The Pentafluorophenylxenon(II) Cation: [C₆F₅Xe]⁺; The First Stable System with a Xenon–Carbon Bond

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Pentafluorophenylxenon(II) pentafluorophenyltrifluoroborate, $[C_6F_5Xe]^+$ $[C_6F_5BF_3]^-$, can be prepared analogously to pentafluorophenylhalogen(III) and (V) fluorides, $C_6F_5HalF_2$ and $C_6F_5HalF_4$ (with Hal = Br or I), by nucleophilic displacement of fluorine in XeF_2 using $B(C_6F_5)_3$ as an aryl-transfer reagent; the resulting colourless solid with a stable xenon–carbon bond is characterised in solution by [129]Xe and [19]F n.m.r. and chemically as an electrophilic transfer reagent for pentafluorophenyl groups.

Since the discovery of the first xenon compound by Bartlett in 1962[1] a large number of xenon compounds with bonds to fluorine, oxygen, and nitrogen have been realised.[2,3] Until today however, there has been no report of a well characterised stable xenon–carbon bond system[4] apart from Lagow's report of $Xe(CF_3)_2$ in 1979.[5]

At a recent Symposium we reported[6] the first synthesis of $[C_6F_5Xe]^+$ $[C_6F_5BF_3]^-$ whereby an excess of XeF_2 was reacted with $B(C_6F_5)_3$ in CH_2Cl_2 at $-30\,°C$ in an FEP-reactor. After separation and purification, $[C_6F_5Xe]^+$ $[C_6F_5BF_3]^-$ was isolated as a colourless solid (yield ~40%) and identified by ^{19}F and [129]Xe n.m.r. spectroscopy in MeCN solution.
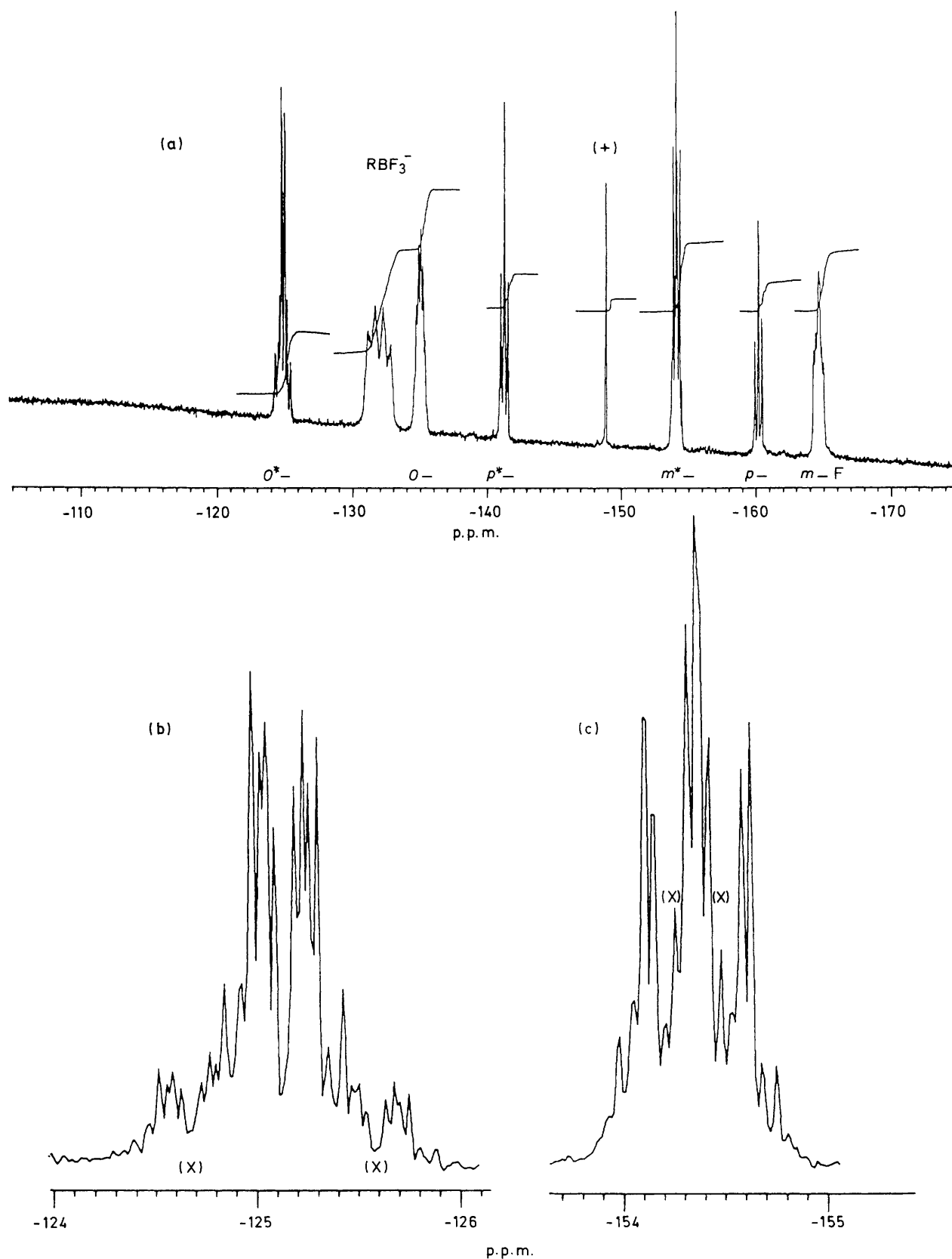
Figure 1. (a—c) ^{19}F n.m.r. spectrum of $[C_6F_5Xe]^+$ $[C_6F_5BF_3]^-$ in MeCN at $-30\,^\circ$C (5 mm tubes with FEP inliner, recorded on a Bruker WP 80 SY spectrometer at 75.39 MHz); shifts are with respect to CCl_3F. In (a) resonances of the $[C_6F_5Xe]^+$ cation are labelled by asterisks ($+$ denotes $[BF_4]^-$ impurity). (b) and (c) represent *ortho*- and *meta*-fluorine resonance. Centres of ^{129}Xe satellites are marked by $\times$.

