Inorganic Chemistry
Article
pubs.acs.org/IC

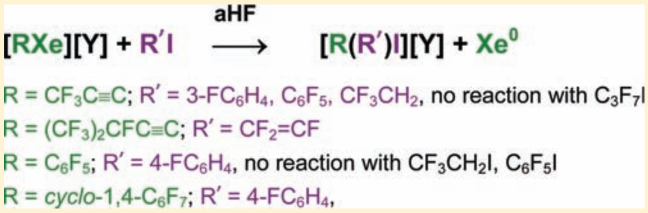
Reaction of Organylxenonium(II) Salts, [RXe][Y], with Organyl Iodides, R′I, in Anhydrous HF: Scope and Limitation of a New Synthetic Approach to Iodonium Salts, [RR′I][Y]

Hermann-Josef Frohn*,† and Vadim V. Bardin‡

†Inorganic Chemistry, University of Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany

‡N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, Acad. Lavrentjev Avenue 9, 630090 Novosibirsk, Russian Federation

ABSTRACT: Perfluoroalkynylxenonium salts, $[RXe][BF_4]$ ($R = CF_3C{\equiv}C$, $(CF_3)_2CFC{\equiv}C$), reacted with organyl iodides, R′I ($R' = 3\text{-}FC_6H_4$, C_6F_5, $CF_2{=}CF$, CF_3CH_2; no reaction with $R' = CF_3CF_2CF_2$) in anhydrous HF to yield the corresponding asymmetric polyfluorinated iodonium salts, [RR′I][Y]. The action of the arylxenonium salt, $[C_6F_5Xe][BF_4]$, and the cycloalkenylxenonium salt, [*cyclo*-1,4-C_6F_7Xe][AsF_6], on $4\text{-}FC_6H_4I$ gave $[C_6F_5(4\text{-}FC_6H_4)I][BF_4]$ and [*cyclo*-1,4-$C_6F_7(4\text{-}FC_6H_4)I$][$AsF_6$], respectively, besides the symmetric iodonium salt, $[(4\text{-}FC_6H_4)_2I][Y]$. But the aryl-, as well as the cycloalkenylxenonium salt, did not react with C_6F_5I, $CF_2{=}CFI$, and CF_3CH_2I.



■ INTRODUCTION

The preparative chemistry of organoxenon compounds was established in 1989 with the syntheses of the first unambiguously characterized salts $[C_6F_5Xe][(C_6F_5)_nBF_{4-n}]$.[1,2] During the last two decades the investigations on organylxenonium(II), organylxenonium(IV) salts, and covalent derivatives of organoxenon(II) concentrated on methodical synthetic aspects, on fundamental reactivities, and on exceptional structural and spectral features. The progress in these fields was discussed in various reviews.[3−6]

Several examples in literature describe the transfer the pentafluorophenyl group from $[C_6F_5Xe][Y]$ to a heteroatom E of an appropriate neutral nucleophile RE under formation of the corresponding onium salt $[C_6F_5(R)E][Y]$. Thus, the molten salt $[C_6F_5Xe][AsF_6]$ (mp 102 °C, dec >125 °C)[7] reacted with $(C_6F_5)_2S$, $(C_6F_5)_3P$, and $(C_6F_5)_3As$ at 130−150 °C to form the corresponding sulfonium, phosphonium, and arsonium salts, $[(C_6F_5)_{n+1}E][AsF_6]$ (E = S, $n = 2$; P and As, $n = 3$) in good yields.[1,8] The interaction of the viscous melt of $[C_6F_5Xe][AsF_6]$ with an excess of C_6F_5I or C_6F_5Br at 140 °C for 1 h gave $[(C_6F_5)_2I][AsF_6]$ and $[(C_6F_5)_2Br][AsF_6]$ in only 20% and 6% yield, respectively.[9] The reaction of $[C_6F_5Xe][(C_6F_5)_3BF]$ with C_6F_5I in acetonitrile at 20 °C was reported to give $[(C_6F_5)_2I][(C_6F_5)_3BF]$.[1] In contrast, $[C_6F_5Xe][AsF_6]$ was found not to react with iodopentafluorobenzene in solution (MeCN, 20 °C, 70 h; MeCN, 80 °C, 4 h) or in suspension (CH_2Cl_2, 80 °C, 4 h).[9,10] A negative result was also presented for the reaction of $[C_6F_5Xe][C_6F_5BF_3]$ with C_6F_5I (MeCN, −30 °C).[2] The interaction of $[C_6F_5Xe][AsF_6]$ with C_6H_5I in MeCN at ≈20 °C gave C_6F_5I (50.0%) besides $C_6F_5C_6H_4I$ (isomeric mixture, 30.2%), $C_6F_5C_6H_5$ (6.5%), and C_6F_5H (6.3%), but bis(aryl)iodonium salts were not obtained.[10] $[2,4,6\text{-}C_6F_3H_2Xe][BF_4]$ showed no reactivity in MeCN at 20 °C toward C_6F_5I over a period of 20 h, while at 60 °C $[2,4,6\text{-}C_6F_3H_2(C_6F_5)I][BF_4]$ was formed besides $1,3,5\text{-}C_6F_3H_3$ and C_6F_5H.[11] Formally, these processes can be described as electrophilic polyfluorophenylations of iodoarenes, but in fact this phenomena should be explained by the intermediate formation of Ar_FXeF for reactions in the melt or in case of reactions of arylxenonium salts with good fluoride donating anions, like $[(C_6F_5)_3BF]^-$. Arylxenonium salts with weakly coordinating anions form adducts between the arylxenonium cation and MeCN solvent, which can be described as $[Ar_FXe\text{---}NCCH_3]^+$.[12] Both structurally related species Ar_FXeF and $[Ar_FXe\text{---}NCCH_3]^+$ have in common the elongation and weakening of the C−Xe bond in comparison with $[Ar_FXe][Y]$.[6,13,14] A "nonsolvated" (or more precisely: a weakly coordinated) $[RXe]^+$ cation in combination with a strongly solvated anion exists in solutions of [RXe][Y] in highly acidic solvents like anhydrous HF (aHF). In this sense, solutions of [RXe][Y] in aHF characterize the reactivity of the nearly "naked" organylxenonium cation. This aspect was demonstrated by few reactions of organylxenonium salts with halide anions.[3,6,14] In the present work we continue our systematic research in this field and investigate the reactivity of a representative choice of perfluoroorganylxenonium(II) salts, [RXe][Y], with a selected series of organyl iodides, R′I, in aHF. The xenonium salts pentafluorophenylxenonium(II) tetrafluoroborate, $[C_6F_5Xe][BF_4]$, heptafluorocyclohexa-1,4-dien-1-ylxenonium(II) hexafluoroarsenate, [*cyclo*-1,4-C_6F_7Xe][AsF_6], trifluoroprop-1-yn-1-ylxenonium(II) tetrafluoroborate, $[CF_3C{\equiv}CXe][BF_4]$, and heptafluoro-3-methylbut-1-yn-1-ylxenonium(II) tetrafluoroborate, $[(CF_3)_2CFC{\equiv}CXe][BF_4]$,

