as long as the aryl group bears at least one electron-withdrawing substituent X (eq 5).

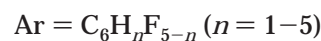
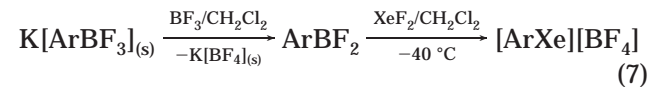


In dichloromethane suspensions the salts [XC<sub>6</sub>H<sub>4</sub>-Xe][(XC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>BF<sub>4−n</sub>] are thermally unstable and decompose already above ca. −40 °C. More stable tetrafluoroborate salts are obtained when the triarylboranes were reacted in the presence of BF<sub>3</sub>·OME<sub>2</sub> (eq 6).

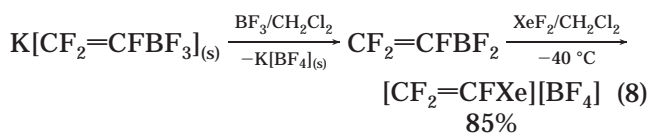


The majority of the salts obtained by this method were not isolated but were characterized unambiguously in solution by their <sup>1</sup>H, <sup>19</sup>F, and <sup>129</sup>Xe NMR spectra.

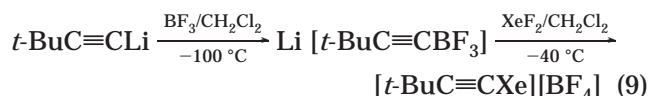
All these routes to arylxenonium(II) salts are based on Ar<sub>3</sub>B and are limited by the availability of the corresponding triarylboranes. The synthesis and purification of arylboranes with electron-poor aryl groups is a delicate procedure which in many cases results in low yields.<sup>37</sup> Recently a convenient access to the salts [ArXe][BF<sub>4</sub>] was developed on the basis of the reaction of XeF<sub>2</sub> with in situ generated aryldifluoroboranes<sup>38</sup> (eq 7).



Evidently, this approach is general and can be used also for the introduction of other organic groups. This was demonstrated by the preparation of trifluorovinylxenonium tetrafluoroborate<sup>39</sup> (eq 8) and the first organic compound of xenon(IV), *trans*-difluoro(pentafluorophenyl)xenonium(IV) tetrafluoroborate,<sup>10</sup> which will be discussed later.



A related procedure was used for the preparation of some alkynylxenonium(II) tetrafluoroborates<sup>40</sup> (eq 9).



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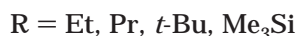
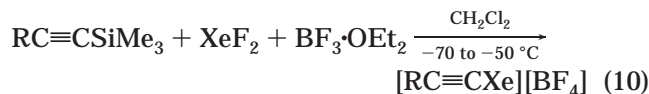
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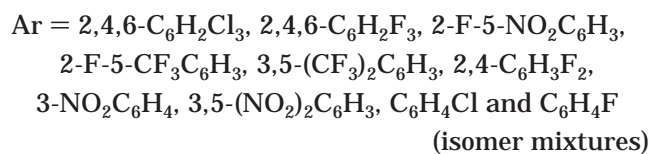
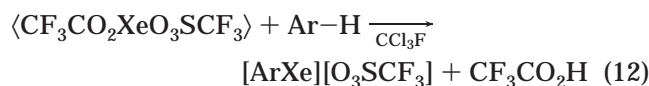
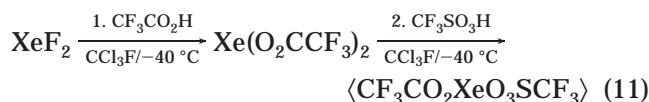
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Stang and Zhdankin assumed that this reaction proceeds via the alkynyltrifluoroborate.<sup>40</sup> However, it should be remembered that all other preparations of organoxenonium salts with electrophilic cations proceed under acidic conditions. Therefore, it seems more probable that in the presence of the excess of  $\text{BF}_3$  the real substrate might be the corresponding alkynyl difluoroborane. The nature of the key reactive alkynyl element intermediate in the reaction of  $\text{RC}\equiv\text{CSiMe}_3$  ( $\text{R} = \text{Et}, \text{Pr}, t\text{-Bu}, \text{Me}_3\text{Si}$ ) with  $\text{XeF}_2$  in the presence of  $\text{BF}_3\cdot\text{OEt}_2$  ( $\text{CH}_2\text{Cl}_2/-70$  to  $-50^\circ\text{C}$ )<sup>40</sup> is not clear (eq 10).



The formation of the alkynylxenonium tetrafluoroborates was proven by their  $^{129}\text{Xe}$  and  $^{13}\text{C}$  NMR spectra. No  $^{129}\text{Xe}$  resonance was observed when  $\text{R}$  was  $\text{Ph-C}\equiv\text{C}$ .<sup>40</sup> None of the alkynylxenonium salts were isolated.

**Arylxenonium(II) Salts by Substitution of Hydrogen in Benzene Derivatives (Xenodeprotonation).** Numerous efforts to replace hydrogen in aromatic compounds by an electrophile generated from  $\text{XeF}_2$  and a Lewis acid were unsuccessful. Usually they led to the addition of fluorine to the C–C double bond or resulted in fluorodeprotonation.<sup>41,42</sup> Naumann et al. offered the unique electrophilic  $\text{Xe}^{\text{II}}$  system generated by the reaction of  $\text{XeF}_2$  in sequence with  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{CF}_3\text{SO}_3\text{H}$  in  $\text{CCl}_3\text{F}$  at  $-40^\circ\text{C}$ . The nature of the resulting reagent was not elucidated. The asymmetric compound  $\text{CF}_3\text{CO}_2\text{-XeO}_3\text{SCF}_3$  or its protonated form was assumed to be the reactive key intermediate in the substitution of hydrogen in benzene derivatives by the  $\text{XeO}_3\text{SCF}_3$  group<sup>43,44</sup> (eqs 11 and 12).



The compounds with  $\text{Ar} = 2,4,6\text{-C}_6\text{H}_2\text{F}_3, 2\text{-F-5-NO}_2\text{C}_6\text{H}_3, 2\text{-F-5-CF}_3\text{C}_6\text{H}_3,$  and  $3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$  were

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(39) Frohn, H.-J.; Bardin, V. V. *Chem. Commun.* **1999**, 919–920.

(40) Zhdankin, V. V.; Stang, P. J.; Zefirov, N. S. *J. Chem. Soc., Chem. Commun.* **1992**, 578–579.

(41) Bardin, V. V.; Yagupol'skii, Y. L. Xenon Difluoride. In *New Fluorinating Agents for Organic Synthesis*; German, L. S., Zemskov, S. V., Eds.; Springer: Berlin, 1989; pp 1–34.

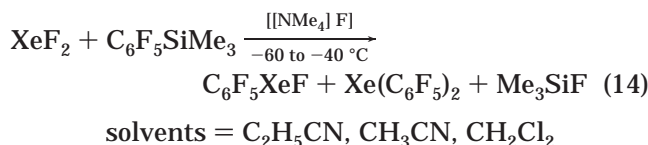
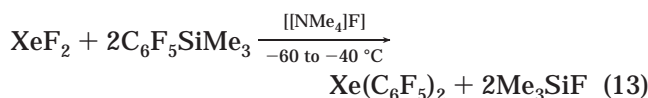
(42) Bardin, V. V.; Shchegoleva, L. N.; Frohn, H.-J. *J. Fluorine Chem.* **1996**, *77*, 153–159.

(43) Naumann, D.; Tyrna, W.; Gnann, R.; Pfohl, D. *J. Chem. Soc., Chem. Commun.* **1994**, 2651–2653.

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isolated in 10–15% yield, whereas the other compounds were only detected in the reaction mixture by means of their  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{129}\text{Xe}$  NMR spectra. No arylxenonium compounds were obtained with benzene, toluene, aniline, phenol or biphenyl or with  $1,3,5\text{-(CF}_3)_3\text{C}_6\text{H}_3$ . The orientation of the xenodeprotonation suggests the electrophilic route of this process. However, the low yields and the nonregiospecificity make the xenodeprotonation inferior as an alternative preparative method to the xenodeborylation approach, despite its scientific interest.

**Diarylxenon,  $\text{XeAr}_2$ , and Arylxenonium Fluoride,  $\text{ArXeF}$ , Derivatives by the Base-Catalyzed Nucleophilic Introduction of the Aryl Group  $\text{C}_6\text{F}_5$  into the  $\text{XeF}_2$  Molecule.** In addition to the previously discussed methods of xenodeborylation and xenodeprotonation in acidic media Naumann et al. reported recently a new method of introducing the  $\text{C}_6\text{F}_5$  group into  $\text{XeF}_2$  using basic catalysis.  $\text{XeF}_2$  reacts with 2 equiv of  $\text{C}_6\text{F}_5\text{SiMe}_3$  after addition of a catalytic amount of  $[\text{NMe}_4]^+\text{F}^-$ , forming  $\text{Xe}(\text{C}_6\text{F}_5)_2$  (eq 13). With 1 equiv of the silane  $\text{C}_6\text{F}_5\text{SiMe}_3$ ,  $\text{C}_6\text{F}_5\text{XeF}$  was formed with an admixture of  $\text{Xe}(\text{C}_6\text{F}_5)_2$ <sup>45</sup> (eq 14). In neither case was a yield reported.



