The First Compound with a Stable Xenon–Carbon Bond: ^{19}F- and ^{129}Xe-N.M.R. Spectroscopic Evidence for Pentafluorophenylxenon(II) Fluoroborates

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Pentafluorophenylxenon(II) fluoroborates have been synthesized by the reaction of xenon difluoride with tris(pentafluorophenyl)borane and characterized by ^{129}Xe- and ^{19}F-n.m.r. spectroscopy and by reaction with bis(pentafluorophenyl)tellurium and pentafluorophenyliodine to yield the novel cations $[(C_6F_5)_3Te]^+$ and $[(C_6F_5)_2I]^+$, respectively.

The formation of $Xe(CF_3)_2$ as an unstable solid with a half-life of 30 min at room temperature was reported in 1979,[1] but no further work on this interesting compound was published. The C–Xe bond strength in the $MeXe^+$ cation had been determined from ion cyclotron resonance methyl cation exchange equilibria[2] as 55.2 ± 2.5 kcal mol^{-1}.

Herein we report the formation of the first xenon compound with a stable xenon–carbon bond. The new compound can be obtained in solution by reacting xenon difluoride with an excess of tris(pentafluorophenyl)borane in acetonitrile at 0 °C; several by-products are also formed, reaction (1).[3] The only boron compounds we can detect using ^{19}F- and ^{11}B-n.m.r. spectroscopy are $B(C_6F_5)_3$, $[B(C_6F_5)_3F]^-$, and $BF_3 \cdot D$ (D = MeCN, F^-). These compounds can be formed in a dismutation reaction of the probably intermediately formed exchange product $B(C_6F_5)_{3-x}F_x$ according to equation (2).