Received: November 30, 2011
Published: January 27, 2012

dx.doi.org/10.1021/ic202576v | *Inorg. Chem.* 2012, 51, 2616−2620

are (a) representative of all actually known types of organylxenonium(II) salts and (b) are stable in aHF at ≈20 °C over a period of days ($[CF_3C{\equiv}CXe][BF_4]$ and $[(CF_3)_2CFC{\equiv}CXe][BF_4]$[15,16]) or years ($[C_6F_5Xe][BF_4]$ and $[\textit{cyclo}\text{-}1,4\text{-}C_6F_7Xe][AsF_6]$[3]).

RESULTS

We examined the synthetic potential of alk-1-yn-1-yl-, alk-1-en-1-yl-, and arylxenonium tetrafluoroborates in model reactions with organyl iodides (3-fluoroiodobenzene, 4-fluoroiodobenzene, iodopentafluorobenzene, iodotrifluoroethene, 1-iodo-2,2,2-trifluoroethane, and 1-iodoheptafluoropropane).

$[CF_3C{\equiv}CXe][BF_4]$ reacted with $3\text{-}FC_6H_4I$ (perfluoroalkynylation) in aHF at ≈20 °C to give trifluoroprop-1-yn-1-yl(3-fluorophenyl)iodonium tetrafluoroborate, $[CF_3C{\equiv}C(3\text{-}FC_6H_4)I][BF_4]$, in 50% isolated yield. Under the same conditions, $[CF_3C{\equiv}C(C_6F_5)I][BF_4]$ (87% yield) was obtained from $[CF_3C{\equiv}CXe][BF_4]$ and the perfluorinated phenyl iodide, C_6F_5I, (Scheme 1).

Scheme 1

$$[CF_3C{\equiv}CXe][BF_4] + R'I \xrightarrow[\approx 20\ ^\circ C,\ 1\ h]{aHF} [CF_3C{\equiv}C(R')I][BF_4] + Xe^0$$

$$R' = 3\text{-}FC_6H_4\ (50\%),\ C_6F_5\ (87\%)$$

The perfluoroalkynylation of iodotrifluoroethene, $CF_2{=}CFI$, with heptafluoro-3-methylbut-1-yn-1-ylxenonium tetrafluoroborate, $[(CF_3)_2CFC{\equiv}CXe][BF_4]$, proceeded slower. After 1.5 h at ≈20 °C, the conversion of $[(CF_3)_2CFC{\equiv}CXe][BF_4]$ was only 50%. After the mixture was stirred overnight, the conversion of both reagents was completed. Heptafluoro-3-methylbut-1-yn-1-yl(trifluoroethenyl)iodonium tetrafluoroborate, $[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]$, was isolated (non-optimized procedure) in 47% yield (Scheme 2).

Scheme 2

$$[(CF_3)_2CFC{\equiv}CXe][BF_4] + CF_2{=}CFI \xrightarrow[\approx 20\ ^\circ C,\ \leq 12\ h]{aHF} \underset{47\%}{[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]} + Xe^0$$

The alkyl iodide 1-iodo-2,2,2-trifluoroethane, CF_3CH_2I, reacted fast with $[CF_3C{\equiv}CXe][BF_4]$ in aHF at ≈20 °C to give trifluoroprop-1-yn-1-yl(2,2,2-trifluoroethyl)iodonium tetrafluoroborate, $[CF_3C{\equiv}C(CF_3CH_2)I][BF_4]$, in practically quantitative yield. In contrast, no reaction was detected between $[CF_3C{\equiv}CXe][BF_4]$ and the perfluorinated alkyl iodide, C_3F_7I, under the same conditions (Scheme 3).

Scheme 3

$$[CF_3C{\equiv}CXe][BF_4] + CF_3CH_2I \xrightarrow[\approx 20\ ^\circ C,\ 1\ h]{aHF} \underset{99\%}{[CF_3C{\equiv}C(CF_3CH_2)I][BF_4]} + Xe^0$$

$$[CF_3C{\equiv}CXe][BF_4] + C_3F_7I \xrightarrow[\approx 20\ ^\circ C,\ 1\ h]{aHF} \text{no reaction}$$

The interaction of the arylxenonium salt, $[C_6F_5Xe][BF_4]$, with $4\text{-}FC_6H_4I$ in aHF at ≈20 °C yielded two principal products, asymmetric pentafluorophenyl(4-fluorophenyl)iodonium tetrafluoroborate, $[C_6F_5(4\text{-}FC_6H_4)I][BF_4]$, and symmetric bis(4-fluorophenyl)iodonium tetrafluoroborate, $[(4\text{-}FC_6H_4)_2I][BF_4]$, besides minor quantities of byproduct (Scheme 4).