It should be mentioned that under similar conditions the silane  $\text{CF}_3\text{SiMe}_3$  gave only  $\text{C}_2\text{F}_6$  and no trifluoromethylxenon(II) compounds were detected.<sup>45</sup>

The intermediate generation of arylxenon(II) compounds in the reactions of  $4\text{-RC}_6\text{H}_4\text{SiMe}_3$  with  $\text{XeF}_2$ <sup>41,46,47</sup> as well as in the fluoride-catalyzed reactions of  $\text{RC}_6\text{F}_4\text{SiX}_3$  ( $\text{X} = \text{Me}, \text{F}$ )<sup>42,46,48</sup> was proposed. Later Ramsden showed that  $4\text{-R-C}_6\text{H}_4\text{SiMe}_3$  forms  $4\text{-R-C}_6\text{H}_4\text{F}$  on reaction with  $\text{XeF}_2$  only in the presence of an acidic Pyrex surface but not in FEP (copolymer of tetrafluoroethylene and hexafluoropropylene) vessels.<sup>49</sup> The Lewis acid catalyzed interaction of  $\text{XeF}_2$  with silyl- and germypentafluorobenzenes  $\text{C}_6\text{F}_5\text{MX}_3$  ( $\text{M} = \text{Si}, \text{Ge}; \text{X} = \text{Me}, \text{Et}, \text{F}$ ) resulted in ring-fluorination products.<sup>50</sup>

**Covalent Compounds  $\text{ArXeY}$  from Arylxenonium(II) Salts.** Despite the weak nucleophilicity of the  $[\text{AsF}_6]^-$  anion, there is a significant cation–anion contact with a distance  $\text{Xe}\cdots\text{F}$  of 2.672(5) Å and a nearly linear C(1)– $\text{Xe}\cdots\text{F}$  triad ( $174.2(3)^\circ$ ) in solid  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$ .<sup>23</sup> This contact is 23% shorter than the sum of

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(46) Bardin, V. V.; Stennikova, I. V.; Furin, G. G.; Leshina, T. V.; Yakobson, G. G. *Zh. Obshch. Khim.* **1988**, *58*, 2580–2588; *J. Gen. Chem. USSR* **1988**, *58*, 2297–2303.

(47) Lothian, A. P.; Ramsden, C. A. *Synlett* **1993**, 753–755.

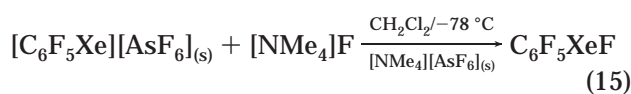
(48) Frohn, H.-J.; Bardin, V. V. *J. Organomet. Chem.* **1995**, *501*, 155–159.

(49) Ramsden, C. A.; Smith, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6842–6843.

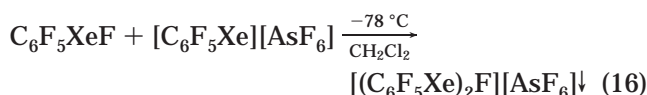
(50) Bardin, V. V.; Frohn, H.-J. *J. Fluorine Chem.* **1993**, *60*, 141–151.

the van der Waals radii of Xe and F of 3.47 Å.<sup>17</sup> The contact to the weakly nucleophilic [AsF<sub>6</sub>]<sup>-</sup> anion emphasizes the electrophilic character of the arylxenonium cation. The linear triad C(1)–Xe···F is best described as an asymmetric hypervalent bond with a nearly 2c–2e C(1)–Xe bond and a mainly electrostatic Xe···F interaction. A similar structural pattern was found for [2,6-C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>Xe][BF<sub>4</sub>].<sup>51</sup>

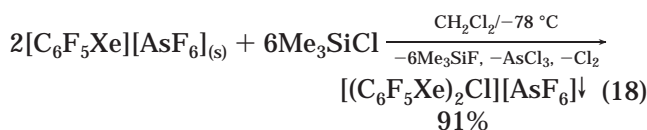
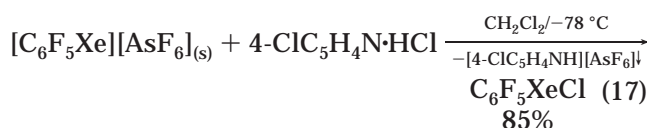
The description of this structural motif as an asymmetric, angled fluoride bridge between the arylxenonium cation and the Lewis acid AsF<sub>5</sub> may be an alternative one. By emphasizing in this way the Lewis acidic nature of the [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> cation, it is understandable that the mononuclear C<sub>6</sub>F<sub>5</sub>XeF molecule can exist as well as the fluoride-bridged dinuclear cation [(C<sub>6</sub>F<sub>5</sub>Xe)<sub>2</sub>F]<sup>+</sup>. The heterogeneous reaction of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with an equimolar amount of [NMe<sub>4</sub>]F in CH<sub>2</sub>Cl<sub>2</sub> leads to C<sub>6</sub>F<sub>5</sub>XeF.<sup>52–54</sup> The latter is not available under acidic conditions from the reaction of a [FXe]<sup>+</sup> source and a [C<sub>6</sub>F<sub>5</sub>]<sup>-</sup> substrate. C<sub>6</sub>F<sub>5</sub>XeF is a covalent compound, which is soluble in CH<sub>2</sub>Cl<sub>2</sub> (eq 15).



The nucleophilic xenon-bonded fluorine atom of C<sub>6</sub>F<sub>5</sub>XeF can react with a further [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> cation to yield [(C<sub>6</sub>F<sub>5</sub>Xe)<sub>2</sub>F][AsF<sub>6</sub>]. This salt is insoluble in CH<sub>2</sub>Cl<sub>2</sub> but soluble in polar CH<sub>3</sub>CN<sup>52–54</sup> (eq 16).



In a similar way, two C<sub>6</sub>F<sub>5</sub>–Xe–Cl compounds had been isolated earlier. The first was the covalent compound C<sub>6</sub>F<sub>5</sub>XeCl, which is soluble in CH<sub>2</sub>Cl<sub>2</sub>. The second is a salt containing the dinuclear [(C<sub>6</sub>F<sub>5</sub>Xe)<sub>2</sub>Cl]<sup>+</sup> cation.<sup>55,56</sup> The latter features a nearly symmetrical, bent Xe–Cl–Xe bridge, with Xe(1)–Cl–Xe(2) = 176.0(3)°, Xe(1)–Cl = 2.847(2) Å, and Xe(2)–Cl = 116.96(8) Å (eqs 17 and 18).



(51) Gilles, T.; Gmann, R.; Naumann, D.; Tebbe, K.-F. *Acta Crystallogr.* **1994**, *C50*, 411–413.

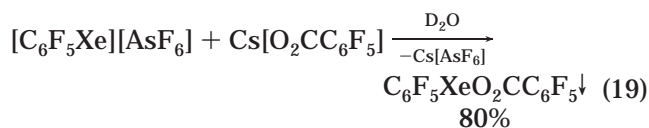
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(Pentafluorophenyl)xenonium acylates were obtained in aqueous solution by the reaction of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with cesium acylates. The pentafluorobenzoate,<sup>57</sup> tetrafluoroterephthalate, and trifluoromethanesulfonate<sup>58</sup> derivatives were prepared in this manner (eq 19).



Alternative routes to arylxenonium triflates involve the reaction of [ArXe][BF<sub>4</sub>] salts with Me<sub>3</sub>SiOTf<sup>59</sup> (eq 20) or the xenodeprotonation reaction of xenon trifluoroacetate triflate with substituted benzene derivatives (see above).<sup>43,44</sup>

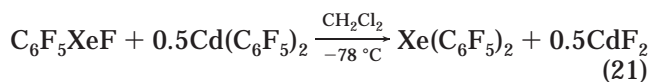


In [2,6-C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>Xe][OTf] there is an asymmetric C–Xe···O triad with a strong Xe···O contact of 2.687(9) Å.<sup>44</sup>

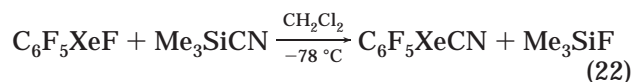
The C–Xe···O triad in (pentafluorophenyl)xenon(II) pentafluorobenzoate becomes significantly more symmetrical and the bond covalent. Consequently, the compound is soluble in CH<sub>2</sub>Cl<sub>2</sub>. The crystal structure shows the xenon atom linearly (178.1(1)°) bonded to carbon and oxygen with a Xe–O distance of 2.367(3) Å, which is 32% shorter than the sum of the van der Waals radii of Xe and O (3.52 Å<sup>17</sup>).

C<sub>6</sub>F<sub>5</sub>XeF is a useful starting material for introducing a second organic group into the C<sub>6</sub>F<sub>5</sub>Xe moiety. The first approach consists of the homogeneous reaction with an organic transfer reagent of weak Lewis acidity such as organocadmium compounds or organotrimethylsilanes. Alternatively, a second aryl group can be introduced under basic conditions (fluoride catalysis;<sup>45</sup> see above).

C<sub>6</sub>F<sub>5</sub>XeF reacts rapidly with Cd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> at low temperature with formation of Xe(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub><sup>54,60</sup> (eq 21).



C<sub>6</sub>F<sub>5</sub>XeCN is formed in the reaction of C<sub>6</sub>F<sub>5</sub>XeF with Me<sub>3</sub>SiCN<sup>54,60</sup> (eq 22).



Similar to the synthesis of bis(pentafluorophenyl)xenon, Xe(2,4,6-C<sub>6</sub>H<sub>2</sub>F<sub>3</sub>)<sub>2</sub> and the asymmetric diaryl-xenon(II) compound C<sub>6</sub>F<sub>5</sub>Xe(2,4,6-C<sub>6</sub>H<sub>2</sub>F<sub>3</sub>) were obtained by reaction of 2,4,6-C<sub>6</sub>H<sub>2</sub>F<sub>3</sub>XeF with Cd(2,4,6-

(56) Frohn, H.-J.; Schroer, T.; Henkel, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 2554–2556.

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(58) Frohn, H.-J.; Klose, A. Unpublished results.

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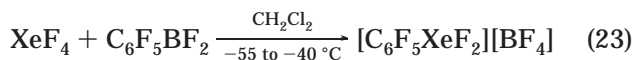
(60) Frohn, H.-J.; Theissen, M. C<sub>6</sub>F<sub>5</sub>XeF: An Important Key Substrate for the Synthesis of New Xenon(II) Compounds. Presented at the 16th International Symposium on Fluorine Chemistry, Durham, U.K., July 2000; Poster 2P-20.

