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Unexpected Reactions of (Heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) Hexafluoroarsenate with Sodium Fluoride and Antimony Pentafluoride

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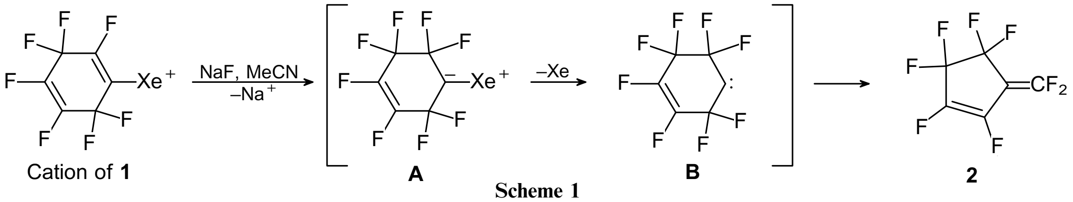
The reactivity of (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) hexafluoroarsenate **1** towards a fluoride donor and acceptor has been investigated; the interaction of **1** with NaF led to perfluoro-3-methylenecyclopentene and xenon. No dication $[C_6F_6Xe]^{2+}$ was detected by ^{19}F NMR spectroscopy when $[1\text{-}Xe^+\text{-}1,4\text{-}C_6F_7]\,[AsF_6]^-$ was treated with SbF_5–SO_2, SbF_5–SO_2FCl or neat SbF_5.

We recently reported the first preparation of the alkenylxenon(II) salts (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) **1** and (nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenates.[1] Both cations were characterized by ^{13}C, ^{19}F and ^{129}Xe NMR spectroscopy and by their conversions into the cycloolefines 1-R-1,4-C_6F_7 or 1-R-C_6F_9 (R = Br, Ph) when they were treated with the bromide anion or benzene, respectively. In both cases replacement of the xenon atom for the halogen atom or the aryl group proceeded in a similar manner to that described for pentafluorophenylxenon(II) hexafluoroarsenate.[2,3] In contrast to the above pattern of reactivity the interaction of $[C_6F_5Xe]^+[AsF_6]^-$ with the fluoride anion (“hardest” nucleophile) in MeCN led to the formation of C_6F_5H and C_6F_5–C_6F_5.[2] In the course of our investigations into organoxenon(II) derivatives we studied the interaction of compound **1** with the fluoride donor NaF as well as with the fluoride acceptor antimony pentafluoride.

Surprisingly, the interaction of diene **1** with sodium fluoride in MeCN under heterogeneous conditions resulted in the formation of perfluoro-3-methylenecyclopentene **2** accompanied by xenon evolution. Olefine **2** was the major component of the reaction mixture and was unambiguously identified by ^{19}F NMR spectroscopy.[4] Minor components were not analysed in detail, but octafluorocyclohexadienes, hydrogen-containing heptafluorocyclohexadienes or perfluorinated bi(hexadienyls) were not found.[†]

The unexpected conversion of the dienyl xenonium cation in salt **1** to cyclopentene **2** may be rationalised by assuming a preferential attack of the “hard” anionic nucleophile fluoride at the “hard” electrophilic centre C(2), rather than at the “soft” electrophilic centre xenon(II). The neutral intermediate **A** eliminated xenon to give the perfluorinated carbene **B** which underwent rearrangement into cyclopentene **2**, Scheme 1. There are related hydrocarbon carbene intermediates in other ring contractions.[5,6]



Scheme 1

Alternative pathways from **1** to **2** seem to be improbable. From the literature[7] it is known that neutral polyfluorinated 1,3- and 1,4-cyclohexadienes convert when treated with CsF in MeCN (room temperature) to thermodynamic mixtures of 1,3- and 1,4-isomers, but show no ring contraction.

The ionisation of polyfluorinated cyclohexadienes into polyfluorobenzenonium cations when they were treated with the strongest fluoride anion acceptor, antimony pentafluoride, is well documented.[8] However, the ^{19}F NMR spectra of solutions of diene **1** in SbF_5–SO_2, SbF_5–SO_2FCl or in neat SbF_5 at -50 to $+35\,^{\circ}C$ showed no observable carbocationic species. A freshly-prepared, pale-red solution in SbF_5–SO_2FCl displayed signals due to SbF_5 at -112 ppm, As-F at -56.6 ppm (very broad) and the cation of **1** at -89.6 (F-2), -93.2 (F-6,6), -146.2 (F-5) and -150.6 (F-4) ppm (the resonance of F-3,3 overlaps with the strong Sb-F signal) together with weak multiplets at -90 to -155 ppm which could not be assigned unambiguously. To our knowledge, diene **1** is the first example of polyfluorinated cyclohexadiene derivatives which did not give remarkable amounts of the corresponding benzenonium cation under the action of SbF_5.

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[†] All experiments were carried out in polytetrafluoroethylene and FEP equipment under an argon atmosphere. *(a)* Sodium fluoride (0.1 mmol) was added to a solution of diene **1** (0.03–0.04 mmol) in MeCN (0.05 ml) at $-30\,^{\circ}C$. Xenon evolution was completed within 5–10 min at room temperature, and excess NaF was filtered off. The yield of perfluoro-3-methylenecyclopentene was 68% (^{19}F NMR). *(b)* A solution of SbF_5 (1.38 mmol) in SO_2FCl (0.5 ml) was added to a suspension of diene **1** (0.095 mmol) in SO_2FCl (0.2 ml) at $-50\,^{\circ}C$. The resulting pale-red solution was analysed by ^{19}F NMR spectroscopy. Removal of SO_2FCl at room temperature gave a viscous solution which was characterized by the same ^{19}F NMR spectrum (all resonances were broadened). Further experiments in SbF_5–SO_2 and neat SbF_5 were carried out in a similar manner.