Scheme 4

$$[C_6F_5Xe][BF_4] + 4\text{-}FC_6H_4I \xrightarrow[\approx 20\ ^\circ C,\ 6\ h]{aHF} \underset{20\%}{[C_6F_5(4\text{-}FC_6H_4)I][BF_4]} + \underset{30\%}{[(4\text{-}FC_6H_4)_2I][BF_4]} + Xe^0 +$$

$$\underset{18\%}{C_6F_5I} + \underset{6\%}{1,4\text{-}C_6F_2H_4} + \underset{3\%}{C_6F_5H} + \underset{\leq 15\%}{C_6F_5\text{-}(F\text{-}C_6H_4)}$$

In contrast to perfluoroalkynylxenonium(II) salts, the arylxenonium salt, $[C_6F_5Xe][BF_4]$, reacted neither with iodopentafluorobenzene nor with 1-iodo-2,2,2-trifluoroethane (Scheme 5).

Scheme 5

$$[C_6F_5Xe][BF_4] + C_6F_5I\ \text{or}\ CF_3CH_2I \xrightarrow[\approx 20\ ^\circ C,\ 24\ \text{or}\ 19\ h]{aHF} \text{no reaction}$$

The reaction of $[\textit{cyclo}\text{-}1,4\text{-}C_6F_7Xe][AsF_6]$ with $4\text{-}FC_6H_4I$ proceeded at 0 °C and was completed after 2 h. The ^{19}F NMR spectrum of the reaction mixture showed the formation of asymmetric heptafluorocyclohexa-1,4-dien-1-yl(4-fluorophenyl)iodonium hexafluoroarsenate, $[\textit{cyclo}\text{-}1,4\text{-}C_6F_7(4\text{-}FC_6H_4)I][AsF_6]$, symmetric bis(4-fluorophenyl)iodonium hexafluoroarsenate, $[(4\text{-}FC_6H_4)_2I][AsF_6]$, 1-iodoheptafluorocyclohexa-1,4-diene, $\textit{cyclo}\text{-}1,4\text{-}C_6F_7I$, 1-*H*-heptafluorocyclohexa-1,4-diene, $\textit{cyclo}\text{-}1,4\text{-}C_6F_7H$, and 1,4-difluorobenzene, $1,4\text{-}C_6F_2H_4$, (Scheme 6). After removal of the volatile aryl and *cyclo*-alkenyl compounds, a mixture of the salts $[\textit{cyclo}\text{-}1,4\text{-}C_6F_7(4\text{-}FC_6H_4)I][AsF_6]$ and $[(4\text{-}FC_6H_4)_2I][AsF_6]$ was isolated.

Scheme 6

$$[\textit{cyclo}\text{-}1,4\text{-}C_6F_7Xe][AsF_6] + 4\text{-}FC_6H_4I \xrightarrow[0\ ^\circ C,\ 2\ h]{aHF} \underset{17\%}{[\textit{cyclo}\text{-}1,4\text{-}C_6F_7(4\text{-}FC_6H_4)I][AsF_6]} +$$

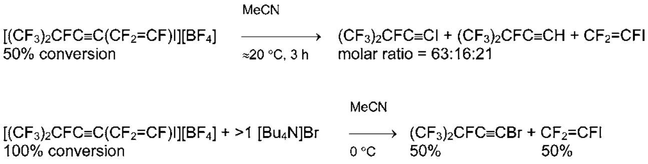
$$\underset{61\%}{[(4\text{-}FC_6H_4)_2I][AsF_6]} + Xe^0 + \textit{cyclo}\text{-}1,4\text{-}C_6F_7I + \textit{cyclo}\text{-}1,4\text{-}C_6F_7H + 1,4\text{-}C_6F_2H_4$$

The iodonium salts $[CF_3C{\equiv}C(3\text{-}FC_6H_4)I][BF_4]$, $[CF_3C{\equiv}C(CF_3CH_2)I][BF_4]$, $[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]$, and $[\textit{cyclo}\text{-}1,4\text{-}C_6F_7(4\text{-}FC_6H_4)I][AsF_6]$ were stable in aHF solutions at ≈20 °C at least one day whereas a solution of $[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]$ in MeCN decomposed at ≈20 °C with a half-life period of 3 h to 1-iodoheptafluoro-3-methylbut-1-yne, $(CF_3)_2CFC{\equiv}CI$, 1-*H*-heptafluoro-3-methylbut-1-yne, $(CF_3)_2CFC{\equiv}CH$, and iodotrifluoroethene, $CF_2{=}CFI$. The potential products with a low boiling point, $CF_2{=}CFH$ and $CF_2{=}CF_2$, were not detected (^{19}F NMR). Treatment of $[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]$ with an excess of $[Bu_4N]Br$ in MeCN at 0 °C gave 1-bromoheptafluoro-3-methylbut-1-yne, $(CF_3)_2CFC{\equiv}CBr$, and iodotrifluoroethene, $CF_2{=}CFI$ (1:1) (Scheme 7).

DISCUSSION

The iodonium salts $[CF_3C{\equiv}C(3\text{-}FC_6H_4)I][BF_4]$, $[CF_3C{\equiv}C(CF_3CH_2)I][BF_4]$, $[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]$, and $[\textit{cyclo}\text{-}1,4\text{-}C_6F_7(4\text{-}FC_6H_4)I][AsF_6]$ can be formed on two principal routes. The first one is characterized by the acid–

Scheme 7



$$\underset{\text{50\% conversion}}{[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]} \xrightarrow[\approx 20\ ^\circ C,\ 3\ h]{MeCN} \underset{\text{molar ratio = 63:16:21}}{(CF_3)_2CFC{\equiv}CI + (CF_3)_2CFC{\equiv}CH + CF_2{=}CFI}$$

$$\underset{\text{100\% conversion}}{[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4] + {>}1\ [Bu_4N]Br} \xrightarrow[0\ ^\circ C]{MeCN} \underset{50\%}{(CF_3)_2CFC{\equiv}CBr} + \underset{50\%}{CF_2{=}CFI}$$

base interaction of the positively charged xenon atom of $[RXe]^+$ with a lone pair of electrons of the iodine atom of R′I. The decomposition of the unstable intermediate **A** can be described as an internal redox reaction under elimination of Xe^0 (Scheme 8).

The alternative route includes a one electron transfer from the iodine atom of R′I to the xenon atom of $[RXe]^+$. After the fast elimination of Xe^0, the radical couple **B** is formed. The *in-cage* recombination of both radical partners leads to the corresponding asymmetric iodonium salt (Scheme 9).