$C_6H_2F_3)_2$  and of  $C_6F_5XeF$  with  $Cd(2,4,6-C_6H_2F_3)_2$ , respectively.<sup>61</sup>

$C_6F_5XeF$  does not react with  $Me_3SiC_6F_5$  alone in  $CH_2Cl_2$  (weakly acidic conditions). The composition of the reaction mixture obtained under  $F^-$  catalysis in  $CH_2Cl_2$  strongly depends on the concentration. In dilute solution the aryl nucleophile generated from  $Me_3SiC_6F_5$  attacks the solvent (protodesilylation) but in highly concentrated solutions the desired product,  $Xe(C_6F_5)_2$ , was obtained.<sup>62</sup>

### III. The First Synthesis of an Arylxenonium(IV) Salt by Substitution of Boron in Organoboranes (Xenoborylation)

Recently, C–Xe bond formation could be extended to  $Xe^{IV}$ . Xenon tetrafluoride is a weaker fluoride donor than  $XeF_2$  and possesses a higher oxidation potential than  $XeF_2$ . An additional disadvantage of  $XeF_4$  is its low solubility in  $aHF$ ,<sup>31</sup> a solvent which is stable toward oxidation. In the reaction of  $XeF_4$  with  $B(C_6F_5)_3$  in  $aHF$  only  $[C_6F_5Xe]^+$  salts were obtained instead of  $Xe(IV)$  salts because of the spontaneous reaction of the electrophilic  $[C_6F_5XeF_2]^+$  cation with the initially formed nucleophilic  $[(C_6F_5)_nBF_{4-n}]^-$  anions. With  $C_6F_5BF_2$  in  $CH_2Cl_2$  the reaction was successful<sup>10</sup> (eq 23), whereas



in  $CH_3CN$  no substitution of a fluorine atom by an aryl group occurred. Probably, in the basic solvent the acidity of the aryldifluoroborane is not high enough to polarize  $XeF_4$  effectively.

The bright yellow compound  $[C_6F_5XeF_2][BF_4]$  is thermally less stable than the analogous  $Xe^{II}$  compound  $[C_6F_5Xe][BF_4]$  and decomposes above  $-20 \text{ } ^\circ C$ .

In addition, recently the formation of the cations  $[C_6F_5XeF_2]^+$  and  $[C_6F_5Xe]^+$  was detected spectroscopically by Schrobilgen in the reaction of  $XeF_6$  with  $B(C_6F_5)_3$  in  $SO_2ClF$ . Also formed were oxidized fluoroaromatic compounds.<sup>63</sup>

### IV. Reactivity of Carbon–Xenon Compounds

At the beginning of this section some general information about the reactivity of organoxenon compounds shall be given. The reactivity of organoxenonium(II) and -(IV) salts is determined by the electrophilic character of the cations. In covalent C–Xe compounds with symmetric or asymmetric 3c–4e bonds the high partial positive charge on Xe has a strong influence on the reactivity. Most information about reactivity deals with reactions of organoxenonium(II) salts with nucleophiles.

The reactivity, as well as the stability, of organoxenonium salts  $[RXe][Y]$  depends on the nature of the organic group R, the counteranion  $[Y]^-$ , and, if in solution, on the nature of the solvent.

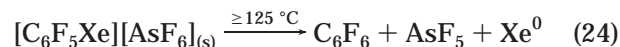
All known organoxenonium salts have in common that  $Xe(II)$  or  $Xe(IV)$  is bonded to a carbon atom which is part of a  $\pi$  system. More extended  $\pi$  systems such as

those in aryl groups increase the relative stability of the C–Xe bond. Aryl groups with  $\sigma$ -electron-withdrawing character prevent the transfer of positive charge from Xe to the aryl group. Reduction of the electron acceptor ability of the aryl group increases the electrophilicity of C(1), which will be accompanied by a weakening of the C–Xe bond. Anions of low nucleophilicity are favored for organoxenonium salts. In the case of kinetically labile anions such as fluoroelementate anions  $[(C_6F_5)_mEF_{n+1}]^-$ , we have to consider additionally the contribution of their solvolysis in basic solvents, which can thereby produce the strongly nucleophilic fluoride anion. The presence of either nucleophilic anions or basic solvents destabilizes the corresponding organoxenonium salt, because the interaction of a nucleophile at  $Xe(II)$  weakens the 2c–2e C–Xe bond.

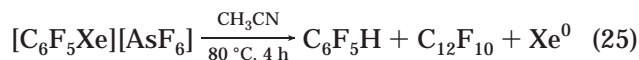
Suitable solvents for ionic  $[RXe][Y]$  compounds are polar basic ones such as  $CH_3CN$ ,  $CH_3NO_2$ ,  $H_2O$ , and  $CF_3CH_2OH$ , which predominantly solvate the cation, or strongly acidic ones such as  $aHF$ ,  $CF_3SO_3H$  or  $SO_2$ , which preferably solvate the anion and result thereby in a comparatively naked cation.

### V. Thermal Stability of Organoxenonium Salts and Covalent Compounds $ArXeY$ (Ar = Aryl)

In many cases the data for the thermal stability of organoxenon compounds are only qualitative, especially for thermally very labile species, because the decomposition points depend strongly on the purity of the compounds, on the rate of heating, and on other experimental details. The most reliable information exists for the salt  $[C_6F_5Xe][AsF_6]$ . The pure salt melts at  $102 \text{ } ^\circ C$  and decomposes slowly above  $125 \text{ } ^\circ C$  (eq 24).

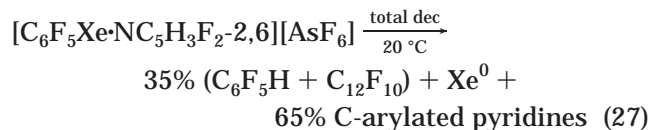
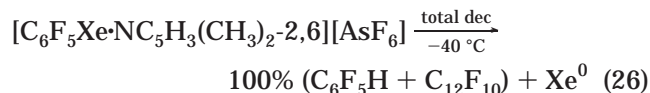


In acetonitrile solution the decomposition already proceeds very slowly even at room temperature and is accelerated on heating to  $80 \text{ } ^\circ C$ , forming  $C_6F_5H$  and  $C_{12}F_{10}$  (6.7:1 at  $20 \text{ } ^\circ C$  and 12:1 at  $80 \text{ } ^\circ C$ ) (eq 25). In



aqueous solution the stability of the salt  $[C_6F_5Xe][AsF_6]$  is significantly lower than in  $CH_3CN$ .<sup>23</sup>

Presumably, if we neglect the interaction of the electrophilic cation with the fluoride ion, possibly present as a solvolysis product of  $[AsF_6]$ , the decomposition of the donor–acceptor complex  $[C_6F_5Xe \cdots NCMel][AsF_6]$  takes place. Related complexes with substituted pyridines in acetonitrile solution show a remarkable dependence of their thermal stability on the basicity of the nitrogen atom and are less thermally stable than the parent salt  $[C_6F_5Xe][AsF_6]$ <sup>64</sup> (eqs 26 and 27).

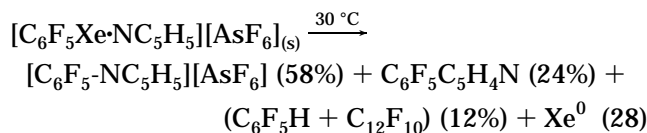


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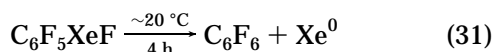
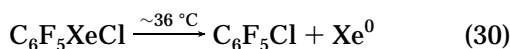
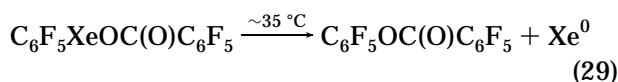
(62) Frohn, H. J.; Theissen, M. Unpublished results.

(63) Schrobilgen, G. J.; Becher, M. Personal communication.

In the thermolysis of the solid adducts  $[\text{C}_6\text{F}_5\text{Xe}\cdot\text{N-base}][\text{AsF}_6]$  (N-bases are substituted pyridines) N- and C-pentafluorophenylation of the corresponding pyridines is preferred over formation of  $\text{C}_6\text{F}_5\text{H}$  and  $\text{C}_{12}\text{F}_{10}$ <sup>64</sup> (eq 28).



The covalent  $\text{Xe}^{\text{II}}$  compounds  $\text{C}_6\text{F}_5\text{XeO}_2\text{CC}_6\text{F}_5$ ,<sup>57</sup>  $\text{C}_6\text{F}_5\text{-XeCl}$ ,<sup>56</sup> and  $\text{C}_6\text{F}_5\text{XeF}^{54}$  in the solid state are thermally less stable than  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  and evolve xenon already at ca. 35 °C (fast heating), whereas in solution the decomposition takes place at significantly lower temperatures (eqs 29–31).

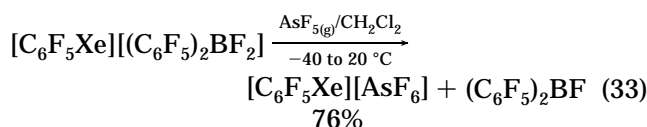
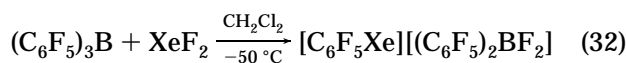


It is interesting that solid  $(\text{C}_6\text{F}_5\text{Xe})_2\text{Cl}][\text{AsF}_6]$  shows a thermal stability similar to that of  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  and decomposes at 100 °C, yielding Xe and  $\text{C}_6\text{F}_5\text{Cl}$ , in addition to  $\text{C}_6\text{F}_6$ ,  $\text{AsF}_5$ , and  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$ .<sup>56</sup>

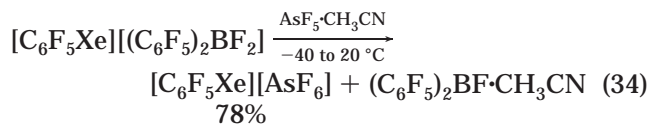
## VI. Anion Metathesis Reactions of Arylxenonium Fluoroborates

The thermal stability of organoxenonium salts  $[\text{RXe}][\text{Y}]$  is strongly influenced by the nucleophilicity of the anion (comparing salts with the same  $[\text{RXe}]$  cation). This influence can be demonstrated with  $[\text{ArXe}][\text{Ar}_n\text{BF}_{4-n}]$  salts. As one goes from  $n = 3$  to  $n = 0$ , the thermal stability under the same conditions increases significantly. It should be mentioned that the anions  $[\text{Ar}_n\text{BF}_{4-n}]^-$  have two sites available for electrophilic attack: the carbon atom C(1) of the aryl group and the fluorine atom bonded to boron.