Table 1. ^{19}F n.m.r. chemical shifts^a δ/p.p.m. of ionic C_6F_5-species.

Species	δ (o-F)	δ (p-F)	δ (m-F)	δ (E-F)
$[C_6F_5Xe]^+$	−125.13	−141.55	−154.34	
$[(C_6F_5)_2Br]^{+\ b}$	−128.91	−139.12	−154.89	−150.58
$[(C_6F_5)_2I]^{+\ b}$	−119.93	−139.92	−155.91	−149.25
$[C_6F_5BF_3]^-$	−135.29	−160.45	−164.87	−132.19

^{a} Recorded in MeCN at −30 °C (5 mm tubes with FEP inliners) using a Bruker WP 80 SY spectrometer (75.39 MHz). ^{b} Measured as BF_4^- salt. (Shifts are with respect to CCl_3F. Negative values describe upfield shifts.)
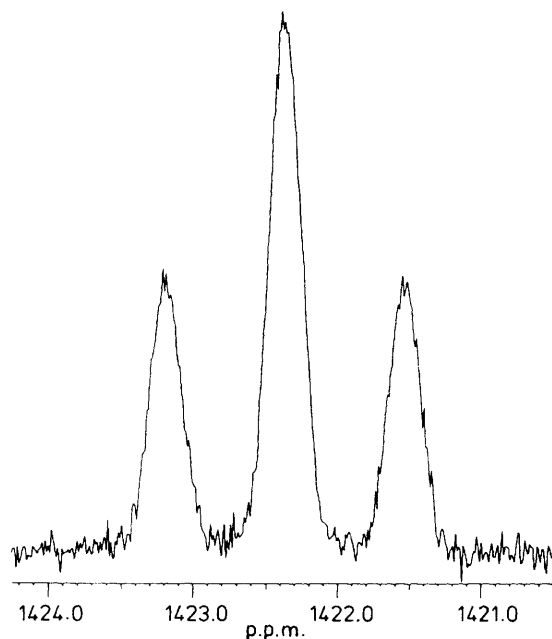

