

## (Heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) and (Nonfluorocyclohexen-1-yl)xenon(II) Hexafluoroarsenates: Synthesis, Spectroscopic Characterization and Reactivity of the First Alkenylxenon(II) Compounds

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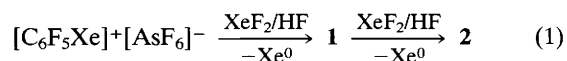
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The first alkenylxenon(II) compounds: (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) hexafluoroarsenate [1-Xe<sup>+</sup>-1,4-C<sub>6</sub>F<sub>7</sub>][AsF<sub>6</sub>]<sup>-</sup> and (nonfluorocyclohexen-1-yl)xenon(II) hexafluoroarsenate [1-Xe<sup>+</sup>-C<sub>6</sub>F<sub>9</sub>][AsF<sub>6</sub>]<sup>-</sup> were obtained by fluorination of [C<sub>6</sub>F<sub>5</sub>Xe]<sup>+</sup>[AsF<sub>6</sub>]<sup>-</sup> with XeF<sub>2</sub> in HF.

Until now, only aryl- and alkynyl-xenon(II) compounds have been prepared. The general route to arylxenon(II) compounds is based on nucleophilic substitution reactions of XeF<sub>2</sub> with Ar<sub>3</sub>B.<sup>1,2</sup> Recently the formation of the unstable alkynylxenon(II) derivatives [RC≡CXe]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> was reported by Stang *et al.*<sup>3</sup> They also used a variant of the above principle: the interaction of XeF<sub>2</sub> with Li<sup>+</sup> [Bu<sup>t</sup>C≡C-BF<sub>3</sub>]<sup>-</sup> or RC≡C-SiMe<sub>3</sub>-BF<sub>3</sub>·OEt<sub>2</sub>. The unstable salts with alkynylxenon(II) cations were characterized without isolation by their <sup>13</sup>C and <sup>129</sup>Xe NMR spectra.<sup>3</sup>

We report here the first synthesis of salts containing alkenylxenon(II) cations. We have found that treatment of pentafluorophenylxenon(II) hexafluoroarsenate with XeF<sub>2</sub> in HF at -10 to +19 °C leads to addition of two to four fluorine atoms to the aromatic ring and (heptafluoro-1,4-cyclohexadien-1-yl)xenon(II) **1** and (nonfluorocyclohexen-1-yl)xenon(II) **2** hexafluoroarsenates are formed in sequence, eqn. (1).



Both new compounds **1** and **2** are colourless solids, stable at room temperature and readily soluble in HF and MeCN. The <sup>19</sup>F NMR spectrum of **1** in HF (-30 °C) exhibits signals at δ -90.6 (F-2), -93.6 (F-6,6), -107.9 (F-3,3), -147.4 (F-5) and -151.5 (F-4) [*J*(F,F)/Hz: 21.9 (2,3), ≤1 (2,4), 3.6 (2,5), 8.6 (2,6), 19.4 (3,4), 9.6 (3,5), 3.5 (3,6), <1 (4,5), 9.5 (4,6),

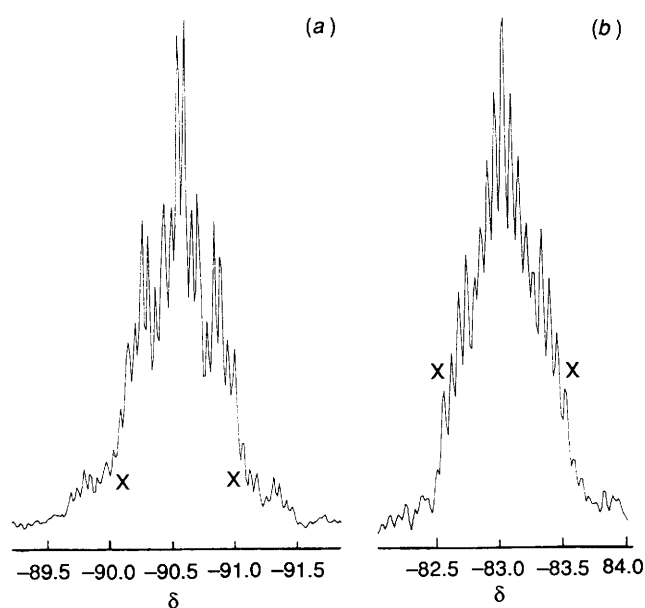


Fig. 1 <sup>19</sup>F NMR signals of the F-2 atom in **1** (a) and **2** (b) (HF, -30 °C, 5 mm tubes with FEP inliner, recorded on a Bruker WP 80 SY spectrometer at 75.4 MHz; shifts with respect to CFCl<sub>3</sub>/HF). Centres of <sup>129</sup>Xe satellites are marked by x.