One route to more thermally stable  $[\text{ArXe}][\text{Y}]$  salts uses the conversion of  $[\text{ArXe}][\text{Ar}_n\text{BF}_{4-n}]$  salts, which were formed initially in the reaction of  $\text{Ar}_3\text{B}$  with  $\text{XeF}_2$  into salts with more weakly nucleophilic anions. This can be achieved, for example, by treatment with fluoride anion acceptors such as  $\text{AsF}_5\cdot\text{CH}_3\text{CN}$ <sup>23,29,65</sup> or  $\text{AsF}_5(\text{g})$ .<sup>23</sup> By this procedure pure arylxenonium(II) hexafluoroarsenates of high thermal stability were obtained (eqs 32–34).



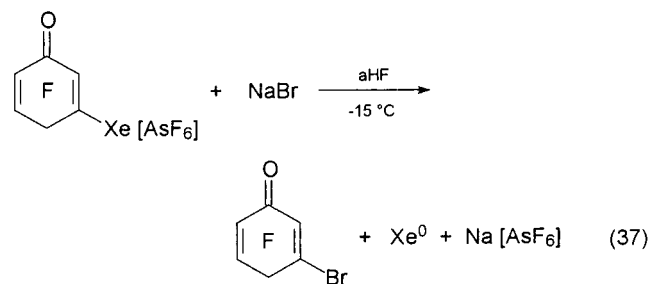
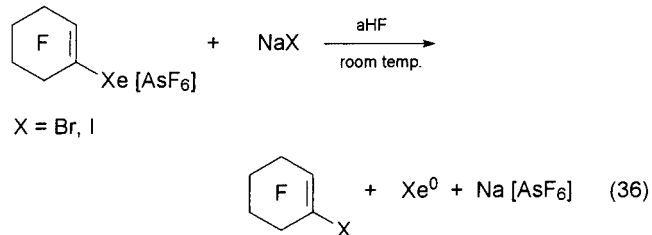
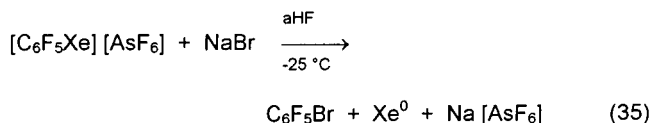
(64) Frohn, H.-J.; Schroer, T.; Henkel, G. *Z. Naturforsch.* **1995**, *50b*, 1799–1810.



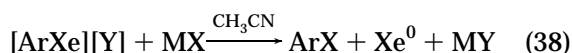
## VII. Reactions of Organoxenonium(II) Salts with Nucleophiles

**Reactions with Halide Anions.** According to NMR spectral data, organoxenonium salts exist in highly acidic media such as superacids as separated ions with solvated anions and nearly naked organoxenonium cations. The latter possess a high electrophilicity and high reactivity toward nucleophiles. On the other hand, the reactivity of nucleophiles is diminished in superacidic media. Thus, (pentafluorophenyl)xenonium hexafluoroarsenate does not react with KF or  $[\text{Me}_4\text{N}]\text{Cl}$  in aHF solution at room temperature over days. The same inertness toward fluoride and chloride anions in aHF is found also for (nonafluorocyclohexen-1-yl)xenonium hexafluoroarsenate.<sup>66</sup>

Alternatively, reactions with bromide and iodide anions occur readily in aHF and lead to the corresponding bromo and iodo derivatives with reductive elimination of  $\text{Xe}^{66-68}$  (eqs 35–37).



In basic solvents such as  $\text{CH}_3\text{CN}$  and  $\text{C}_2\text{H}_5\text{CN}$ , fluorine-containing aryl-, cycloalkenyl-, and vinyl-xenonium salts show similar reactivity patterns toward “soft” anionic nucleophiles such as bromide and iodide (eqs 38 and 39).

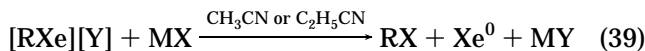
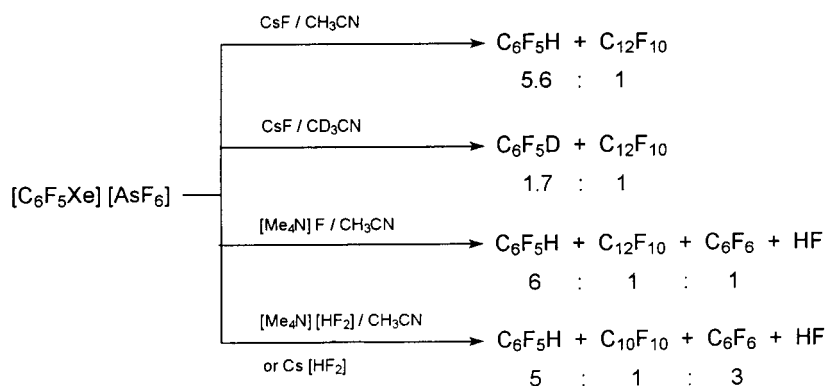


X = I, Y =  $\text{ArBF}_3$ , Ar =  $\text{C}_6\text{F}_5$ ,<sup>9</sup> 3- $\text{CF}_3\text{C}_6\text{H}_4$ ,

4- $\text{CF}_3\text{C}_6\text{H}_4$ , 4- $\text{C}_6\text{H}_4\text{F}$ ;<sup>33,32</sup> X = I, Y =  $\text{AsF}_6$ ,

Ar =  $\text{C}_6\text{F}_5$ ,<sup>69</sup> X = Br, Ar =  $\text{C}_6\text{F}_5$ , Y =  $\text{ArBF}_3$ ,<sup>9</sup>  $\text{AsF}_6$ <sup>69</sup>

Scheme 2

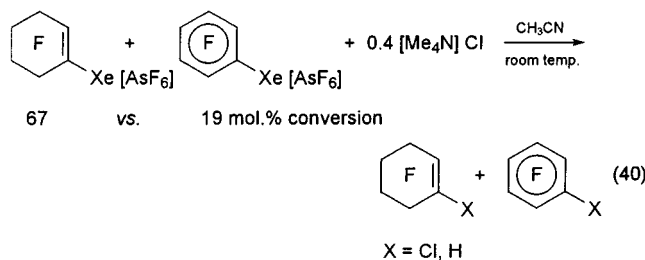


X = Br, I, R = cyclo-1,4-C<sub>6</sub>F<sub>7</sub>, cyclo-C<sub>6</sub>F<sub>9</sub>,

cyclo-2-HC<sub>6</sub>F<sub>8</sub>, Y = AsF<sub>6</sub>,<sup>70,68</sup> X = I,

R = CF<sub>2</sub>=CF, Y = BF<sub>4</sub><sup>39</sup>

The reaction of the cycloalkenylxenonium salt [cyclo-C<sub>6</sub>F<sub>9</sub>Xe][AsF<sub>6</sub>] with Cl<sup>-</sup> leads to 1-H-nonafluorocyclohexene as the major product in addition to 1-chlorononafluorocyclohexene (ca. 4:3).<sup>66</sup> Under the same conditions, chloropentafluorobenzene and pentafluorobenzene (traces) are obtained from the salt [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>],<sup>9</sup> whereas the slow reaction of [2,4,6-C<sub>6</sub>H<sub>2</sub>F<sub>3</sub>Xe][BF<sub>4</sub>] with Cl<sup>-</sup> results in 1,3,5-trifluorobenzene and 2,4,6-trifluorobenzene (4:1).<sup>35</sup> The competitive reaction of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] and [cyclo-C<sub>6</sub>F<sub>9</sub>Xe][AsF<sub>6</sub>] with chloride anions in CH<sub>3</sub>CN results in the faster conversion of the unsaturated derivative in comparison to the aromatic salt.<sup>66</sup> (eq 40).



The interaction of the salt [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with the “hardest” nucleophile fluoride in acetonitrile proceeds in a more complex way. The treatment of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with an excess of CsF at room temperature leads to the evolution of xenon and the formation of C<sub>6</sub>F<sub>5</sub>H and C<sub>6</sub>F<sub>5</sub>C<sub>6</sub>F<sub>5</sub> in a 5.6:1 molar ratio (in CH<sub>3</sub>CN) or of C<sub>6</sub>F<sub>5</sub>D and C<sub>6</sub>F<sub>5</sub>C<sub>6</sub>F<sub>5</sub> (1.7:1) (in CD<sub>3</sub>CN).<sup>69</sup> No C<sub>6</sub>F<sub>6</sub> was detected in either case, which is in contrast to the reported reaction of [C<sub>6</sub>F<sub>5</sub>Xe][(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>BF] with KF in CH<sub>3</sub>CN.<sup>8</sup>

(65) Frohn, H.-J.; Klose, A.; Henkel, G. *GIT Fachz. Lab.* **1993**, *37*, 752–755.

(66) Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **1996**, *622*, 2031–2034.

(67) Frohn, H.-J.; Bardin, V. V. *Z. Naturforsch.* **1996**, *51b*, 1011–1014.

(68) Frohn, H.-J.; Bardin, V. V. *Z. Naturforsch.* **1998**, *53b*, 562–564.

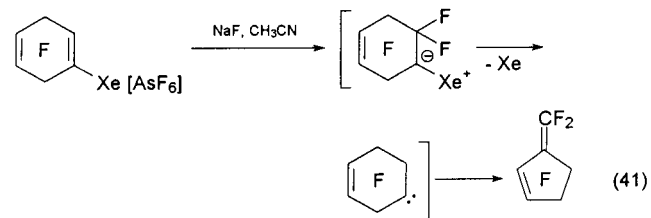
(69) Frohn, H.-J.; Klose, A.; Bardin, V. V.; Kruppa, A. J.; Leshina, T. V. *J. Fluorine Chem.* **1995**, *70*, 147–154.

(70) Frohn, H.-J.; Bardin, V. V. *J. Chem. Soc., Chem. Commun.* **1993**, 1072–1074.

