Preparation, Spectral Identification and Chemical Reaction of Alkynyl Xenonium Tetrafluoroborates, R–C≡C–Xe$^+$ BF$_4^-$: Novel Organoxenonium Species

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Spectroscopic and chemical evidence for the formation of alkynyl xenonium tetrafluoroborates in a low temperature reaction between lithium acetylides XeF_2 and BF_3 is reported.

Since the discovery of the first stable xenon compounds in 1962 numerous xenon(II) derivatives have been synthesized.[1] However, only a single example of a relatively stable compound with a Xe–C bond has been observed,[2] namely the pentafluorophenylxenonium salt $[C_6F_5Xe]^+[C_6F_5BF_3]^-$. Spectroscopic[3] and chemical[4] evidence for the existence of unstable alkylxenonium derivatives has also been reported. Recent theoretical calculations predict special stability for alkynyl noble gas compounds not only for Xe but even for Ne and Ar,[5] although it is known[6] that the alkynyl He species decomposes *via* loss of He and an alkynyl cation.

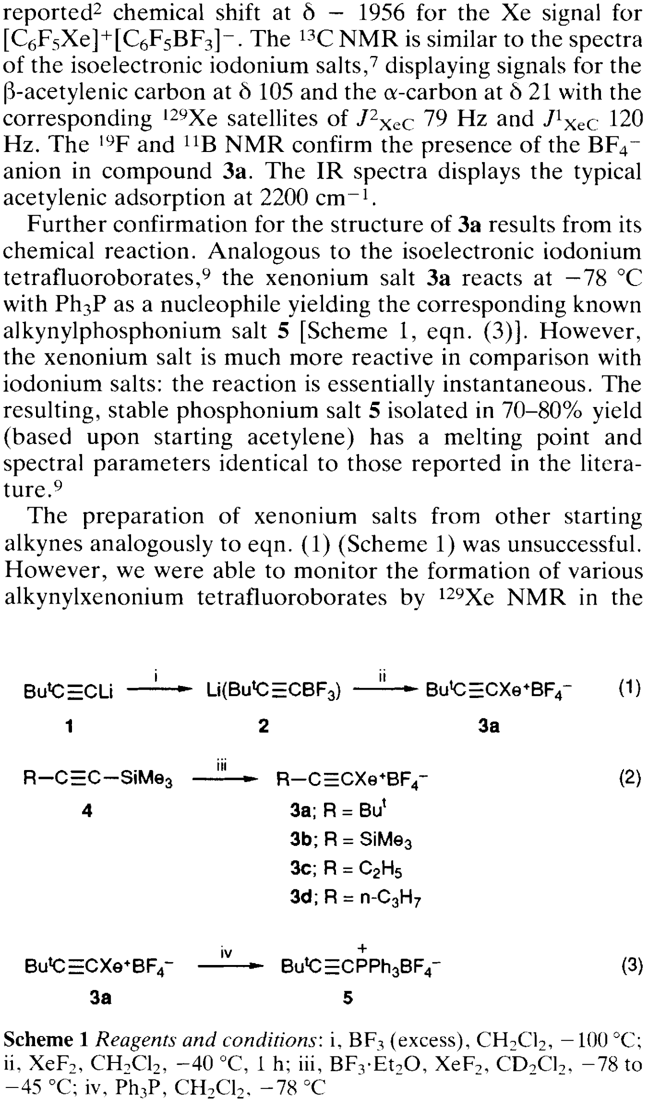
Xe^{II} species are isoelectronic with I^{III} species. In light of our recent experience with stable alkynyl iodonium salts[7] RC≡CIPh·OTf and the considerable interest in Xe–C bonds, in the present paper we report a synthetic approach to alkynyl xenonium tetrafluoroborates, their spectral identification and reaction with triphenylphosphine. We have found that the trifluoroborate complex **2**, which can be generated *in situ* from lithium *tert*-butylacetylide **1** and BF_3,[8] reacts at −40 °C with XeF_2 yielding alkynyl xenonium salt **3a** [Scheme 1, eqn. (1)].

A typical procedure for the preparation of the xenonium salt **3a** is as follows. A 2.5 mol dm^{-3} solution of n-butyllithium in hexane (0.4 ml, 1 mmol) is added to a stirred solution of *tert*-butylacetylene (0.12 ml, 1 mmol) in dry CH_2Cl_2 (20 ml) at −78 °C under nitrogen. The mixture is stirred for 10 min at −20 to −10 °C, then cooled to −100 °C and first an excess (5–10 mmol) of gaseous BF_3 followed by a solution of XeF_2 (0.17 g, 1 mmol) in CH_2Cl_2 (10 ml) is added. The resulting yellow mixture is stirred for 1 h at −40 °C; the precipitated inorganic lithium salt is filtered off at −78 °C under nitrogen and the solution concentrated in vacuum at a temperature not exceeding −40 °C yielding a dark oily residue. According to low temperature spectral data† this oil consists essentially of *tert*-butylethynylxenonium tetrafluoroborate **3a** with minor impurities (10–20%) of the decomposition products. We were not able to isolate **3a** in pure crystalline form because of its instability at temperatures above −30 °C.