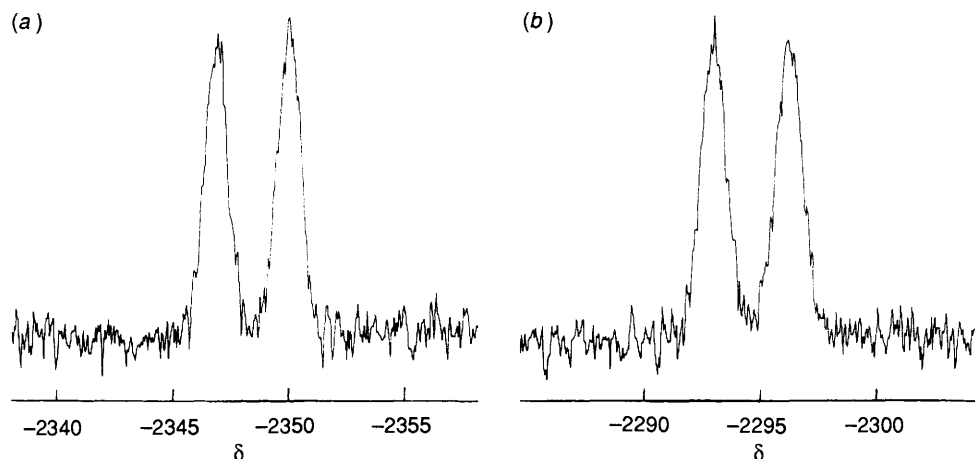


Fig. 2  $^{129}\text{Xe}$  NMR signals of **1** (a) and **2** (b) (HF,  $-30^\circ\text{C}$ , 10 mm tubes with FEP inliner, recorded on a Bruker WP 80 SY spectrometer at 22.17 MHz; shifts with respect to  $\text{XeF}_2/\text{HF}$ )

21.4 (5,6)] which are attributed to 1-(*R*)-heptafluoro-1,4-cyclohexadienes.<sup>4,5</sup> The solution of **1** in  $\text{CD}_3\text{CN}$  ( $-30^\circ\text{C}$ ) is characterized by significantly differing  $\delta(\text{F})$  values equal to  $-95.8$  (F-2,6,6),  $-110.0$  (F-3,3),  $-147.9$  (F-5), and  $-153.0$  (F-4) [ $J(\text{F},\text{F})/\text{Hz}$ : 20 (2,3), 20.5 (3,4), 12 (3,5),  $\leq 1$  (3,6), 3.6 (4,5), 9.4 (4,6), 26.8 (5,6)]. The resonance of the  $\text{AsF}_6^-$  anion appears as a relatively sharp group of four signals (1:1:1:1) in MeCN solution, whereas in HF these peaks are very broad owing to fast exchange with HF. A similar phenomenon is observed in the  $^{19}\text{F}$  NMR spectra of compound **2** in HF ( $-30^\circ\text{C}$ ) [ $\delta$   $-83.0$  (F-2),  $-99.0$  (F-6,6),  $-115.3$  (F-3,3),  $-127.7$  (F-5,5),  $-131.3$  (F-4,4);  $J(\text{F},\text{F})/\text{Hz}$ : 22.5 (2,3), 5 (2,4), 9.4 (2,6)] and in  $\text{CD}_3\text{CN}$  ( $-30^\circ\text{C}$ ) [ $\delta$   $-87.9$  (F-2),  $-101.2$  (F-6,6),  $-117.4$  (F-3,3),  $-129.7$  (F-5,5),  $-132.3$  (F-4,4);  $J(\text{F},\text{F})/\text{Hz}$ : 24 (2,3), 5 (2,4), 9.5 (2,6)]. The signals of the fluorine atom F-2 in **1** and **2** contain  $^{129}\text{Xe}$ -satellites corresponding to the natural abundance of  $^{129}\text{Xe}$  ( $I = 1/2$ ) of 26% (Fig. 1). The spin-spin coupling constant  $^3J(^{19}\text{F}-2)-(^{129}\text{Xe})$  is measured as  $70.6 \pm 1.1$  Hz for **1** (in HF) and  $72.8 \pm 1.1$  Hz (in HF) or  $84.5 \pm 1.5$  Hz (in  $\text{CD}_3\text{CN}$ ) for **2** [in  $\text{CD}_3\text{CN}$  solution of **1** the signal of F-2 overlaps with the signal of F-6,6 and is not available for  $^3J(^{19}\text{F}-2)-(^{129}\text{Xe})$  determination]. No  $^{129}\text{Xe}$ -satellites are observable in the signals of the other fluorine atoms.