However, in reactions with [Me<sub>4</sub>N][HF<sub>2</sub>] or anhydrous [Me<sub>4</sub>N]F in CH<sub>3</sub>CN (the latter is not really stable at room temperature) hexafluorobenzene, pentafluorobenzene, and decafluorobiphenyl are obtained in addition to HF<sup>69</sup> (Scheme 2).

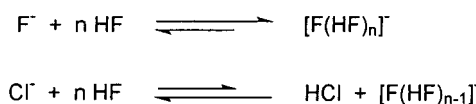
It is likely that the reaction of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with CsF in acetonitrile proceeds via the [(C<sub>6</sub>F<sub>5</sub>Xe)<sub>2</sub>F]<sup>+</sup> cation (see section II). Its decomposition at –20 °C is accompanied by the chemically induced dynamic nuclear polarization (CIDNP) of the <sup>19</sup>F NMR signals of C<sub>6</sub>F<sub>5</sub>H (C<sub>6</sub>F<sub>5</sub>D) and C<sub>12</sub>F<sub>10</sub>, indicating the intermediate generation of pentafluorophenyl radicals. The generation of the latter species is supported by the formation of a mixture of C<sub>6</sub>F<sub>5</sub>C<sub>6</sub>H<sub>4</sub>F isomers when the reaction was performed in the presence of fluorobenzene (see later).<sup>69</sup>

A peculiar reaction route was found in the case of (perfluorocycloalken-1-yl)xenonium hexafluoroarsenates with the fluoride anion in CH<sub>3</sub>CN.<sup>71,66</sup> Treatment of the salt [cyclo-1,4-C<sub>6</sub>F<sub>7</sub>Xe][AsF<sub>6</sub>] with sodium fluoride results in a contraction of the ring, and perfluoro-3-methylenecyclopentene is formed. This conversion can be rationalized in terms of a preferential attack of the “hard” anionic nucleophile fluoride at the “hard” electrophilic C(2) site, rather than at the “softer” electrophilic xenon(II) site<sup>71</sup> (eq 41).



The different behavior of the “hard” chloride anion and the “hardest” fluoride anion in aHF compared with CH<sub>3</sub>CN toward electrophilic organoxenonium compounds arises from the higher degree of protonation of F<sup>-</sup> in aHF, which diminishes sufficiently the nucleophilicity of F<sup>-</sup>, and, on the other hand, from the lower reducing potential of HCl compared to Cl<sup>-</sup> (Scheme 3).

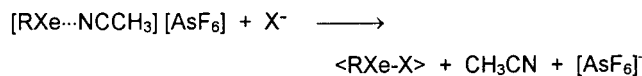
Scheme 3



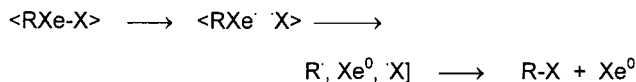
The reaction of (nonafluorocyclohexen-1-yl)xenonium hexafluoroarsenate as well as of the arylxenonium salt



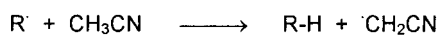
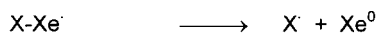
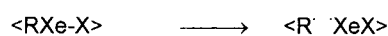
## Scheme 4



reaction path 1 (X = Br<sup>-</sup>, I<sup>-</sup>):



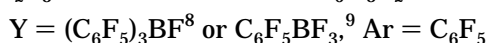
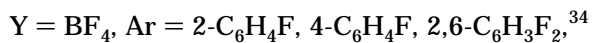
path 2 (X = F<sup>-</sup>, Cl<sup>-</sup>):



[C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with chloride, bromide, and iodide anions in the basic CH<sub>3</sub>CN proceeds via the displacement of coordinated CH<sub>3</sub>CN in [R-Xe<sup>+</sup>NCCH<sub>3</sub>]<sup>+</sup> by the anionic nucleophile.

As a result of such displacement, the intermediate [RXe-Hal] (R = C<sub>6</sub>F<sub>5</sub>, cyclo-C<sub>6</sub>F<sub>9</sub>) is formed. The further fate of [RXe-Hal] depends on the nature of Hal. For Hal = Br, I a single electron transfer (Scheme 4, path 1) with elimination of Xe<sup>0</sup> from RXe<sup>+</sup> was proposed, followed by the in-cage recombination of R<sup>•</sup> and Hal<sup>-</sup> to RHal. When the halide anion is more nucleophilic and more stable toward oxidation (Hal = Cl, F), the carbon-xenon bond in the intermediate RXe-Hal (asymmetric hypervalent bond) will be elongated and cleaved preferably (Scheme 4, path 2). The escaping radical R<sup>•</sup> abstracts hydrogen from solvent molecules. In the case of the chloride anion both paths seem to compete. This consideration is in agreement with data obtained from the interaction of (pentafluorophenyl)xenonium hexafluoroarsenate with pyridine derivatives of different nucleophilicity<sup>64</sup> and with the generation of the FXe<sup>•</sup> radical in CH<sub>3</sub>CN.<sup>72</sup>

**Reactions with Chalcogen Nucleophiles.** The salt [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] is soluble in water and decomposes slowly in aqueous solution at room temperature over 12 h.<sup>23</sup> (Polyfluorophenyl)xenonium salts react with aqueous acetonitrile formally by replacement of xenon by hydrogen (eq 42).



These reactions may not all proceed by the same route, because the list of examples contains both thermally unstable as well as thermally stable salts. Additionally, the formation of F<sup>-</sup> or [HF<sub>2</sub>]<sup>-</sup> in the hydroly-

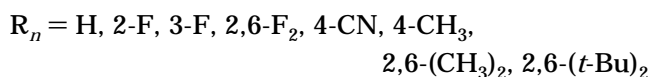
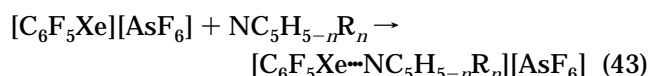
ysis of the [(C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>BF<sub>4-n</sub>] anions cannot be excluded. It is known that different products result in the reaction of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with F<sup>-</sup> or [HF<sub>2</sub>]<sup>-</sup> anions in CH<sub>3</sub>CN.

The consumption of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] in CD<sub>3</sub>CN at 80 °C is accelerated and is complete in 1 h in the presence of H<sub>2</sub>O (1 equiv), forming C<sub>6</sub>F<sub>5</sub>D (main product) and (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>. A similar acceleration was found in the presence of CH<sub>3</sub>OH (1 equiv) at room temperature, but instead of C<sub>6</sub>F<sub>5</sub>D, pentafluorobenzene (C<sub>6</sub>F<sub>5</sub>H) was the main product.<sup>58</sup> In the presence of C<sub>6</sub>F<sub>5</sub>OH in CD<sub>3</sub>CN the salt [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] decomposes rapidly at ≥ -20 °C and more than 10 pentafluorophenyl derivatives are formed, including C<sub>6</sub>F<sub>5</sub>D, (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, and C<sub>6</sub>F<sub>5</sub>OC<sub>6</sub>F<sub>5</sub>. The last ether becomes the main product in neat H<sub>2</sub>O at 0 °C.<sup>58</sup>

[C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] reacts spontaneously with C<sub>6</sub>F<sub>5</sub>SH as well as with [NMe<sub>4</sub>][C<sub>6</sub>F<sub>5</sub>S] in CD<sub>3</sub>CN even at -40 °C and forms (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>S, (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub>, and C<sub>6</sub>F<sub>5</sub>H. A CIDNP effect is observed in the produced C<sub>6</sub>F<sub>5</sub>H when the reaction is monitored by <sup>19</sup>F NMR spectroscopy. The nucleophilicity of the sulfur atom in the disulfide (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub> is lower than that in C<sub>6</sub>F<sub>5</sub>SH or in [C<sub>6</sub>F<sub>5</sub>S]<sup>-</sup>. Thus, the reaction of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub> proceeds in CH<sub>3</sub>CN only at 80 °C and is complete within 1 h, yielding (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>S (main product) and C<sub>6</sub>F<sub>5</sub>H (minor product). The more nucleophilic disulfide (NCS)<sub>2</sub> reacts already at -40 °C, spontaneously forming C<sub>6</sub>F<sub>5</sub>SCN, C<sub>6</sub>F<sub>5</sub>H, and (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>S. The last species is not a product due to C<sub>6</sub>F<sub>5</sub>SCN attack on [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] because neither C<sub>6</sub>F<sub>5</sub>SCN nor (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>S react with the [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> cation in CH<sub>3</sub>CN at 80 °C. The arylxenonium salt is converted only to C<sub>6</sub>F<sub>5</sub>H and (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>.<sup>58</sup>

**Reactions with Pnictide Nucleophiles.** Adduct formation between the [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup> cation and neutral N-bases was investigated in detail. The molecular structure of the salt [C<sub>6</sub>F<sub>5</sub>Xe<sup>+</sup>NCCH<sub>3</sub>][(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>BF<sub>2</sub>]<sup>-</sup> shows a nearly linear asymmetric hypervalent triad C-Xe<sup>+</sup>⋯N with a C-Xe<sup>+</sup>⋯N angle of 174.5(3)° and distances C-Xe = 2.092(8) Å and Xe<sup>+</sup>⋯N = 2.681(8) Å. These can be regarded in a borderline description as a weak 2c-2e C-Xe bond and a strong ion-dipole Xe<sup>+</sup>⋯N interaction.<sup>29</sup>

Pyridines react with solutions of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] in CH<sub>3</sub>CN and H<sub>2</sub>O or with its dichloromethane suspension to form the corresponding adducts<sup>64</sup> (eq 43).