Compound **3a** is identified by low temperature multinuclear NMR and IR spectra. The ^{129}Xe NMR shows an intense signal at δ − 1818 (standard XeF_2), which is close to the previously reported[2] chemical shift at δ − 1956 for the Xe signal for $[C_6F_5Xe]^+[C_6F_5BF_3]^-$. The ^{13}C NMR is similar to the spectra of the isoelectronic iodonium salts,[7] displaying signals for the β-acetylenic carbon at δ 105 and the α-carbon at δ 21 with the corresponding ^{129}Xe satellites of J^2_{XeC} 79 Hz and J^1_{XeC} 120 Hz. The ^{19}F and ^{11}B NMR confirm the presence of the BF_4^- anion in compound **3a**. The IR spectra displays the typical acetylenic adsorption at 2200 cm^{-1}.

Further confirmation for the structure of **3a** results from its chemical reaction. Analogous to the isoelectronic iodonium tetrafluoroborates,[9] the xenonium salt **3a** reacts at −78 °C with Ph_3P as a nucleophile yielding the corresponding known alkynylphosphonium salt **5** [Scheme 1, eqn. (3)]. However, the xenonium salt is much more reactive in comparison with iodonium salts: the reaction is essentially instantaneous. The resulting, stable phosphonium salt **5** isolated in 70–80% yield (based upon starting acetylene) has a melting point and spectral parameters identical to those reported in the literature.[9]

The preparation of xenonium salts from other starting alkynes analogously to eqn. (1) (Scheme 1) was unsuccessful. However, we were able to monitor the formation of various alkynylxenonium tetrafluoroborates by ^{129}Xe NMR in the



Scheme 1 *Reagents and conditions*: i, BF_3 (excess), CH_2Cl_2, −100 °C; ii, XeF_2, CH_2Cl_2, −40 °C, 1 h; iii, $BF_3{\cdot}Et_2O$, XeF_2, CD_2Cl_2, −78 to −45 °C; iv, Ph_3P, CH_2Cl_2, −78 °C

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† *Spectral data* for **3a**: NMR data ($CDCl_3$, −40 °C, Varian XL-300): ^{129}Xe NMR (standard XeF_2) δ −1818; ^{13}C NMR δ 26.9 (s, J^1_{C-Xe} 120 Hz, C≡*C*–Xe), 28.9, 30.1 (Bu^t), 105.2 (s, J^2_{C-Xe} 79 Hz, *C*≡C–Xe), the spectrum also contains signals of by-products at 40–20 ppm; ^{1}H NMR δ 1.7 (s, Bu^t); ^{19}F NMR δ − 149.9 (BF_4^-); ^{11}B NMR (standard HBF_4) δ 0.0. IR (at 0 °C, cm^{-1}) 2971 (Bu^t), 2200 (C≡C), 1060 (BF_4^-).

reaction of trimethylsilylalkynes with XeF_2 and $BF_3 \cdot Et_2O$‡ according to eqn. (2) (Scheme 1). The most intense signals in the ^{129}Xe NMR spectra in the region δ −1800 to −1900, which correspond to the organoxenonium species, are observed for the *tert*-butyl and trimethylsilyl derivatives **3a** and **3b** respectively; gradual warming of the samples usually causes evolution of Xe gas and disappearance of the signals at −20–0 °C. The ethyl and n-propyl derivatives **3c, d** are even less stable and decompose at −40 to −45 °C in 20–30 min. An attempt to prepare a xenonium salt from phenylacetylene according to this procedure resulted in an immediate formation of black tar even at −78 °C. Xe containing compounds were not observed, as monitored by ^{129}Xe NMR according to eqn. (2) (Scheme 1), with R = H, Me, CF_3, p-$MeC_6H_4SO_2$, $(Pr^i)_3Si$, $PhMe_2Si$ presumably owing either to the low stability of the products or the low reactivity of the starting trimethylsilyl substituted acetylenes.

In conclusion, the spectroscopic data and the reaction with a nucleophile support the formation of alkynyl xenonium tetrafluoroborates in a low temperature reaction between lithium or trimethylsilyl acetylides, XeF_2 and BF_3. We believe that this simple *in situ* synthetic approach to alkynyl xenonium compounds will stimulate further investigation of these compounds and related Xe–C species.

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‡ *Typical experiment*: XeF_2 (85 mg, 0.5 mmol) is dissolved in CD_2Cl_2 (0.6 ml) in an NMR tube under stirring. The solution is cooled to −78 °C and the corresponding trimethylsilylacetylene **4** (0.5 mmol) and $BF_3 \cdot Et_2O$ (0.15 ml) are added. The solution is stirred for 10 min at −50 to −45 °C and analysed by ^{129}Xe NMR (standard XeF_2, −45 °C, Varian XL-300, spectrometer frequency 83.1 MHz); δ for **3a**: −1818; **3b**: −1802; **3c**: −1810; **3d**: −1883.