For a successful reaction via the second route each $[RXe]^+$ oxidizer in Scheme 9 needs to have a higher electron affinity (EA) than the ionization potential (IP) of the reducer R′I. The IP-values of iodohalobenzenes cover the range of 8.8−8.9 eV[17] (by the best of our knowledge we could not find the IP-values of individual F−C_6H_4−I molecules) and are significantly lower than those of the other organyl iodides under investigation: $CF_2{=}CFI$ (IP = 9.55 eV)[18] < C_6F_5I (IP = 9.84 eV)[19] < CF_3CH_2I (IP = 9.99 eV)[19] < C_3F_7I (IP = 10.61 eV)[19] (from photoelectron spectra). All three types of $[RXe]^+$ oxidizer in this investigation reacted with the most easily oxidizable F−C_6H_4−I molecules. The fact that $[C_6F_5Xe][BF_4]$ and [*cyclo*-1,4-$C_6F_7Xe][AsF_6]$ did not react with the weaker reducing molecules, for example, $CF_2{=}CFI$ allows to suggest the sequence of EA values of $[RXe]^+$ cations in aHF: $[(CF_3)_2CFC{\equiv}CXe][BF_4]$, $[CF_3C{\equiv}CXe][BF_4]$ > [*cyclo*-1,4-$C_6F_7Xe][AsF_6]$, $[C_6F_5Xe][BF_4]$.

Furthermore, the formation of the byproduct C_6F_5I, C_6F_5H, C_6F_5-(F-C_6H_4), and 1,4-$C_6F_2H_4$ in the reaction of $[C_6F_5Xe][BF_4]$ with 4-FC_6H_4I is in agreement with Scheme 9 and can be explained by reactions of the escaping radicals $[R]^\bullet$ and $[R'I]^{+\bullet}$ (see lower part of Scheme 9). The route of the aryl- and alkenylxenonium salt with 4-FC_6H_4I to the observed symmetric product $[(4\text{-}FC_6H_4)_2I][Y]$ in a remarkable yield is less certain. It may be the product of the reaction of the oxidizing radical cation $[4\text{-}FC_6H_4I]^{+\bullet}$ with the precursor molecule 4-FC_6H_4I. This assumption is based on the experimental result that the fluorooxidizer SbF_5 reacted with C_6F_5I under formation of the iodonium salt $[(C_6F_5)_2I][SbF_6]$.[20] The formation of substantial amounts of $[(4\text{-}FC_6H_4)_2I][Y]$ (Scheme 4 and 6) in the reaction of $[C_6F_5Xe][BF_4]$ and [*cyclo*-1,4-$C_6F_7Xe][AsF_6]$ with 4-FC_6H_4I should proceed on a similar route. We can exclude the formation of $[(R')_2I][Y]$ by symmetrization of $[R(R')I][Y]$ in both cases, because the corresponding product $[R_2I][Y]$ was absent.

■ CONCLUSIONS

Perfluoroorganylxenonium cations $[RXe]^+$, which are weakly solvated in aHF, enable the electrophilic organylation of fluorinated organyl iodides R′I under formation of iodonium cations $[R(R')I]^+$. The process is based on the higher electron affinity of $[RXe]^+$/aHF compared with the ionization potential of R′I and likely involves a single electron transfer (SET) step.

The scope of this electrophilic organylation process allowed to deduce the ranking of [RXe][Y] salts in aHF by their electron affinity. Our results permit to conclude a sequence of electron affinity of perfluoroorganylxenonium cations: $[R_FC{\equiv}CXe]^+$ > [*cyclo*-1,4-$C_6F_7Xe]^+$, $[C_6F_5Xe]^+$. Obviously, the electron affinity of perfluoroorganylxenonium salts is higher than that of polyfluoroorganyliodonium salts in aHF, because the excess of R′I at the end of the reactions was not attacked by polyfluoroorganyliodonium salts.

■ EXPERIMENTAL SECTION

Apparatus and Materials. The NMR spectra were measured on the Bruker spectrometer AVANCE 300 (^1H at 300.13 MHz, ^{19}F at 282.40 MHz, ^{13}C at 75.46 MHz). The chemical shifts are referenced to TMS (^1H, ^{13}C) and CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)). The composition of the reaction mixtures and the yields of products in solution were determined by ^1H or ^{19}F NMR spectroscopy using internal integral standards. As a convention for NMR spectra of [R(R′)I][Y] salts, the numeration of carbon and connected fluorine or hydrogen nuclei of the R moiety (deriving from [RXe][Y] starting materials) is presented as C-1, F-1, H-1, etc., and of the R′ moiety (deriving from [R′I starting materials) by C^1, F^1, H^1, etc.

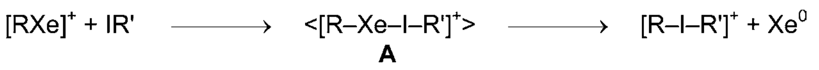
Dichloromethane (Baker) was purified by sequential treatment with conc. H_2SO_4, aqueous Na_2CO_3, and water. After drying and distillation over P_4O_{10}, it was stored over molecular sieve 3 Å. Trichlorofluoromethane (Solvay Fluor and Derivate GmbH), 1,1,2-trichlorotrifluoroethane (Merck), C_6F_5I (Aldrich), 3-FC_6H_4I (ABCR), 4-FC_6H_4I (Fluorochem), CF_3CH_2I (ABCR), and C_3F_7I (ABCR) were used as supplied. Organylxenonium(II) salts $[CF_3C{\equiv}CXe][BF_4]$, $[(CF_3)_2CFC{\equiv}CXe][BF_4]$[16], $[C_6F_5Xe][BF_4]$,[21] and [*cyclo*-1,4-$C_6F_7Xe][AsF_6]$[22] were prepared as described. $CF_2{=}CFI$, which was kindly donated by Dr. V. Cherstkov (INEOS RAN, Moscow), was stored at 4 °C in a sealed tube in the dark. Anhydrous hydrogen fluoride, aHF, was obtained by electrolysis (stainless steel cell, Ni-electrodes).