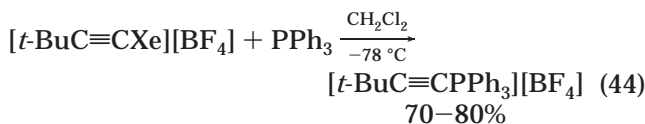


The X-ray structural analysis of the [C<sub>6</sub>F<sub>5</sub>Xe<sup>+</sup>2,6-C<sub>5</sub>H<sub>3</sub>F<sub>2</sub>N][AsF<sub>6</sub>]<sup>-</sup> salt shows a linear C-Xe<sup>+</sup>⋯N arrangement and distances C-Xe = 2.087(5) Å and Xe<sup>+</sup>⋯N = 2.694(5) Å. The <sup>1</sup>H, <sup>19</sup>F, and <sup>129</sup>Xe NMR spectra of the adduct give evidence for a significant charge transfer from nitrogen to xenon, and there is a good correlation between the chemical shifts δ(F-4, C<sub>6</sub>F<sub>5</sub>) and the pK<sub>a</sub> values of the pyridine bases.<sup>64</sup>

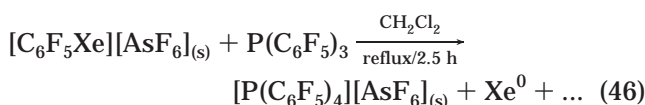
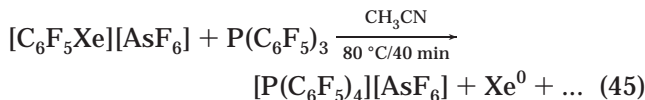
A triphenyl(alkynyl)phosphonium tetrafluoroborate was obtained by the electrophilic alkynylation of triphenylphosphine<sup>40</sup> (eq 44).

(71) Frohn, H.-J.; Bardin, V. V. *Mendeleev Commun.* **1995**, 114-115.

(72) Bucher, G.; Scaiono, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 10076-10079.

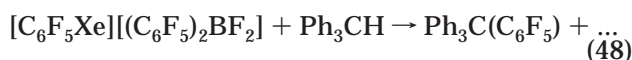
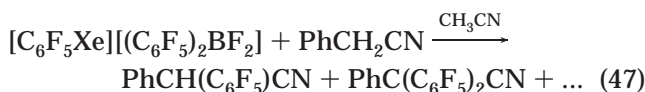


The less electron-rich phosphine  $\text{P}(\text{C}_6\text{F}_5)_3$  is arylated by an electrophilic route using  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  in  $\text{CH}_3\text{CN}$  solution or  $\text{CH}_2\text{Cl}_2$  suspension (eqs 45 and 46).

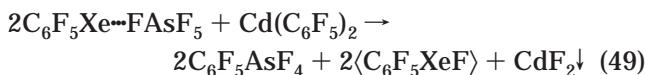


Such quaternization of  $\text{As}(\text{C}_6\text{F}_5)_3$  by  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  to give  $[\text{As}(\text{C}_6\text{F}_5)_4][\text{AsF}_6]$  was not detected in refluxing  $\text{CH}_3\text{CN}$  or in  $\text{CH}_2\text{Cl}_2$ .<sup>58</sup>

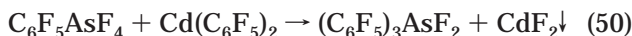
**Reactions with CH Acids and Organoelement and Aromatic Compounds.** The reactions of organoxenonium salts with negatively charged nucleophiles and heteroatomic neutral  $n$ -electron donors as discussed before result primarily in formation of donor adducts at the xenon atom and/or the formal transfer of the organic cation to the nucleophile. Formal similarity is found in reactions of  $[\text{C}_6\text{F}_5\text{Xe}][(\text{C}_6\text{F}_5)_2\text{BF}_2]$  with some CH acids in which the pentafluorophenyl group is added to the deprotonated anionic species with elimination of  $\text{Xe}^0$ <sup>33</sup> (eqs 47 and 48).



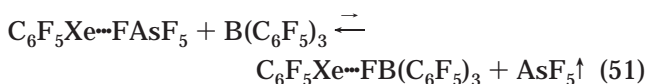
The organoelement compounds  $\text{Cd}(\text{C}_6\text{F}_5)_2$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  have in common a nucleophilic ipso-C atom, but they react with  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  by different routes, due to their different Lewis acidities. In refluxing  $\text{CD}_2\text{Cl}_2$  solution  $\text{Cd}(\text{C}_6\text{F}_5)_2$  reacts by two different paths. First, nucleophilic attack of the  $\text{C}_6\text{F}_5$  group on the electrophilic  $[\text{C}_6\text{F}_5\text{Xe}]^+$  cation results in formation of  $\text{C}_6\text{F}_5\text{D}$ ,  $(\text{C}_6\text{F}_5)_2$ , and  $\text{Xe}^0$ . Second, the  $\text{C}_6\text{F}_5$  group adds to the polarized



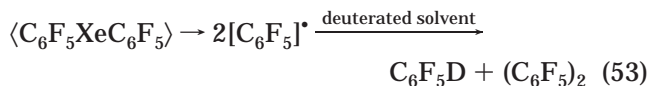
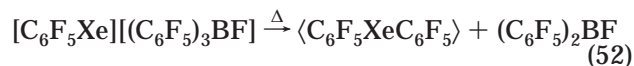
$[\text{AsF}_6]^-$  anion in  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  (eq 49), forming pentavalent arsoranes,  $(\text{C}_6\text{F}_5)_n\text{AsF}_{5-n}$  ( $n = 2, 3$ ) (eq 50).



$[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  reacts with the Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  in  $\text{CD}_2\text{Cl}_2$  at reflux to give  $\text{C}_6\text{F}_5\text{D}$ ,  $\text{C}_6\text{F}_5\text{BF}_2$ ,  $(\text{C}_6\text{F}_5)_2$ ,  $(\text{C}_6\text{F}_5)_2\text{BF}$ , and  $\text{AsF}_3$  (reduction product of  $\text{AsF}_5$ ). The result can be explained by the competition of the Lewis acids  $\text{AsF}_5$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  for the fluoride anion attached to the  $[\text{C}_6\text{F}_5\text{Xe}]^+$  cation (eq 51). In a subsequent step,

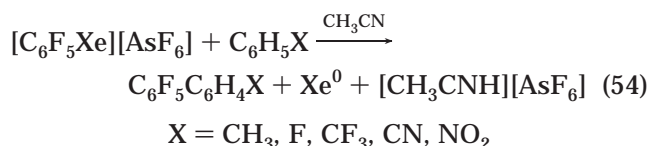


the electrophilic arylxenonium cation can abstract  $\text{C}_6\text{F}_5$  groups from the fluoroborate anion (eqs 52 and 53). The



fluoroborane  $(\text{C}_6\text{F}_5)_2\text{BF}$  reacts like  $\text{B}(\text{C}_6\text{F}_5)_3$ .

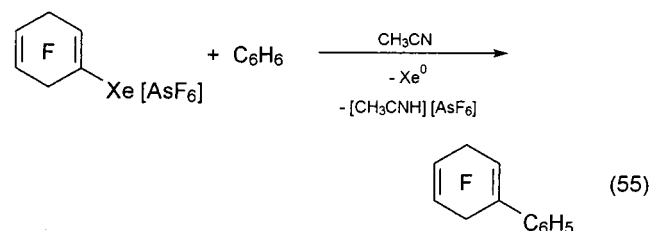
Aromatic compounds  $\text{C}_6\text{H}_5\text{X}$  also undergo pentafluorophenylation in reactions with  $[\text{C}_6\text{F}_5\text{Xe}][\text{Y}]$  to give 2,3,4,5,6-pentafluorobiphenyls  $\text{C}_6\text{F}_5\text{C}_6\text{H}_4\text{X}$ .<sup>33,73</sup> The reaction rates diminish in the series  $\text{X} = \text{CH}_3 > \text{F} > \text{CF}_3 \approx \text{CN} > \text{NO}_2$ , which does not contradict the electrophilic nature of the process. However, detailed investigation of the isomer distribution in the  $\text{C}_6\text{F}_5\text{C}_6\text{H}_4\text{X}$  products shows unambiguously the radical character of the pentafluorophenylation reaction<sup>73</sup> (eq 54).



It is noteworthy that these reactions are accelerated by the fluoride anion. For instance, the total conversion of the salt  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  to  $\text{C}_6\text{F}_5\text{C}_6\text{H}_4\text{F}$  is achieved within 14 h at room temperature, while the  $\text{CsF}$ -catalyzed process is complete within a few minutes.<sup>69</sup>

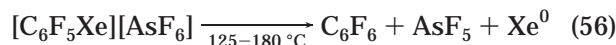
Pentafluorobenzenes  $\text{C}_6\text{F}_5\text{X}$  ( $\text{X} = \text{F}, \text{H}, \text{CN}, \text{SiMe}_3$ ) as well as  $\text{C}_6\text{F}_5\text{I}$  are not reactive under these conditions.<sup>9,73</sup> The reported formation of the iodonium salt  $[(\text{C}_6\text{F}_5)_2\text{I}][\text{Y}]^-$  in the reaction of  $[\text{C}_6\text{F}_5\text{Xe}][\text{Y}]$  ( $\text{Y} = (\text{C}_6\text{F}_5)_3\text{BF}$ ) with  $\text{C}_6\text{F}_5\text{I}$ <sup>8</sup> may be explained by the presence of the anion  $\text{Y}^-$  which can act as a  $\text{F}^-$  donor or via the formation of  $\text{C}_6\text{F}_5\text{IF}_2$  from  $\text{C}_6\text{F}_5\text{I}$  and residual  $\text{XeF}_2$  followed by interaction with  $(\text{C}_6\text{F}_5)_3\text{B}$ .<sup>73</sup> Moreover, the reaction of the salt  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  with  $\text{C}_6\text{H}_5\text{I}$  gives  $\text{C}_6\text{F}_5\text{I}$  (major product) in addition to  $\text{C}_6\text{F}_5\text{C}_6\text{H}_4\text{I}$ ,  $\text{C}_6\text{F}_5\text{H}$ , and  $\text{C}_6\text{F}_5\text{C}_6\text{H}_5$ .<sup>73</sup> A similar reaction mixture is obtained by the radical pentafluorophenylation of iodobenzene using  $\text{C}_6\text{F}_5\text{NH}_2$  and  $\text{C}_5\text{H}_{11}\text{ONO}$ . The predominant formation of iodopentafluorobenzene here may be rationalized in terms of attack of the electrophilic  $\text{C}_6\text{F}_5$  radical on  $\text{C}_6\text{H}_5\text{I}$  with subsequent decomposition of the unstable diaryliodonium radical  $[\text{C}_6\text{F}_5(\text{C}_6\text{H}_5)\text{I}]^\bullet$  with  $[\text{C}_6\text{H}_5]$  elimination (cf. ref 74).  $\text{C}_6\text{F}_5\text{I}$  is favored over  $\text{C}_6\text{H}_5\text{I}$  by the stronger bond of iodine to the  $\text{C}_6\text{F}_5$  group because of the additional high electrostatic bonding component.<sup>75</sup>

Perfluorocycloalkenylxenonium salts react with aromatic compounds such as arylxenonium salts<sup>70</sup> (eq 55).