Figure 2. ^{129}Xe n.m.r. spectrum of $[C_6F_5Xe]^+$ $[C_6F_5BF_3]^-$ in MeCN at −30 °C (10 mm tubes with FEP inliner, recorded on a Bruker WM 300 spectrometer at 83.03 MHz); shift with respect to Xe^0.
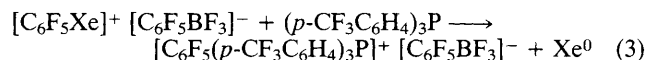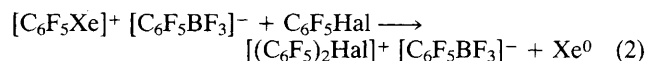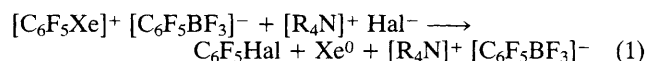
The ^{19}F n.m.r. spectrum shows two C_6F_5 groups of equal intensity with typical patterns for *ortho-*, *meta-* and *para-*fluorine positions (Figure 1). Resonances at −125.13 (*o*-, rel. int. 2), −154.34 (*m*-, rel. int. 2), and −141.55 p.p.m. (*p*-, rel. int. 1) are assigned to the $[C_6F_5Xe]^+$ cation. An argument in favour of the Xe–C_6F_5 bond is the n.m.r. pattern of the *ortho-* and *meta-*fluorine atoms which shows ^{129}Xe-satellites corresponding to the natural abundance of ^{129}Xe (I = 1/2) of 26%. Spin–spin coupling constants $|^3J(^{129}Xe-^{19}F)|$ of 67.8 ± 1.1 Hz and $|^4J(^{129}Xe-^{19}F)|$ of 19.5 ± 1.1 Hz are measured [Figure 1(b) and 1(c)]. There are two factors in the n.m.r. which are significant to the cationic species $[C_6F_5Xe]^+$. Firstly, the low-field *ortho-*fluorine position is typical for C_6F_5-groups bonded to low co-ordinated heavy elements like Zn, Cd, Hg, or I. Secondly the low field *para-*fluorine position is found in

the same region as in the cationic species $[(C_6F_5)_2I]^+$ ^{7} and $[(C_6F_5)_2Br]^+$ ^{8} (Table 1) and can be interpreted in terms of an aryl back-bond to xenon(II). The ^{129}Xe n.m.r. (Figure 2) consists of a triplet at 1422 p.p.m. downfield from Xe^0 (or 1950 p.p.m. upfield from XeF_2) caused by the $|^3J(^{129}Xe-^{19}F)|$ spin–spin coupling of 69.1 ± 2.7 Hz which is in agreement with the ^{19}F n.m.r. results (Figure 1). The half width ($w_{\frac{1}{2}}$) of 22 Hz does not allow the detection of $^4J(^{129}Xe-^{19}F)$ in the ^{129}Xe spectrum.

The $[C_6F_5BF_3]^-$ anion is characterised by ^{19}F n.m.r. resonances at −135.29 (*o*-, rel. int. 2), −164.87 (*m*-, rel. int. 2), −160.45 (*p*-, rel. int. 1), and −132.19 p.p.m. ($[RBF_3]^-$, rel. int. 3).

We also report for the first time some of the chemical properties of $[C_6F_5Xe]^+$ $[C_6F_5BF_3]^-$, concerning its thermal stability in solution, reactions with nucleophiles, and hydrolysis.

In MeCN solution at 35 °C, $[C_6F_5Xe]^+$ $[C_6F_5BF_3]^-$ shows a half-life of >2 h. Decomposition products are $(C_6F_5)_2$ and C_6HF_5, formed by radical attack on the solvent. No decomposition occurred during storage at −60 °C. $[C_6F_5Xe]^+$ reacts with halide ions (Hal^- = I^- and Br^-) in MeCN at −30 °C with formation of C_6F_5Hal [equation (1)]. At −30 °C, no electrophilic attack of $[C_6F_5Xe]^+$ on soft basic centres in C_6F_5Hal or $(p\text{-}CF_3C_6H_4)_3P$ according to equations (2) or (3) can be observed. In MeCN solution, hydrolysis with formation of C_6HF_5 occurs spontaneously when water is present.

$$[C_6F_5Xe]^+\ [C_6F_5BF_3]^- + [R_4N]^+\ Hal^- \longrightarrow$$
$$C_6F_5Hal + Xe^0 + [R_4N]^+\ [C_6F_5BF_3]^- \quad (1)$$

$$[C_6F_5Xe]^+\ [C_6F_5BF_3]^- + C_6F_5Hal \longrightarrow$$
$$[(C_6F_5)_2Hal]^+\ [C_6F_5BF_3]^- + Xe^0 \quad (2)$$

$$[C_6F_5Xe]^+\ [C_6F_5BF_3]^- + (p\text{-}CF_3C_6H_4)_3P \longrightarrow$$
$$[C_6F_5(p\text{-}CF_3C_6H_4)_3P]^+\ [C_6F_5BF_3]^- + Xe^0 \quad (3)$$

We are continuing our preparative work on aryl–xenon compounds and their reaction chemistry, as well as structural investigations on this new class of compounds.

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