All manipulations with organylxenonium salts in aHF were performed in FEP-equipment (block copolymer of tetrafluoroethylene and hexafluoropropylene) under an atmosphere of dry argon. CAUTION: Adequate precaution is necessary when handling anhydrous hydrogen fluoride (aHF).[23] When aHF solutions were stirred at ≈20 °C in a closed FEP-trap in an intensively ventilated hood the Teflon-stopper was fixed. For subsequent operations like taking portions or working up, the solutions were cooled to 0 or −10 °C.

Reaction of $[CF_3C{\equiv}CXe][BF_4]$ with 3-FC_6H_4I in aHF. A cold (−30 °C) solution of $[CF_3C{\equiv}CXe][BF_4]$ (0.2 mmol) in aHF (0.5 mL) was added in one portion to stirred neat 3-FC_6H_4I (−20 °C, 33 mg, 0.15 mmol) in a FEP-trap. The reaction mixture was subsequently stirred in the closed trap at ≈20 °C (bath) for 1 h. All volatiles were evaporated in vacuum at ≈20 °C and the residue was washed with CH_2Cl_2 and dried. The salt $[CF_3C{\equiv}C(3\text{-}FC_6H_4)I][BF_4]$ (30 mg, 50%) was isolated as a white solid.

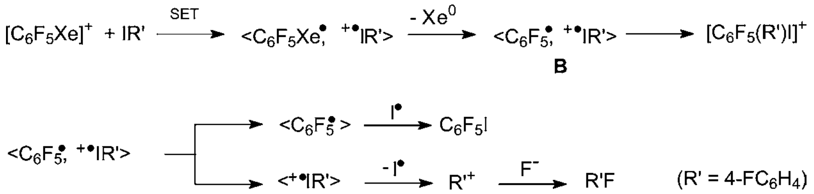
$[CF_3C{\equiv}C(3\text{-}FC_6H_4)I][BF_4]$. ^1H spectrum (aHF, 0 °C): $\delta(^1H)$ = 7.62 (m, 2H, $H^{2,6}$), 7.33 (d, 6 Hz, t, 8 Hz, 1H, H^4), 7.21 (d, 1 Hz, d, 2 Hz, t, 8 Hz, 1H, H^5) ppm. $^{13}C\{^{19}F\}$ spectrum (aHF, 0 °C): $\delta(^{13}C)$ = 116.0 (C-3), 94.1 (C-2), 24.3 (C-1) ppm; the signals of the R′ group were too weak to be measured. $^{13}C\{^1H\}$ spectrum (aHF, 0 °C): $\delta(^{13}C)$ = 115.8 (q, ^1J(C-3, F-3) = 277 Hz, C-3), 94.1 (q, ^2J(C-2, F-3) = 58 Hz,

Scheme 8



$$[RXe]^+ + IR' \longrightarrow \underset{\mathbf{A}}{<[R\text{–}Xe\text{–}I\text{–}R']^+>} \longrightarrow [R\text{–}I\text{–}R']^+ + Xe^0$$

Scheme 9



C-2), 24.3 (q, ${}^3J$(C-1, F-3) = 8 Hz, C-1), 164.1 (d, ${}^1J$(C^3, F^3) = 259 Hz, C^3), 135.1 (d, ${}^3J$(C^5, F^3) = 8 Hz, C^5), 132.2 (d, ${}^4J$(C^6, F^3) = 4 Hz, C^6), 123.4 (d, ${}^2J$(C^2, F^3) = 28 Hz, C^2), 123.2 (d, ${}^2J$(C^4, F^3) = 21 Hz, C^4), 110.7 (d, ${}^3J$(C^1, F^3) = 10 Hz, C^1) ppm. ^{19}F spectrum (aHF, 0 °C): δ(^{19}F) = −51.7 (s, 3F, F-3), −100.8 (t, 6 Hz, d, 8 Hz, 1F, F^3), −147.8 (s, 4F, $[BF_4]^-$) ppm.

Reaction of $[CF_3C{\equiv}CXe][BF_4]$ with C_6F_5I in aHF. A cold (−30 °C) solution of $[CF_3C{\equiv}CXe][BF_4]$ (0.32 mmol) in aHF (0.51 mL) was added in one portion to stirred neat C_6F_5I (−30 °C, 80 mg, 0.27 mmol). The reaction mixture was stirred in the closed trap at ≈20 °C (bath) for 1 h. The ^{19}F and ^{13}C{^{19}F} spectra showed the resonances of $[CF_3C{\equiv}C(C_6F_5)I][BF_4]$ and traces of C_6F_5I, while such of $[CF_3C{\equiv}CXe][BF_4]$ were absent. The volatiles were evaporated in vacuum at ≈20 °C and the residue was washed with CH_2Cl_2 and dried in vacuum. $[CF_3C{\equiv}C(C_6F_5)I][BF_4]$ (129 mg, 87%) was obtained as a white solid.

$[CF_3C{\equiv}C(C_6F_5)I][BF_4]$. ^{13}C{^{19}F} spectrum (aHF, 0 °C): δ(^{13}C) = 111.9 (C-3), 92.6 (C-2), 23.8 (C-1), 148.0 (C^4), 146.6 ($C^{2,6}$), 138.1 ($C^{3,5}$), 82.8 (C^1) ppm. ^{19}F spectrum (aHF, 0 °C): δ(^{19}F) = −52.0 (s, 3F, F-3), −117.3 (m, 2F, $F^{2,6}$), −134.7 (tt, ${}^4J$(F^4, F^2) = 9 Hz, ${}^3J$(F^4, F^3) = 19 Hz, 1F, F^4), −152.2 (m, 2F, $F^{3,5}$), −147.5 ppm (s, 4F, $[BF_4]^-$) (cf., ref 24).