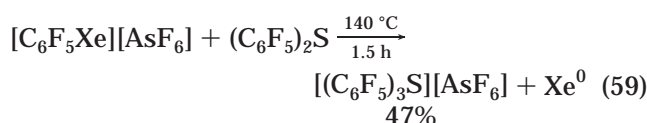
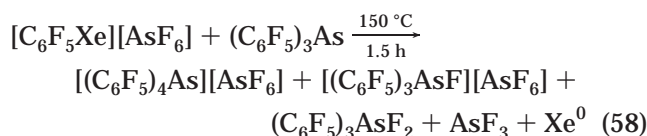
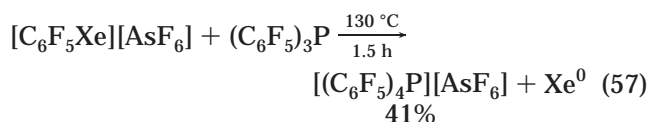


**Reactions of the Molten Salt  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  with Nucleophiles.** The salt  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  is one of the

most thermally stable organoxenon compounds. It melts at 102 °C, forming a viscous liquid which decomposes slowly above 125 °C with an electrophilic transfer of the C<sub>6</sub>F<sub>5</sub> group from xenon to one of the fluorine atoms of the counteranion<sup>23</sup> (eq 56).

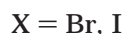
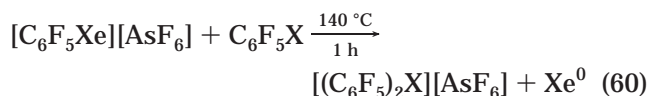


The thermal stability to 125 °C and the slow decomposition of the melt until 180 °C can be used for electrophilic pentafluorophenylation reactions of less nucleophilic organoelement compounds. For instance, the reactions of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P, (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-As, and (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>S in the melt result in the formation of the corresponding phosphonium, arsonium, and sulfonium salts in good yield<sup>58,65,76</sup> (eqs 57–59).



In all cases C<sub>6</sub>F<sub>6</sub> was found among the products. However, heating [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Sb or (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Bi did not effect the electrophilic arylation of Sb<sup>III</sup> or Bi<sup>III</sup>. The main products were (C<sub>6</sub>F<sub>5</sub>)<sub>n</sub>AsF<sub>5-n</sub> (n = 2, 3), which probably arise from aryl-fluorine redistribution between [AsF<sub>6</sub>]<sup>-</sup> and tris(pentafluorophenyl)antimony or -bismuth at elevated temperature (see for comparison the reaction of [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>).

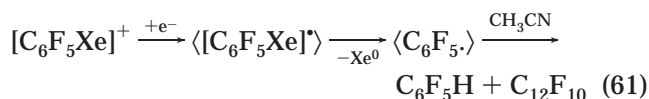
Bromo- and iodopentafluorobenzenes underwent electrophilic pentafluorophenylation in the molten salt [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>]<sup>76</sup> (eq 60).



**Electrochemical Reduction of Arylxenonium(II) Salts.** Although the mechanisms of reactions of arylxenonium salts with π- or n-electron donors have not been investigated in detail, many processes can be described in terms of the reduction–oxidation terminology. To determine the oxidation ability of arylxenonium salts, their electrochemical reduction in acetonitrile solution was studied using cyclic voltammetry.

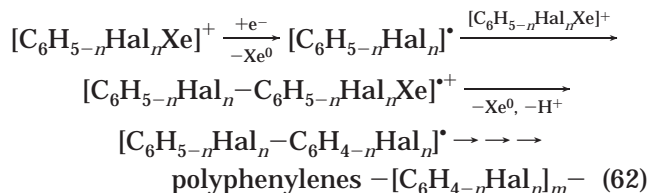
The cyclic voltammograms of [C<sub>6</sub>F<sub>5</sub>Xe][Y] (Y = BF<sub>4</sub>, AsF<sub>6</sub>) were measured in CH<sub>3</sub>CN on a glassy-carbon electrode and on a platinum-disk electrode. They showed

only one reduction peak, which reflects the irreversible electrochemical reduction of the arylxenonium cation to the arylxenonium radical. The latter then undergoes rapid elimination of xenon, generating the pentafluorophenyl radical. As a result, pentafluorobenzene and decafluorobiphenyl are the observed products<sup>77</sup> (eq 61).



The reduction potentials of both (pentafluorophenyl)-xenonium tetrafluoroborate and hexafluoroarsenate are equal to +0.45 V on a glassy-carbon electrode or +0.20 V on a platinum-disk electrode.

For the partially fluorinated salts [2,4,6-C<sub>6</sub>H<sub>2</sub>F<sub>3</sub>Xe][BF<sub>4</sub>] and [2,6-C<sub>6</sub>H<sub>3</sub>F<sub>2</sub>Xe][BF<sub>4</sub>] substantially lower potentials (Pt-disk electrode, -1.13 and -0.87 V, respectively) were measured.<sup>78</sup> However, the values of [C<sub>6</sub>H<sub>4-n</sub>R<sub>n</sub>Xe][Y] salts do not reflect the real redox properties of these salts, as also is the case for the salts [2-C<sub>6</sub>H<sub>4</sub>FXe][BF<sub>4</sub>], [4-C<sub>6</sub>H<sub>4</sub>FXe][BF<sub>4</sub>], and [4-C<sub>6</sub>H<sub>4</sub>ClXe][BF<sub>4</sub>].<sup>78</sup> The early deposition of a polyphenylene film on the surface of the cathode as a result of a radical oligomerization was assumed to be responsible for the measured low potential values<sup>77</sup> (eq 62).



### VIII. Reactions of Organoxenonium(II) Salts with Electrophiles

Polyfluoroaryl groups in arylxenonium cations are resistant toward most electrophiles. The electron-withdrawing effect of the fluorine substituents and especially the influence of the positively charged xenon atom are responsible for this behavior. No reactions were detected between [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] and the superacids aHF, FSO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H (at room temperature, during the course of some years), (Cl<sub>2</sub> + SbF<sub>5</sub>/HSO<sub>3</sub>F) (-35 °C, 1 h), and [NO<sub>2</sub>][BF<sub>4</sub>] in FSO<sub>3</sub>H (90 °C, 36 h) and between [2,3,4,5-C<sub>6</sub>HF<sub>4</sub>Xe][BF<sub>4</sub>] and Br<sub>2</sub> (excess) in CH<sub>3</sub>CN (room temperature, 22 h) or 100% HNO<sub>3</sub>-aHF (room temperature, 12 h).<sup>79</sup>

However, treatment of the salt [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] with XeF<sub>2</sub> in aHF results in xenon evolution and formation of (perfluoro-1,4-cyclohexadien-1-yl)xenonium hexafluoroarsenate. Further fluorination leads to (perfluorocyclohexen-1-yl)xenonium hexafluoroarsenate in high yield<sup>70</sup> (eq 63).

Similar ring fluorination reactions take place in the case of the [2,3,4,5-C<sub>6</sub>HF<sub>4</sub>Xe][Y] salts (Y = AsF<sub>6</sub>, BF<sub>4</sub>),

(76) Frohn, H.-J.; Klose, A.; Henkel, G. Thermally Stable Arylxenon(II) Compounds: The Salt [C<sub>6</sub>F<sub>5</sub>Xe][AsF<sub>6</sub>] and the Molecule C<sub>6</sub>F<sub>5</sub>XeO<sub>2</sub>C<sub>6</sub>F<sub>5</sub>. Presented at the 11th Winter Fluorine Conference, St. Petersburg, FL, January 1993; Paper 58.

(77) Datsenko, S.; Ignat'ev, N.; Barthen, P.; Frohn, H.-J.; Scholten, T.; Schroer, T.; Welting, D. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1669–1673.

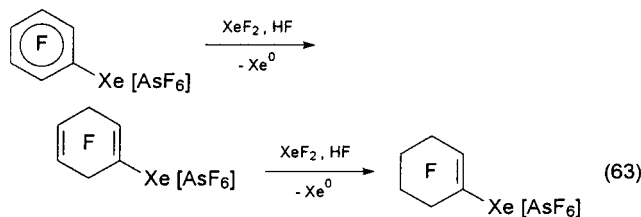
(78) Naumann, D.; Gnam, R.; Ignat'ev, N.; Datsenko, S. *Z. Anorg. Allg. Chem.* **1995**, *621*, 851–853.

(79) Frohn, H.-J.; Bardin, V. V. Unpublished results.

(73) Frohn, H.-J.; Klose, A.; Bardin, V. V. *J. Fluorine Chem.* **1993**, *64*, 201–215.

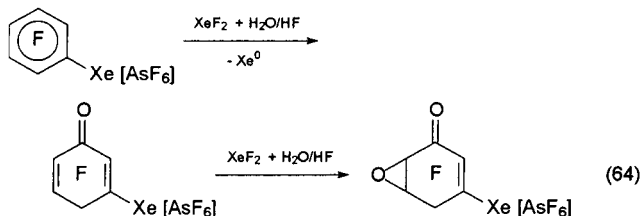
(74) Beringer, F. M.; Falk, R. A. *J. Chem. Soc.* **1964**, 4442–4451.

(75) Bailly, F.; Barthen, P.; Frohn, H.-J.; Köckerling, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2419–2427.