The  $^{129}\text{Xe}$  NMR signal of compound **1** represents a doublet at  $\delta$   $-2348.5$  [ $^3J(^{129}\text{Xe})-(^{19}\text{F}-2)$   $68.5 \pm 1.1$  Hz] in HF [Fig. 2(a)] and at  $\delta$   $-1975.1$  [ $^3J(^{129}\text{Xe})-(^{19}\text{F}-2)$   $82.1 \pm 1.1$  Hz] in  $\text{CD}_3\text{CN}$ . The  $^{129}\text{Xe}$  NMR resonance of (nonafluorocyclohexen-1-yl) xenon(II) hexafluoroarsenate **2** is located at a higher frequency:  $\delta$   $-2294.6$  [ $^3J(^{129}\text{Xe})-(^{19}\text{F}-2)$   $69.7 \pm 1.1$  Hz] in HF [Fig. 2(b)] and at  $\delta$   $-1914.0$  [ $^3J(^{129}\text{Xe})-(^{19}\text{F}-2)$   $83.1 \pm 1.1$  Hz] in  $\text{CD}_3\text{CN}$ . Absence of observable spin-spin interactions  $^>3J(^{129}\text{Xe})-(^{19}\text{F})$  is limited by the half width  $w_{1/2} \geq 25$  Hz for **1** and **2**.

Comparing the  $\delta(^{129}\text{Xe})$  shift values of **1** and **2** with those of  $[\text{C}_6\text{F}_5\text{Xe}]^+ [\text{AsF}_6]^-$  in  $\text{CD}_3\text{CN}$  ( $-30^\circ\text{C}$ ) [ $\delta$   $-2010.1$ ,  $^3J(^{129}\text{Xe})-(^{19}\text{F}-2,6)$   $69.0 \pm 1.1$  Hz,  $w_{1/2} = 31$  Hz] and  $[\text{C}_6\text{F}_5\text{Xe}]^+ [\text{AsF}_6]^-$  in HF ( $-10^\circ\text{C}$ ) [ $\delta$   $-2380.4$ ,  $^3J(^{129}\text{Xe})-(^{19}\text{F}-2,6)$   $60.4 \pm 1.1$  Hz,  $w_{1/2} = 20$  Hz] shows a significant, high frequency chemical shift from perfluoroaromatic to perfluorocycloalkene derivatives of xenon(II) independently of solvent and their specific coordination. The deshielding of the F-2 fluorine atoms of **1** and **2** in HF relative to  $\text{CD}_3\text{CN}$  means probably a stronger coordination of the xenon atom by the nitrogen atom of  $\text{CD}_3\text{CN}$  (*cf.* ref. 6) than by the fluorine atom of  $[\text{HF}]_n$ . The stronger coordination causes a partial 'quenching' of the positive charge at  $\text{Xe}^{\text{II}}$  and diminishes the interaction of the F-2 fluorine atom with the less positively charged xenon atom.

The  $^{13}\text{C}$  NMR spectra of **1** and **2** in HF solution at  $-10^\circ\text{C}$  give resonances at  $\delta$  93.35 (C-1), 155.02 (C-2), 104.82 (C-3), 136.87 (C-4), 135.58 (C-5) and 105.45 (C-6) for **1** and at 96.28 (C-1), 155.84 (C-2), 105.60 (C-3), 105.68 (C-4), 106.73 (C-5) and 106.99 (C-6) for **2**. From the  $^{19}\text{F}$  decoupled  $^{13}\text{C}$  NMR spectrum of **2**  $^1J(^{13}\text{C}-1)-(^{129}\text{Xe})$  was determined as 113.9 Hz (doublet).