Reaction of $[(CF_3)_2CFC{\equiv}CXe][BF_4]$ with $CF_2{=}CFI$ in aHF. A cold (−40 °C) solution of $[(CF_3)_2CFC{\equiv}CXe][BF_4]$ (0.50 mmol) in aHF (0.5 mL) was added in one portion to stirred neat $CF_2{=}CFI$ (−40 °C, 134 mg, 0.64 mmol). After the mixture was stirred at 0 °C for 1 h and at ≈20 °C for 1.5 h, the conversion of $[(CF_3)_2CFC{\equiv}CXe][BF_4]$ was ≈50% (^{19}F). Full conversion was achieved by further stirring at ≈20 °C (bath) overnight (≤12 h). After removing of the volatiles in vacuum at ≈20 °C, the residue was washed with cold (4 °C) pentane (2x 2 mL) and dried in vacuum at 4 °C to yield $[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]$ as a colorless viscous oil (116 mg, 47%). No decomposition of $[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]$ occurred in aHF at ≈20 °C over 48 h (^{19}F).

$[(CF_3)_2CFC{\equiv}C(CF_2{=}CF)I][BF_4]$. ^{11}B spectrum (aHF, −20 °C): δ(^{11}B) = −2.2 ppm (s, $[BF_4]^-$). ^{13}C{^{19}F} spectrum (aHF, −20 °C): δ(^{13}C) = 119.3 (C-4), 90.2 (C-2), 85.6 (C-3), 30.6 (C-1), 154.8 (C^2), 102.4 ppm (C^1). ^{19}F spectrum (aHF, −20 °C): δ(^{19}F) = −74.0 (d, ${}^3J$(F-4, F-3) = 10 Hz, 6F, 2CF_3), −169.2 (sept, ${}^3J$(F-3, F-4) = 10 Hz, 1F, F-3), −71.8 (dd, ${}^2J$(F^{2trans}, F^{2cis}) = 16 Hz, ${}^3J$(F^{2trans}, F^1) = 71 Hz, 1F, F^{2trans}), −90.6 (dd, ${}^2J$(F^{2cis}, F^{2trans}) = 16 Hz, ${}^3J$(F^{2cis}, F^1) = 127 Hz, 1F, F^{2cis}), −154.2 (dd, ${}^3J$(F^1, F^{2trans}) = 71 Hz, ${}^3J$(F^1, F^{2cis}) = 127 Hz, 1F, F^1), −147.8 ppm (s, 4F, $[BF_4]^-$).

Reaction of $[CF_3C{\equiv}CXe][BF_4]$ with CF_3CH_2I in aHF. A cold (−20 °C) solution of $[CF_3C{\equiv}CXe][BF_4]$ (0.30 mmol) in aHF (0.5 mL) was added in one portion to stirred neat CF_3CH_2I (−20 °C, 77 mg, 0.36 mmol). After stirring at ≈15 °C (bath) for 1 h, the volatiles were evaporated in vacuum at ≈20 °C. The residue was washed with cold (5 °C) CH_2Cl_2 and dried in vacuum. $[CF_3C{\equiv}C(CF_3CH_2)I][BF_4]$ (116 mg, 99%) was obtained as a colorless oil and identified by ^{1}H, ^{13}C{^{19}F}, ^{19}F (aHF, 0 °C).[24]

Attempted reaction of $[CF_3C{\equiv}CXe][BF_4]$ with C_3F_7I in aHF. 1-Iodoheptafluoropropane (88 mg, 0.30 mmol) was added in one portion to a stirred cold (−78 °C) solution of $[CF_3C{\equiv}CXe][BF_4]$ (0.30 mmol) in aHF (0.5 mL). Following the reaction mixture was stirred in the closed trap at ≈20 °C (bath) for 1 h. The ^{19}F and ^{13}C{^{19}F} spectra showed only the presence of the starting reagents $[CF_3C{\equiv}CXe][BF_4]$ and C_3F_7I.

Reaction of $[C_6F_5Xe][BF_4]$ with $4\text{-}FC_6H_4I$ in aHF. 4-Fluoroiodobenzene (49 mg, 0.21 mmol) was added to a solution of $[C_6F_5Xe][BF_4]$ (82 mg, 0.21 mmol) in aHF (0.8 mL) and subsequently the solution was stirred at ≈20 °C for 6 h. The ^{19}F spectrum (aHF, 0 °C) showed the complete conversion of $[C_6F_5Xe][BF_4]$ under formation of $[C_6F_5(4\text{-}FC_6H_4)I][BF_4]$ and $[(4\text{-}FC_6H_4)_2I][BF_4]$ besides byproduct. The reaction mixture was extracted with CCl_3F (1 mL) and dried in vacuum. After an additional extraction with $CClF_2CCl_2F$ the residue was dried again and consisted of $[C_6F_5(4\text{-}FC_6H_4)I][BF_4]$[25] (20% yield) and $[(4\text{-}FC_6H_4)_2I][BF_4]$[26] (30% yield) (^{1}H, ^{19}F). The combined chlorofluorocarbon extracts contained C_6F_5H, C_6F_5I, 1,4-$C_6F_2H_4$ (yields 3%, 18%, and 6%, respectively), 4-FC_6H_4I (conversion >90%), and probably, three hexafluorobiphenyls (^{19}F signals at −114.0 (1F, F^1), −139.9 (2F, F-2,6), −153.4 (1F, F-4), −161.0 ppm (2F, F-3,5); −118.0 (1F, F^1), −140.2 (2F, F-2,6), −153.5 (1F, F-4), −161.0, F-3,5); −118.7 (1F, F^1), −140.5 (2F, F-2,6), −153.6 (1F, F-4), −161.0 (2F, F3,5) (molar ratio 1:2:2; total yield 10−15%).

Attempted Reaction of $[C_6F_5Xe][BF_4]$ with C_6F_5I in aHF. Iodopentafluorobenzene (59 mg, 0.20 mmol) was added to a solution of $[C_6F_5Xe][BF_4]$ (79 mg, 0.20 mmol) in aHF (0.6 mL), and the emulsion was stirred at ≈20 °C for 24 h. The quantity of both reagents did not change (^{19}F).

Attempted Reaction of $[C_6F_5Xe][BF_4]$ with CF_3CH_2I in aHF. CF_3CH_2I (46 mg, 0.22 mmol) was added to a solution of $[C_6F_5Xe][BF_4]$ (79 mg, 0.20 mmol) in aHF (1 mL), and the solution was stirred at ≈20 °C for 19 h without change of the quantities of both reagents (^{19}F).