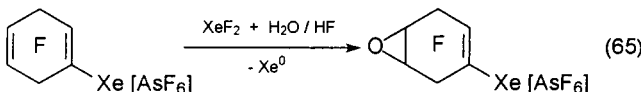


but this reaction is additionally accompanied by the partial replacement of a hydrogen atom by fluorine<sup>68</sup> (Scheme 5). It is noteworthy that under similar conditions the tetrafluorobenzenes  $\text{C}_6\text{HF}_4\text{X}$  ( $\text{X} = \text{H, F, Br, CF}_3, \text{NO}_2$ ) also undergo both reactions, ring fluorination as well as fluorodeprotonation.<sup>42</sup>

When the salt  $[\text{C}_6\text{F}_5\text{Xe}][\text{AsF}_6]$  reacts with  $\text{XeF}_2$  in  $\text{HF}$  which contains 1–2 equiv of  $\text{H}_2\text{O}$ , new types of oxygenation reactions are encountered. (Pentafluoro-1,4-cyclohexadien-3-on-1-yl)xenonium hexafluoroarsenate is the initially isolated product. In an excess of  $\text{XeF}_2$  and  $\text{H}_2\text{O}$  the latter salt undergoes epoxidation<sup>67</sup> (eq 64).



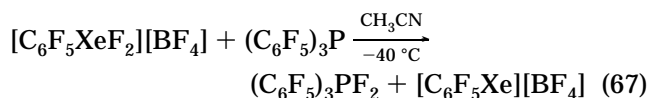
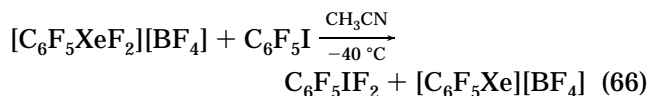
As the reactive key intermediate,  $[\text{HOXeF} \cdot n\text{HF}]$  or a related electrophilic species was assumed. Similar electrophilic oxygenation reactions proceed with the dienyloxenonium salt  $[\text{cyclo-C}_6\text{F}_7][\text{AsF}_6]$ <sup>67</sup> (eq 65) as well



as with the polyfluoroarenes  $\text{C}_6\text{F}_5\text{R}$  ( $\text{R} = \text{F, H, CF}_3, \text{NMe}_3^+, \text{OCH}_2\text{CF}_3$ , etc.)<sup>80</sup> and demonstrate the generality of this process. It is noteworthy that the  $\text{CF}=\text{CXe}^+$  moiety in cyclohexenyl derivatives in all cases is not attacked.

### IX. $[\text{C}_6\text{F}_5\text{XeF}_2][\text{BF}_4]$ , a Potential Electrophilic Fluorinating Agent

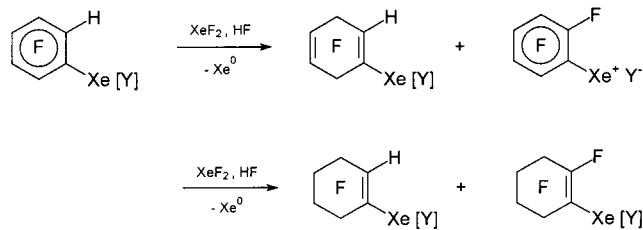
High fluorinating ability is characteristic of the salt  $[\text{C}_6\text{F}_5\text{XeF}_2][\text{BF}_4]$ . The reactions with iodopentafluorobenzene or with  $\text{P}(\text{C}_6\text{F}_5)_3$  result in the oxidative fluorination of the heteroatom with formation of the salt  $[\text{C}_6\text{F}_5\text{Xe}][\text{BF}_4]$  as the other product (eqs 66 and 67). This



means that in the competition between the fluorine

(80) Frohn, H.-J.; Bardin, V. V. *Z. Naturforsch.* **1996**, *51b*, 1015–1021.

### Scheme 5

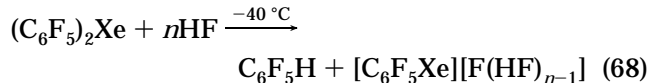


$\text{Y} = \text{AsF}_6, \text{BF}_4$ .

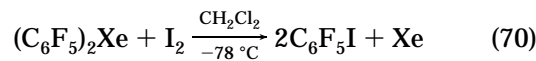
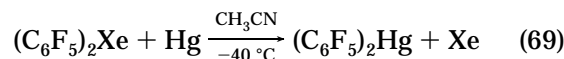
atom and the pentafluorophenyl group for the formal addition to the electron pair of I or P only the addition of fluorine is observed.<sup>10</sup>

### X. Reactions of the Covalent Xenon(II) Compounds $\text{R}_2\text{Xe}$ , $\text{RXeR}'$ , and $\text{RXeHal}$

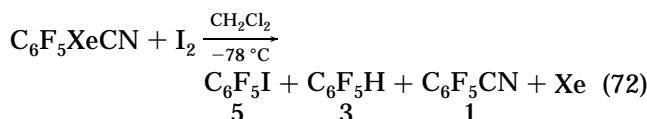
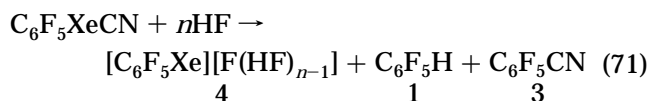
These organoxenon derivatives were synthesized only a short while ago. Consequently, only few examples of their reactivity have been studied to date. Similar to the fluorine atoms in  $\text{XeF}_2$ , both organic groups in  $(\text{C}_6\text{F}_5)_2\text{Xe}$  carry a high negative charge which is concentrated on C(1). However, only one C–Xe bond is cleaved by the action of  $\text{aHF}$  (eq 68) because in the initially formed cation  $[\text{C}_6\text{F}_5\text{Xe}]^+$  the negative charge on C(1) is strongly diminished.<sup>54</sup>



The carbon–xenon bond in  $(\text{C}_6\text{F}_5)_2\text{Xe}$  with bond order 0.5 is weaker than that in the cation  $[\text{C}_6\text{F}_5\text{Xe}]^+$  (bond order 1). In  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2$  solution total decomposition takes place within 24 or 9 h, respectively. In  $\text{CH}_3\text{CN}$   $(\text{C}_6\text{F}_5)_2$  is reported as the main product in addition to  $\text{C}_6\text{F}_5\text{H}$ ,<sup>45</sup> whereas in  $\text{CH}_2\text{Cl}_2$  a 10:1 ratio of  $\text{C}_6\text{F}_5\text{H}$  to  $(\text{C}_6\text{F}_5)_2$  was found.<sup>54</sup> Reactions of  $(\text{C}_6\text{F}_5)_2\text{Xe}$  with mercury<sup>45</sup> and with iodine<sup>54</sup> proceed formally with addition of  $\text{C}_6\text{F}_5$  radicals to Hg or I (eqs 69 and 70).

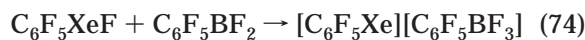
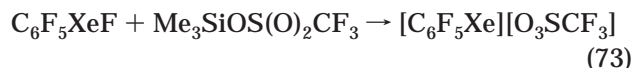


The solution of  $\text{C}_6\text{F}_5\text{XeCN}$  in dichloromethane is less stable than that of  $(\text{C}_6\text{F}_5)_2\text{Xe}$ . At  $-40^\circ\text{C}$  total decomposition proceeds within 2 h, forming  $\text{C}_6\text{F}_5\text{CN}$  and  $\text{C}_6\text{F}_5\text{H}$  (4:1) as fluoroaromatic products. Reactions of  $\text{C}_6\text{F}_5\text{XeCN}$  with  $\text{aHF}$  and  $\text{I}_2$  give the fluoroaromatic products in the indicated ratio<sup>54</sup> (eqs 71 and 72).



A remarkable decomposition of  $\text{C}_6\text{F}_5\text{XeF}$  in  $\text{CH}_2\text{Cl}_2$  proceeds above  $-30^\circ\text{C}$ .  $\text{C}_6\text{F}_5\text{H}$  and traces of  $\text{C}_6\text{F}_5\text{Cl}$  are formed.<sup>54</sup> The higher thermodynamic stability of  $[\text{C}_6\text{F}_5$

Xe][Y] salts compared to  $C_6F_5XeF$  becomes obvious in the reaction of the covalent  $C_6F_5XeF$  with Lewis acids such as  $Me_3SiOS(O)_2CF_3$ ,<sup>45</sup>  $C_6F_5BF_2$ , and  $SiF_4$ <sup>54</sup> (eqs 73–75).



### XI. Conclusions and Prospects

At the present time the following types of organoxenon compounds are known: the mononuclear xenonium(II) salts  $[RXe]^+[Y]^-$  (R = aryl, polyfluoroalkenyl, alkynyl), the binuclear xenonium(II) salts  $[(C_6F_5Xe)_2Z]^+ [AsF_6]^-$  (Z = F, Cl), the arylxenonium(IV) salt  $[C_6F_5XeF_2]^+[BF_4]^-$ , the covalent xenon(II) compounds  $C_6F_5XeZ$  (Z = F, Cl, CN, OC(O)C<sub>6</sub>F<sub>5</sub>), the symmetric diorganoxenon(II) compounds  $R_2Xe$  (R = C<sub>6</sub>F<sub>5</sub>, 2,4,6-C<sub>6</sub>H<sub>2</sub>F<sub>3</sub>), and the unsymmetrical diorganoxenon(II) compounds  $RXeR'$  (R = C<sub>6</sub>F<sub>5</sub>, R' = 2,4,6-C<sub>6</sub>H<sub>2</sub>F<sub>3</sub>).

To date there is no evidence for the existence of alkylxenon derivatives (salts or covalent species). However, recent experimental and theoretical data do not

preclude their existence and the preparation of these two classes of xenon compounds is one of the “hot” points in this field.

Additionally, organoxenonium salts offer a promising access to new xenon-element compounds because of their lower oxidation potential in comparison to the  $[FXe]^+$  cation which has been used traditionally as basis for the preparation of new xenon-element bonds.

Further progress in carbon–xenon chemistry also will deal with the application of organoxenon compounds in synthesis: for instance, in the radical and, in particular, the electrophilic introduction of organic groups R into organic molecules and organoelement compounds. The first examples of such applications have been given here. They promise a good perspective for organoxenon compounds as useful synthetic reagents.

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