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Alkynylxenon(II) Fluorides

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Alkynylxenon(II) fluorides, RC≡CXeF, have been prepared from the reactions of the corresponding trimethyl(alkynyl)silanes, $Me_3SiC{\equiv}CR$, and XeF_2 in the presence of $[NMe_4]F$ in common organic solvents at low temperature. The existence of the linear unit C≡C—Xe—F was proved for PhC≡CXeF by the ^{19}F–^{13}C NMR correlation method using the HMBC pulse sequence.

Alkynylxenon(II) derivatives were first mentioned 1992 by Zhdankin et al.[1] They reported evidence for several alkynylxenon(II) tetrafluoroborates from which [t-BuC≡CXe][BF_4] turned out as most stable and was analyzed by multinuclear NMR spectroscopic means.

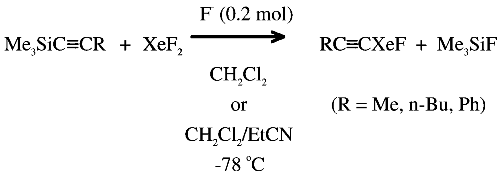
The first isolated alkynylxenon(II) compound, [$CF_3C{\equiv}CXe$][BF_4], was reported by Frohn and Bardin.[2] Salt-like [$CF_3C{\equiv}CXe$][BF_4] prepared from $CF_3C{\equiv}CBF_2$ and XeF_2 in 1,1,1,3,3-pentafluoropropane is described as a solid, stable at ambient temperature for 2−3 h,[2] while the nonfluorinated derivatives rapidly decompose at temperatures below −20 °C.[1]

Several further alkynylkrypton(II) and -xenon(II) compounds have been predicted from ab initio calculations, and structures of HC≡CNgH (Ng = Kr, Xe) have been examined by FTIR spectroscopy after UV photolysis of acetylene/noble gas mixtures at 8−40 K.[3,4]

Fluoride ion initiated arylations starting with XeF_2 and Me_3SiAr_f were successful in several cases.[5] Among those compounds, $Xe(C_6F_5)_2$[6] turned out to be the most stable one, and its molecular structure was determined from powder data.[7]

In a similar manner as trimethyl(aryl)silanes, trimethyl(alkynyl)silanes, $Me_3SiC{\equiv}CR$, can be used as transfer reagents in fluoride substitutions.[8] Reactions of trimethyl(alkynyl)silanes under fluoride ion initiation in organic synthesis were reported by Abele et al.[9,10] The reactions of several trimethyl(alkynyl)silanes with xenon difluoride and tetramethylammonium fluoride in dichloromethane or a dichloromethane/propionitrile mixture were investigated at temperatures between −78 and −30 °C by multinuclear NMR spectroscopy (Scheme 1).

Scheme 1



$$Me_3SiC{\equiv}CR + XeF_2 \xrightarrow[CH_2Cl_2 \text{ or } CH_2Cl_2/EtCN,\ -78\ ^\circ C]{F^- (0.2\ mol)} RC{\equiv}CXeF + Me_3SiF$$

(R = Me, n-Bu, Ph)

Unfortunately, the reaction of trimethyl(ethynyl)silane with xenon difluoride and tetramethylammonium fluoride in dichloromethane at −78 °C leads to indefinite decomposition products. Neither an alkynylxenon(II) compound nor xenon difluoride could be detected in the ^{19}F NMR and ^{129}Xe NMR spectra.

Trimethyl(propynyl)silane reacts with xenon difluoride under similar conditions to give propynylxenon(II) fluoride, MeC≡CXeF, (^{19}F, −24.9 ppm; $^1J(^{19}F-^{129}Xe)$, 4241 Hz). Further characterization of the compound failed due to bad reaction rates.

Trimethyl(1-hexynyl)silane reacts under these conditions with better reaction rates to give 1-hexynylxenon(II) fluoride, n-BuC≡CXeF, (^{19}F, −24.0 ppm; ^{129}Xe, −1943 ppm; $^1J(^{19}F-^{129}Xe)$, 4231 Hz).

A consecutive reaction with trimethylsilyl-trifluoromethanesulfonate, $Me_3SiOSO_2CF_3$, gave evidence for 1-hexynylxenon(II) trifluoromethanesulfonate, [n-BuC≡CXe][OSO_2CF_3] (^{129}Xe, −2197 ppm).