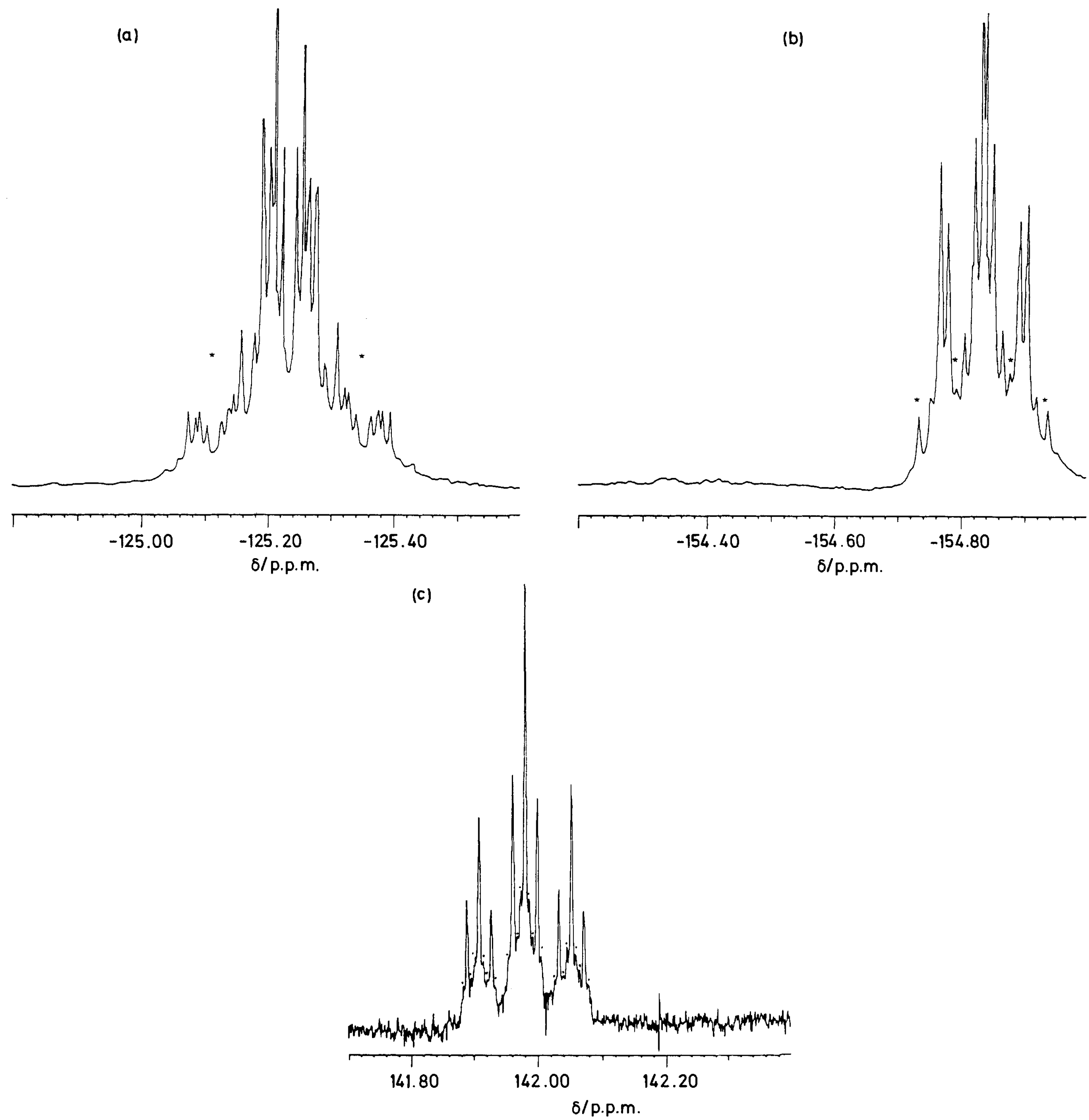

Figure 1. ^{19}F N.m.r. spectrum of the pentafluorophenylxenon cation in acetonitrile solution: (a) *o*-fluorine resonance; (b) *m*-fluorine resonance; (c) *p*-fluorine resonance. Asterisks (*) denote ^{129}Xe satellites

The resulting boron trifluoride forms weak complexes with xenon difluoride.[4] The xenon difluoride–boron trifluoride adduct is known to be a strong fluorinating reagent, which readily reacts with pentafluorobenzene derivatives to give 1-R-heptafluorocyclohexa-1,4-dienes (R = H, F, Cl, Br, C_6F_5).[5] 1-H-Heptafluorocyclohexa-1,4-diene and octafluorocyclohexa-1,4-diene have been unambiguously identified as by-products from their ^{19}F n.m.r. spectra.

$$XeF_2 + B(C_6F_5)_3 \xrightarrow{MeCN} [C_6F_5Xe][B(C_6F_5)_3F] + BF_3{\cdot}MeCN + BF_4^- \quad (1)$$

$$3\,B(C_6F_5)_{3-x}F_x \rightarrow (3-x)\,B(C_6F_5)_3 + x\,BF_3\ (x = 1,2) \quad (2)$$

The new xenon compound can easily be identified by recording ^{19}F- and ^{129}Xe-n.m.r. spectra of the reaction mixture when XeF_2 has reacted quantitatively and XeF_2 resonances are no longer detectable in the reaction mixture. The patterns of the *o*-, *m*-, and *p*-fluorine resonances show ^{129}Xe satellites (^{129}Xe: natural abundance 26.44%; I = 1/2) with the absolute values of coupling constants $^3J(^{129}Xe–F_o)$ 67.8 ± 0.4 Hz (Figure 1a), $^4J(^{129}Xe–F_m)$ 18.6 ± 0.4 Hz (Figure 1b), and $^5J(^{129}Xe–F_p)$ 4.2 ± 0.4 Hz (Figure 1c), respectively. The downfield shifts, especially for the *p*-fluorine resonance, indicate the presence of a cationic species with a large cation–anion interaction (Table 1).