The spectral proof of compounds **1** and **2** is supported by specific chemical reactions. The interaction of the organoxenon(II) compounds of the new type with the bromide anion in acetonitrile immediately leads to xenon evolution and formation of 1-bromoheptafluoro-1,4-cyclohexadiene **3** or 1-bromononafluorocyclohexene **4**, respectively. Addition of benzene to the solution of **1** in MeCN results in 1-phenylheptafluoro-1,4-cyclohexadiene **5**, whereas 1-phenylnonafluorocyclohexene **6** is obtained from compound **2**.<sup>†</sup> It is noteworthy that the formation of bromo-olefins **3**, **4** and phenyl-olefins **5**, **6** occurs in the same way as the reaction of  $[\text{C}_6\text{F}_5\text{Xe}]^+ [\text{AsF}_6]^-$  with bromide anion or aromatic compounds.<sup>1,7</sup> Further investigations of properties and reactivity of the new type of organoxenon(II) compounds are in progress.

(Heptafluoro-1,4-cyclohexadien-1-yl) xenon(II) hexafluoroarsenate **1**. The FEP tube reactor was charged with  $[\text{C}_6\text{F}_5\text{Xe}]^+ [\text{AsF}_6]^-$  ( $523 \mu\text{mol}$ ) and HF (2 ml) and cooled to  $-15^\circ\text{C}$ .  $\text{XeF}_2$  ( $598 \mu\text{mol}$ ) in HF (1 ml) was added gradually. The resulting solution was warmed up carefully to room temp. In a few minutes  $\text{Xe}^0$  evolution was completed, and the clear colourless solution was cooled down to  $-15^\circ\text{C}$  and HF was removed in vacuum to give the white solid **1** ( $447 \mu\text{mol}$ , 85%).

<sup>†</sup> Reactions of **1** and **2** with  $\text{Br}^-$ : solution of the 3:1 mixture of **1** and **2** in MeCN was added to a stirred suspension of  $[\text{Me}_4\text{N}]\text{Br}$  (excess) in an equal volume of MeCN at room temp. In a few minutes xenon evolution was complete and bromo-olefins **3** and **4** were formed in the same ratio (quantitative yield) (identified by their  $^{19}\text{F}$  NMR spectra).<sup>5,8</sup> Reactions of **1** or **2** with benzene: benzene (50  $\mu\text{l}$ ) was dropped into the solution of **1** ( $78 \mu\text{mol}$ ) in MeCN (0.2 ml) at room temp. After 40 min the reaction mixture was treated with NaF (0.2 g), the liquid phase separated from the solid and evaporated to dryness, yielding 17 mg (77%) of 1-phenylheptafluoro-1,4-cyclohexadiene **5** [ $^1\text{H}$  NMR (acetone),  $\delta$  7.5–7.7 ( $\text{C}_6\text{H}_5$ ),  $^{19}\text{F}$  NMR (acetone),  $\delta$   $-102.2$  (F-6,6),  $-111.7$  (F-3,3),  $-131.9$  (F-2),  $-153.2$  (F-5),  $-159.1$  (F-4);  $J(\text{F},\text{F})/\text{Hz}$ : 22.4 (2,3),  $<1.5$  (2,4) and (2,5), 10.2 (2,6), 19.4 (3,4), 10.2 (3,5), 6 (3,6), 6 (4,5), 10.2 (4,6), 20.9 (5,6)]. 1-Phenylnonafluorocyclohexene **6** (26 mg, 79%) [Olefin **6** was described previously<sup>9</sup> (b.p., elemental analysis, IR spectrum) without NMR spectral data] was obtained by reaction of **2** ( $104 \mu\text{mol}$ ) with benzene (100  $\mu\text{l}$ ) in MeCN in a similar manner. [ $^1\text{H}$  NMR (acetone),  $\delta$  7.5–7.7 ( $\text{C}_6\text{H}_5$ ),  $^{19}\text{F}$  NMR (acetone),  $\delta$   $-107.4$  (F-6,6),  $-117.7$  (F-3,3),  $-125.8$  (F-2),  $-133.0$  (F-4,4,5,5)].

(Nonafluorocyclohexen-1-yl)xenon(II) hexafluoroarsenate **2** (293  $\mu\text{mol}$ , 81% yield) was obtained from  $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$  (363  $\mu\text{mol}$ ) and  $\text{XeF}_2$  (1106  $\mu\text{mol}$ ) in HF (2 ml) in a similar manner.

We gratefully acknowledge Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

Received, 31st March 1993; Com. 3/01846F

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