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(1) Zhdankin, V. V.; Stang, P. J.; Zefirov, N. S. *J. Chem. Soc., Chem. Commun.* **1992**, 578.
(2) Frohn, H.-J.; Bardin, V. V. *Chem. Commun.* **2003**, 2352.
(3) Khriachtchev, L.; Tanskanen, H.; Lundell, J.; Pettersson, M.; Kiljunen, H.; Raesanen, M. *J. Am. Chem. Soc.* **2003**, *125*, 4696.
(4) Khriachtchev, L.; Tanskanen, H.; Cohen, A.; Gerber, R. B.; Lundell, J.; Pettersson, M.; Kiljunen, H.; Raesanen, M. *J. Am. Chem. Soc.* **2003**, *125*, 6876.
(5) Bock, H. Dissertation, Universität zu Köln, 2003.
(6) Maggiarosa, N.; Naumann, D.; Tyrra, W. *Angew. Chem.* **2000**, *112*, 4759. Maggiarosa, N.; Naumann, D.; Tyrra, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4588.
(7) Bock, H.; Hinz-Huebner, D.; Ruschewitz, U.; Naumann, D. *Angew. Chem.* **2002**, *114*, 465. Bock, H.; Hinz-Huebner, D.; Ruschewitz, U.; Naumann, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 448.
(8) Tyrra, W. *Heteroat. Chem.* **2002**, *13*, 561.
(9) Abele, E.; Rubina, K.; Popelis, J.; Mazeika, I.; Lukevics, E. *J. Organomet. Chem.* **1999**, *586*, 184.
(10) Abele, E.; Rubina, K.; Arsenyan, P.; Grinberga, S.; Popelis, J.; Lukevics, E. *Main Group Met. Chem.* **2000**, *23*, 243.

10.1021/ic035394k CCC: $27.50

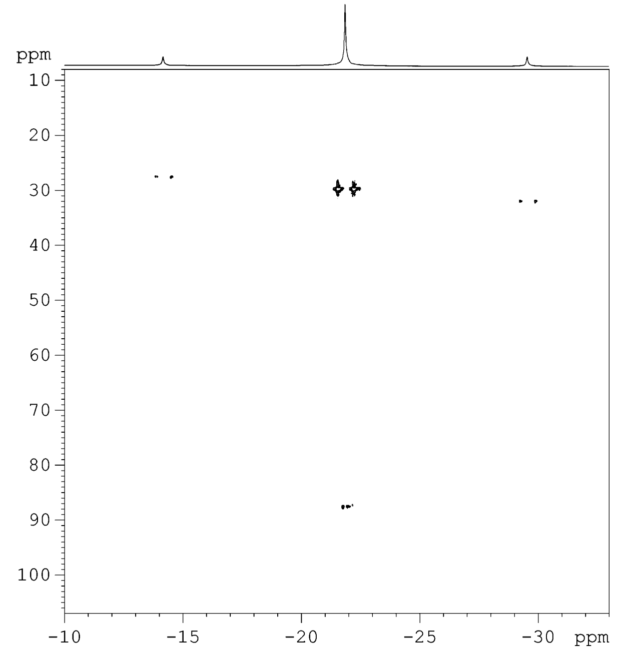

Figure 1. $^{19}F-^{13}C$ NMR HMBC spectrum of phenylethynylxenon(II) fluoride (CH_2Cl_2/EtCN, 203 K, ^{19}F (282.35 MHz), ^{13}C (75.47 MHz)).

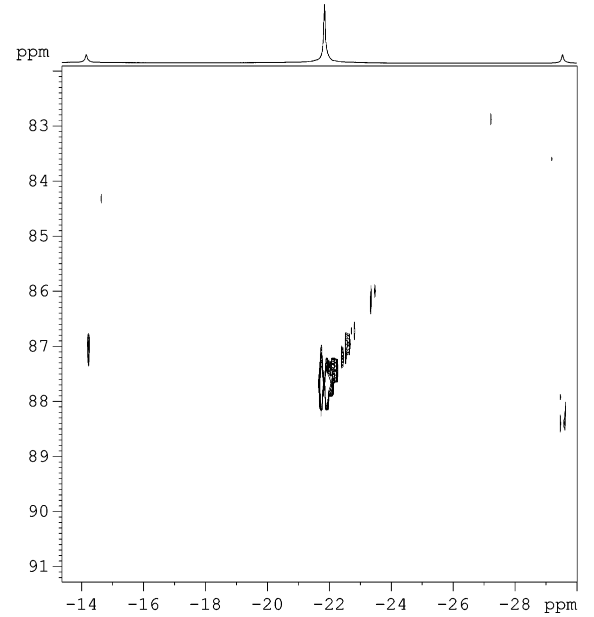

Figure 2. $^{19}F-^{13}C$ NMR HMBC spectrum of phenylethynylxenon(II) fluoride (CH_2Cl_2/EtCN, 203 K, ^{19}F (282.35 MHz), ^{13}C (75.47 MHz)), inspecting the spectrum from Figure 1 in the region of the signal of C2 of the alkynyl fragment at a lower level.

The most intensively investigated compound, phenylethynylxenon(II) fluoride, PhC≡CXeF, is formed from the reaction of trimethyl(phenylethynyl)silane, xenon difluoride, and tetramethylammonium fluoride in dichloromethane (^{19}F, −23.1 ppm; ^{129}Xe, −1887 ppm; $^{1}J(^{19}F-^{129}Xe)$, 4301 Hz) or a dichloromethane/propionitrile mixture (^{19}F, −21.9 ppm; ^{129}Xe, −1885 ppm; $^{1}J(^{19}F-^{129}Xe)$, 4331 Hz) at −78 °C.