Reaction of [*Cyclo*-1,4-C_6F_7Xe][AsF_6] with $4\text{-}FC_6H_4I$ in aHF. A cold solution of [*cyclo*-1,4-C_6F_7Xe][AsF_6] (94 mg, 0.18 mmol) in aHF (0.6 mL) was added to a solution of 4-FC_6H_4I (51 mg, 0.23 mmol) in aHF (0.5 mL) at 0 °C and the brown reaction mixture was stirred at 0 °C for 2 h and formed a two-phase system. The ^{19}F spectrum of the upper aHF phase at 0 °C showed the complete conversion of [*cyclo*-1,4-C_6F_7Xe][AsF_6] and the presence of [*cyclo*-1,4-$C_6F_7(4\text{-}FC_6H_4)I$][$AsF_6$] and $[(4\text{-}FC_6H_4)_2I][AsF_6]$ besides byproduct. Further maintaining of the dark mixture at ≈20 °C for 16 h did not affect on the composition of products in the upper aHF phase (^{19}F). After extraction of the reaction mixture with CCl_4 (1 mL), the aHF phase was evaporated under reduced pressure and the resulting residue was dissolved in MeCN (1 mL). The freshly prepared solution contained [*cyclo*-1,4-$C_6F_7(4\text{-}FC_6H_4)I$][$AsF_6$] (0.03 mmol, 17%) and $[(4\text{-}FC_6H_4)_2I][AsF_6]$ (0.07 mmol, 61%), besides signals of unknown minor products. The carbon tetrachloride extract contained *cyclo*-1,4-C_6F_7I, *cyclo*-1,4-C_6F_7H, and 1,4-$C_6F_2H_4$.

[cyclo-1,4-$C_6F_7(4\text{-}FC_6H_4)I$][$AsF_6$]. ^{19}F spectrum (aHF, 10 °C): δ(^{19}F) = −92.5 (ttd, ${}^5J$(F-6, F-3) = 4 Hz, ${}^4J$(F-6, F-2,4) = 10 Hz, ${}^3J$(F-6, F-5) = 21 Hz, 2F, F-6), −101.0 (m, 1F, F-2), −108.5 (tdt, ${}^5J$(F-3, F-6) = 4 Hz, ${}^4J$(F-3, F-5) = 10 Hz, ${}^3J$(F-3, F-2,4) = 21 Hz, 2F, F-3), −147.1 (tt, ${}^4J$(F-5, F-3) = 11 Hz, ${}^3J$(F-5, F-6) = 21 Hz, 1F, F-5), −152.4 (tt, ${}^4J$(F-4, F-6) = 10 Hz, ${}^3J$(F-4, F-3) = 19 Hz, 1F, F-4), −96.3 (tt, ${}^4J$(F^4, $H^{2,6}$) = 4 Hz, ${}^3J$(F^4, $H^{3,5}$) = 8 Hz, 1F, F^4), −64 ppm (br, 6F, $[AsF_6]^-$). ^{19}F spectrum (MeCN): δ(^{19}F) = −95.3 (ttd, ${}^5J$(F-6, F-3) = 4 Hz, ${}^4J$(F-6, F-2,4) = 9 Hz, ${}^3J$(F-6, F-5) = 22 Hz, 2F, F-6), −94.1 (dtt, ${}^5J$(F-2, F-5) = 3 Hz, ${}^4J$(F-2, F-6) = 10 Hz, ${}^3J$(F-2, F-3) = 24 Hz, 1F, F-2), −110.5 (tddd, ${}^5J$(F-3, F-6) = 4 Hz, ${}^4J$(F-3, F-5) = 10 Hz, ${}^3J$(F-3, F-2) = 24 Hz, ${}^3J$(F-3, F-4) = 20 Hz, 2F, F-3), −148.9 (m, 1F, F-5), −155.1 (dtt, ${}^3J$(F-4, F-5) = 4 Hz, ${}^4J$(F-4, F-6) = 10 Hz, ${}^3J$(F-4, F-3) =

20 Hz, 1F, F-4), −101.6 (tt, $^4J(F^4, H^{2,6})$ = 5 Hz, $^3J(F^4, H^{3,5})$ = 8 Hz, 1F, F^4), −64.4 ppm (q(1:1:1:1), ^1J(F, As) = 931 Hz, 6F, $[AsF_6]^-$).

Decomposition of $[(CF_3)_2CFC\equiv C(CF_2{=}CF)I][BF_4]$ in MeCN Solution. Salt $[(CF_3)_2CFC\equiv C(CF_2{=}CF)I][BF_4]$ (116 mg, 0.23 mmol) was dissolved in cold (0 °C) MeCN (0.5 mL). Half of the solution was diluted with MeCN (0.3 mL) and kept at ≈20 °C for 3 h. The ^{19}F spectrum showed 50% conversion of $[(CF_3)_2CFC\equiv C(CF_2{=}CF)I][BF_4]$ under formation of $(CF_3)_2CFC\equiv CI$, $(CF_3)_2CFC\equiv CH$,[27] and $CF_2{=}CFI$ (molar ratio = 63:16:21).

$[(CF_3)_2CFC\equiv C(CF_2{=}CF)I][BF_4]$. ^{19}F spectrum (MeCN): $\delta(^{19}F)$ = −75.3 (d, ^3J(F-4, F-3) = 10 Hz, 6F, $2CF_3$), −169.1 (sept, ^3J(F-3, F-4) = 10 Hz, 1F, F-3), −77.7 (dd, $^2J(F^{2trans}, F^{2cis})$ = 27 Hz, $^3J(F^{2trans}, F^1)$ = 64 Hz, 1F, F^{2trans}), −95.4 (dd, $^2J(F^{2cis}, F^{2trans})$ = 27 Hz, $^3J(F^{2cis}, F^1)$ = 125 Hz, 1F, F^{2cis}), −157.8 (dd, $^3J(F^1, F^{2trans})$ = 64 Hz, $^3J(F^1, F^{2cis})$ = 125 Hz, 1F, F^1), −149.0 ppm (s, 4F, $[BF_4]^-$).