The ^{129}Xe n.m.r. spectrum in acetonitrile shows a triplet of

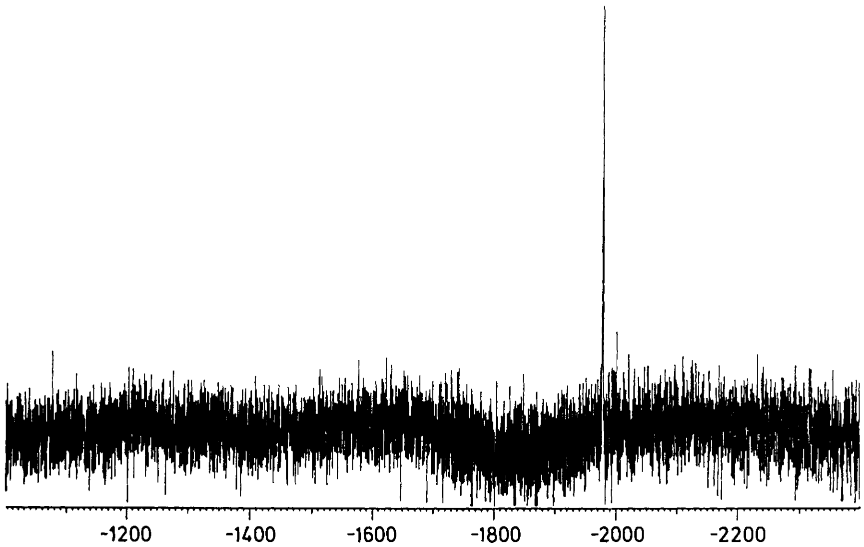

Figure 2. [129]Xe N.m.r. spectrum of the reaction mixture (chemical shift relative to internal XeF_2).

Table 1. [19]F N.m.r. parameters of the C_6F_5 derivatives.[a]

Compound	δ(*o*-F)	δ(*m*-F)	δ(*p*-F)	δ(EF)
$[C_6F_5Xe]^+$	−125.23	−154.84	−141.98	
$[(C_6F_5)_2I]^+$	−120.65	−155.67	−141.49	
$[(C_6F_5)_3Te]^+$	−122.05	−156.32	−141.47	
$[B(C_6F_5)_3F]^-$	−135.17	−166.39	−161.54	−188.91
$C_6F_5IF_2$	−123.34	−157.63	−144.87	−160.99
$(C_6F_5)_2IF$	−123.37	−157.27	−145.76	−161.12

[a] Spectra were recorded in MeCN at 20 °C using 4 mm tubes at 7.06 T, and a spectrometer frequency of 282.4 MHz. All chemical shifts were referenced to external CCl_3F. A negative chemical shift denotes a resonance occurring to low frequency (high field) of the reference compound.

multiplets 1 980 p.p.m. upfield from external xenon difluoride in CD_3CN.† The expected resonance for the $XeC_6F_5^+$ cation is a triplet of triplets of doublets resulting from the spin–spin interaction of the xenon nucleus with two *o*-, two *m*-, and one *p*-fluorine atoms of a single pentafluorophenyl group bound to xenon. Due to the signal width of approximately 40 Hz (Figure 2) we could only observe the main splitting $^3J(^{129}Xe–F_o)$ 68 Hz for the triplet resulting from the spin–spin coupling of xenon with the *o*-fluorine atoms. The formation of $Xe(C_6F_5)_2$ can be excluded, because we would expect a primary splitting of the Xe signal into a quintet. Whether the xenon cation forms a 1 : 1 adduct with acetonitrile[6] can neither be proved nor disproved from the n.m.r. spectra.

The [13]C n.m.r. spectrum in CH_2Cl_2–MeCN (1 : 1 mixture) at −12 °C external ref. Me_4Si gives resonances at δ83.5 (C-1), 144.2 (C-2,-6), 138.3 (C-3,-5), and 142.5 (C-4), respectively. Owing to the low intensity of the C-1 resonance no splittings