Although phenylethynylxenon(II) fluoride appears to be the most stable of the neutral compounds which can be stored in solution at −78 °C for several weeks, NMR studies show that onset of significant decomposition occurs at temperatures above −60 °C.

The existence of the alkynylxenon fluoride moiety in these compounds is exemplarily proved by $^{19}F-^{13}C$ NMR correlation spectroscopy on phenylethynylxenon(II) fluoride in dichloromethane/propionitrile solution. For this purpose a concentrated solution was purified over two steps at −78 °C. The sample was investigated by ^{129}Xe, ^{19}F, ^{13}C NMR and $^{19}F-^{13}C$ NMR correlation spectroscopy.

The correlation spectrum was obtained by usage of an HMBC pulse sequence (Figure 1).[11]

In the $^{19}F-^{13}C$ HMBC spectrum (Figure 1), correlations are observed between the fluorine bound to xenon, easy to identify by its chemical shift and the $^{1}J(^{19}F-^{129}Xe)$ coupling of 4331 Hz, and carbon resonances at 29.8 and 87.6 ppm. Because no decoupling was performed during the acquisition time, the doublet splitting along the F2 axis gives the value of the ($^{19}F-^{13}C$) coupling constants. Additionally, correlations between the ^{129}Xe satellites of the fluorine and the ^{129}Xe satellites of the carbons occur. The ^{13}C signal at 29.8 ppm shows a ($^{129}Xe-^{13}C$) coupling of 336 Hz (Figure 1), the signal at 87.6 ppm a ($^{129}Xe-^{13}C$) coupling of 98 Hz (Figure 2). These experimental results unambiguiously prove the existence of a C≡C−Xe−F moiety in PhC≡CXeF which must be regarded as a hypervalent 3c−4e bond with respect to the C−Xe−F unit. Because of its chemical shift and its larger ($^{19}F-^{13}C$) and ($^{129}Xe-^{19}F$) couplings, the signal at 29.8 ppm must be assigned to the carbon directly bound to xenon. The signal of the carbon atom detected at 87.6 ppm is consequently assigned to the second carbon of the alkynyl group. The cross-peak of this carbon shows a lower intensity in the spectrum because the experiment was optimized on the larger ($^{19}F-^{13}C$) coupling.

From the cross-peaks and their xenon satellites in the $^{19}F-^{13}C$ NMR correlation as well as the ^{129}Xe NMR spectra, the following chemical shifts and coupling constants were obtained.

^{129}Xe:	-C≡C-**Xe**-**F**	$^{1}J(^{129}Xe-^{19}F)$:	4331	Hz
$^{19}F-^{13}C$:	-C≡**C**-Xe-F	^{13}C:	29.8	ppm
	-**C**≡C-Xe-F	^{13}C:	87.6	ppm
	-C≡**C**-**Xe**-F	$^{1}J(^{129}Xe-^{13}C)$:	336	Hz
	-**C**≡C-**Xe**-F	$^{2}J(^{129}Xe-^{13}C)$:	98	Hz
	-C≡**C**-Xe-**F**	$^{2}J(^{19}F-^{13}C)$:	182	Hz
	-**C**≡C-Xe-**F**	$^{3}J(^{19}F-^{13}C)$:	46	Hz

The observation of the $^{3}J(^{19}F-^{13}C)$ coupling between C2 of the alkyne fragment and the fluorine atom and the large value of 336 Hz for the $^{1}J(^{129}Xe-^{13}C)$ coupling between C1 and Xe is remarkable. This value is very close to that reported by Frohn and Bardin[2] (343 Hz) for $[CF_3C≡CXe][BF]_4$.

The following references were used to record the NMR spectra: ^{19}F, CCl_3F at room temperature; ^{13}C, TMS at room temperature; ^{129}Xe, XeF_2 (1 M) in CD_3CN at room temperature. All measurements were performed on a Bruker AMX300 NMR spectrometer with 10 mm broad band probe

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[11] Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

head. In the $^{19}F-^{13}C$ HMBC experiment the broad band coil was tuned to the ^{13}C frequency and the decoupler coil to ^{19}F frequency.

The reactions of trimethyl(alkynyl)silanes and XeF_2 in the presence of $[NMe_4]F$ allow the synthesis of alkynylxenon(II) fluorides, $RC\equiv CXeF$ ($R = Me$, n-Bu, Ph). These compounds are stable in solution up to −60 °C. Among those derivatives, $PhC\equiv CXeF$ was chosen for NMR spectroscopic investigations. On the basis of a complete data set, the covalent nature of the hypervalent (3c−4e) C−Xe−F unit is confirmed.

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Supporting Information Available: Plot of the ^{129}Xe NMR spectrum of phenylethinylxenon(II) fluoride and typical experimental procedures for the preparation of phenylethinylxenon(II) fluoride (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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