$(CF_3)_2CFC\equiv CI$. ^{19}F spectrum (MeCN): $\delta(^{19}F)$ = −76.3 (d, ^3J(F-4, F-3) = 10 Hz, 6F, $2CF_3$),−164.5 ppm (sept, ^3J(F-3, F-4) = 10 Hz, 1F, F-3). $^{13}C\{^{19}F\}$ spectrum (CD_3CN): $\delta(^{13}C)$ = 119.0 (C-4), 85.3 (C-3), 77.3 (C-2), 25.6 ppm (C-1).

Reaction of $[(CF_3)_2CFC\equiv C(CF_2{=}CF)I][BF_4]$ with $[Bu_4N]Br$ in MeCN. A cold (0 °C) solution of $[(CF_3)_2CFC\equiv C(CF_2{=}CF)I][BF_4]$ (58 mg, 0.11 mmol) in MeCN (0.5 mL) was treated for 15 min with a large excess of $[Bu_4N]Br$ to give $(CF_3)_2CFC\equiv CBr$ and $CF_2{=}CFI$ (1:1) (^{19}F and $^{13}C\{^{19}F\}$). $(CF_3)_2CFC\equiv CBr$. ^{19}F spectrum (MeCN): $\delta(^{19}F)$ = −76.4 (d, ^3J(F-4, F-3) = 10 Hz, 6F, $2CF_3$), −165.5 ppm (sept, ^3J(F-3, F-4) = 10 Hz, 1F, F-3). $^{13}C\{^{19}F\}$ spectrum (CD_3CN): $\delta(^{13}C)$ = 119 (C-4), 85.3 (C-3), 64.3 (C-2), 61.4 ppm (C-1).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: h-j.frohn@uni-due.de.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft, the Russian Foundation for Basic Research, and the Fonds der Chemischen Industrie.

■ REFERENCES

(1) Naumann, D.; Tyrra, W. *J. Chem. Soc., Chem. Commun.* **1989**, 47−50.

(2) Frohn, H.-J.; Jakobs, S. *J. Chem. Soc., Chem. Commun.* **1989**, 625−627.

(3) Frohn, H.-J.; Bardin, V. V. *Organometallics* **2001**, *20*, 4750−4762.

(4) (a) Brel, V. K.; Pirguliyev, N. Sh.; Zefirov, N. S. *Usp. Khim.* **2001**, *70*, 262−298. (b) Brel, V. K.; Pirguliyev, N. Sh.; Zefirov, N. S. *Russ. Chem. Rev.* **2001**, *70*, 231−264.

(5) Tyrra, W.; Naumann, D. Organoxenon compounds. In: *Inorganic Chemistry Highlights*; Meyer, G., Naumann, D., Wesemann, L., Eds.; Wiley-VCH: Weinheim, Germany, 2002; pp 297−316.

(6) Frohn, H.-J.; Bardin, V. V. Organoxenonium salts. Synthesis by "Xenodeborylation", Reactivities, and NMR Spectroscopic Properties. In *Recent Developments in Carbocation and Onium Ion Chemistry*; Laali, K. K., Ed.; ACS Symposium Series 965; American Chemical Society: Washington, DC2007; pp 428−457.

(7) Frohn, H.-J.; Klose, A.; Schroer, T.; Henkel, G.; Buss, V.; Opitz, D.; Vahrenhorst, R. *Inorg. Chem.* **1998**, *37*, 4884−4890.

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

(9) Helber, J.; Frohn, H.-J.; Klose, A.; Scholten, T. *Arkivoc* **2003**, 71−82, http://www.arkat-usa.org/ark/journal/2003/Varvoglis/AV-682A/682.pdf.

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

(11) Butler, H.; Naumann, D.; Tyrra, W. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 739−758.

(12) Koppe, K.; Frohn, H.-J.; Mercier, H. P. A; Schrobilgen, G. J. *Inorg. Chem.* **2008**, *47*, 3205−3217.

(13) Frohn, H.-J.; Bilir, V.; Bläser, D.; Boese, R. Reactions of $[C_6F_5Xe][EF_{n+1}]$ (E = B, As) and C_6F_5XeF with Alk_3SiY. Presented at the 16th European Symposium on Fluorine Chemistry, Ljubljana, Slovenia, July 18−23, 2010, oral contribution B2, abstract p 96.

(14) Koppe, K.; Bilir, V.; Frohn, H.-J.; Mercier, H. P. A; Schrobilgen, G. J. *Inorg. Chem.* **2007**, *46*, 9425−9437.

(15) Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1627−1632.

(16) Frohn, H.-J.; Bardin, V. V. *Eur. J. Inorg. Chem.* **2006**, 3948−3953.

(17) (a) Novak, I.; Kovač, B. *J. Phys. Chem.* **2005**, *109A*, 3318−3324. (b) Novak, I.; Potts, A. W. *J. Phys. Chem.* **1998**, *102A*, 3532−3536. (c) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1), 220−223.

(18) Schander, J.; Russell, B. R. *J. Mol. Spectrosc.* **1977**, *65*, 379−387.

(19) Angelo, R.; Boschi, A.; Salahub, D. R. *Can. J. Chem.* **1974**, *52*, 1217−1228.

(20) Frohn, H.-J.; Bailly, F.; Welting, D.; Bardin, V. V. *J. Fluorine Chem.* **2009**, *130*, 301−307.

(21) Frohn, H.-J.; Franke, H.; Bardin, V. V. *Z. Naturforsch., B: Chem. Sci.* **1999**, *54*, 1495−1498.

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

(23) (a) Howells, R. D.; Gilman, H. *J. Fluorine Chem.* **1975**, *5*, 99−114. (b) Peters, D.; Miethchen, R. *J. Fluorine Chem.* **1996**, *79*, 161−165.

(24) Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2008**, *634*, 82−86.

(25) Bailly, F.; Barthen, P.; Frohn, H.-J.; Koeckerling, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2419−2427.

(26) Zefirov, N. S.; Kasumov, T. M.; Koz'min, A. S.; Sorokin, V. D.; Stang, P. J.; Zhdankin, V. V. *Synthesis* **1993**, 1209−1210.

(27) Bardin, V. V.; Adonin, N. Yu.; Frohn, H.-J. *Organometallics* **2005**, *24*, 5311−5317.