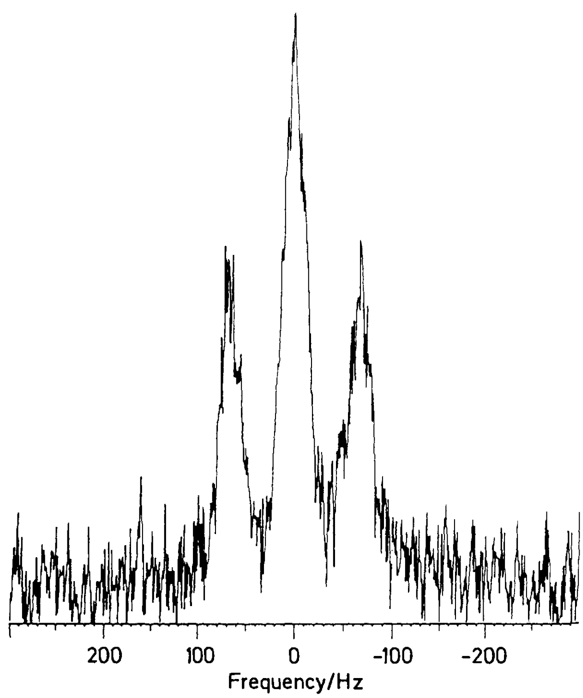

Figure 3. [129]Xe Resonance of C_6F_5Xe.

can be observed. The chemical shift of the C-1 atom and the unexpected upfield shift of the Xe atom can be explained by a partial Xe–C double bond.

In order to investigate the reactivity of the new compound, the XeF_2-free solution was reacted with water, potassium fluoride, bis(pentafluorophenyl)tellurium, and pentafluorophenyl iodine. In the presence of water or deuterium oxide the pentafluorophenylxenon cation rapidly hydrolyses to give pentafluorobenzene or deuteropentafluorobenzene, respectively. The reaction with potassium fluoride gives elemental xenon, hexafluorobenzene, and potassium tris(pentafluorophenyl)fluoroborate. The formation of hexafluorobenzene

† The previously recorded value of 1 014 p.p.m. downfield relative to internal XeF_2 must be corrected. Referring to discussions with H. J. Frohn[3] at the 12th International Symposium on Fluorine Chemistry in Santa Cruz, U.S.A. (August 1988), we re-investigated the [129]Xe n.m.r. spectrum and found that we had measured a folding of the XeF_2 signal, which was not detectable in our spectrum. So we have to state that the value measured by H. J. Frohn is correct.

indicates the presence of an unstable intermediate pentafluorophenylxenon fluoride, which decomposes according to equations (3) and (4). With bis(pentafluorophenyl)tellurium and pentafluorophenyl iodine the novel tris(pentafluorophenyl)tellurium and bis(pentafluorophenyl)iodine cations are formed, equations (5) and (6).

$$[C_6F_5Xe][B(C_6F_5)_3F] + KF \rightarrow \langle C_6F_5XeF \rangle + K[B(C_6F_5)_3F] \quad (3)$$

$$\langle C_6F_5XeF \rangle \rightarrow C_6F_6 + Xe \quad (4)$$

$$[C_6F_5Xe][B(C_6F_5)_3F] + Te(C_6F_5)_2 \rightarrow [(C_6F_5)_3Te][B(C_6F_5)_3F] + Xe \quad (5)$$

$$[C_6F_5Xe][B(C_6F_5)_3F] + C_6F_5I \rightarrow [(C_6F_5)_2I][B(C_6F_5)_3F] + Xe \quad (6)$$

The new iodine compound can also be prepared by reacting pentafluorophenyliodine difluoride with tris(pentafluorophenyl)boron under conditions comparable to those required for the formation of the pentafluorophenylxenon cation. The resulting bis(pentafluorophenyl)iodonium tris(pentafluorophenyl)fluoroborate can be converted into bis(pentafluorophenyl)iodine fluoride by adding KF, equation (7).

$$[(C_6F_5)_2I][B(C_6F_5)_3F] + KF \rightarrow (C_6F_5)_2IF + K[B(C_6F_5)_3F] \quad (7)$$

These reactions, as well as the n.m.r. spectra, lead to the conclusion that when xenon difluoride reacts with tris(pentafluorophenyl)boron under certain conditions pentafluorophenylxenon tris(pentafluorophenyl)fluoroborate is formed.

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