Fluoro(nitrile)xenon(II) Cations, $RC{\equiv}N{-}XeF^+$ AsF_6^- (R = H, CH_3, CH_2F, C_2H_5, C_2F_5, C_3F_7, or C_6F_5); Novel Examples of Xenon–Nitrogen Bonds and $^{129}Xe{-}^{13}C$, $^{129}Xe{-}^{1}H$, and $^{129}Xe{-}^{14}N$ Nuclear Spin–Spin Couplings

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A new class of Xe–N bonded compound results from the interaction of the electron lone pair of a nitrile with the Lewis acid, XeF^+; the cationic adducts, $RC{\equiv}N{-}XeF^+$, have been derived from the interaction of the appropriate nitrile with either $XeF^+AsF_6^-$ or $Xe_2F_3^+AsF_6^-$ in anhydrous HF at low temperature and characterized in the solid state by Raman spectroscopy (for R = H and Me) and in HF solution by ^{129}Xe, ^{19}F, ^{14}N, ^{13}C, and ^{1}H n.m.r. spectroscopy.

Herein we report a new ligand group for xenon which is bonded to the noble gas atom through nitrogen. In choosing a likely ligand precursor for a Xe–C or Xe–N bond, the very weak protonic acid HCN was considered and initially found to be unreactive towards XeF_2 in SO_2ClF at room temperature by the usual HF displacement to give the Xe–C and Xe–N bonded compounds, FXe(CN) and $Xe(CN)_2$. Although the conventional HF displacement is not a viable route to xenon(II) cyanides and isocyanides, we have found that HCN, and nitriles in general, behave as nitrogen bases towards the XeF^+ cation.

The reactions of $XeF^+AsF_6^-$ and $Xe_2F_3^+AsF_6^-$ with HCN, CH_3CN, CH_2FCN, C_2H_5CN, C_2F_5CN, C_3F_7CN, and C_6F_5CN were carried out by combining stoicheiometric amounts of the reactants in anhydrous HF and warming to −20 to −10 °C to effect reaction and dissolution in the solvent (HCN reactions were also conducted in SO_2ClF solvent). The reactions proceed according to equations (1) and (2).

$$\underset{(\mathbf{1})}{XeF^+AsF_6^-} + RC{\equiv}N{:} \longrightarrow \underset{(\mathbf{2})}{RC{\equiv}N{-}XeF^+AsF_6^-} \qquad (1)$$

$$Xe_2F_3^+AsF_6^- + (\mathbf{1}) \longrightarrow (\mathbf{2}) + XeF_2 \qquad (2)$$

Multinuclear magnetic resonance spectra were recorded for the nitrile cations in HF solvent, and in the case of the ^{1}H and ^{129}Xe n.m.r. spectra of the $HC{\equiv}N{-}XeF^+$ cation, in BrF_5 solvent. As every element in the $RC{\equiv}N{-}XeF^+$ cations studied possesses at least one nuclide which is suitable for observation by n.m.r. spectroscopy, n.m.r. studies using both naturally abundant and ^{13}C enriched compounds were undertaken and have provided unambiguous proof for the structures of a majority of the cations in solution (Table 1). In the case of $HC{\equiv}N{-}XeF^+$, the chemical shifts of all five nuclei and eight of the ten possible spin–spin couplings that have been observed are listed in Table 1. The ^{129}Xe, ^{14}N, ^{13}C, and ^{1}H spectra are illustrated in Figures 1 and 2. The couplings, $^{1}J(^{129}Xe{-}^{14}N)$, $^{2}J(^{129}Xe{-}^{13}C)$, and $^{3}J(^{129}Xe{-}^{1}H)$, represent the first examples of nuclear spin–spin couplings observed between these nuclides. Owing to the cylindrical symmetry of the $C{\equiv}N{-}Xe{-}F$ moiety in the new cation series, low viscosity of the HF solvent medium, and the small quadrupole moment of ^{14}N, quadrupole relaxation of the $^{129}Xe{-}^{14}N$ coupling is found to be minimal giving rise to slightly quadrupole collapsed 1 : 1 : 1 triplets in the ^{129}Xe spectra and ^{129}Xe satellites in the ^{14}N spectra (Figures 1 and 2). The similarities of $^{1}J(^{129}Xe{-}^{14}N)$ and $^{1}J(^{129}Xe{-}^{19}F)$ values to those of the $HC{\equiv}N{-}XeF^+$ cation

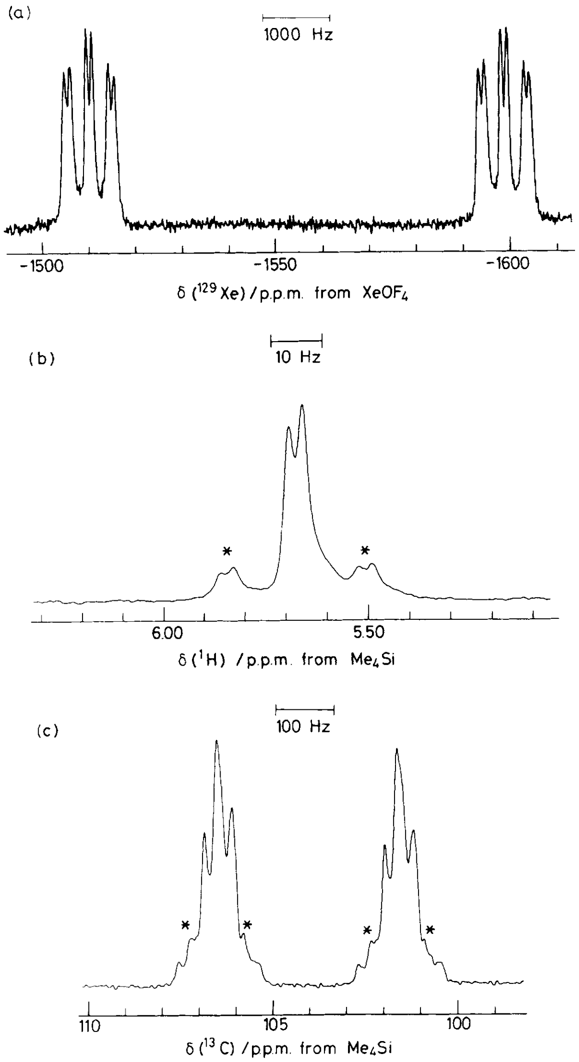

Figure 1. N.m.r. spectra of $HC{\equiv}N{-}XeF^+AsF_6^-$: (a) ^{129}Xe spectrum for a 99.2% ^{13}C enriched sample recorded in HF solvent at −10 °C; (b) ^1H spectrum for a natural abundance sample recorded in BrF_5 solvent at-58 °C at 1.8790 T; (c) ^{13}C spectrum for a 99.2% ^{13}C enriched sample recorded in HF at −10 °C. Asterisks (*) denote ^{129}Xe satellites.

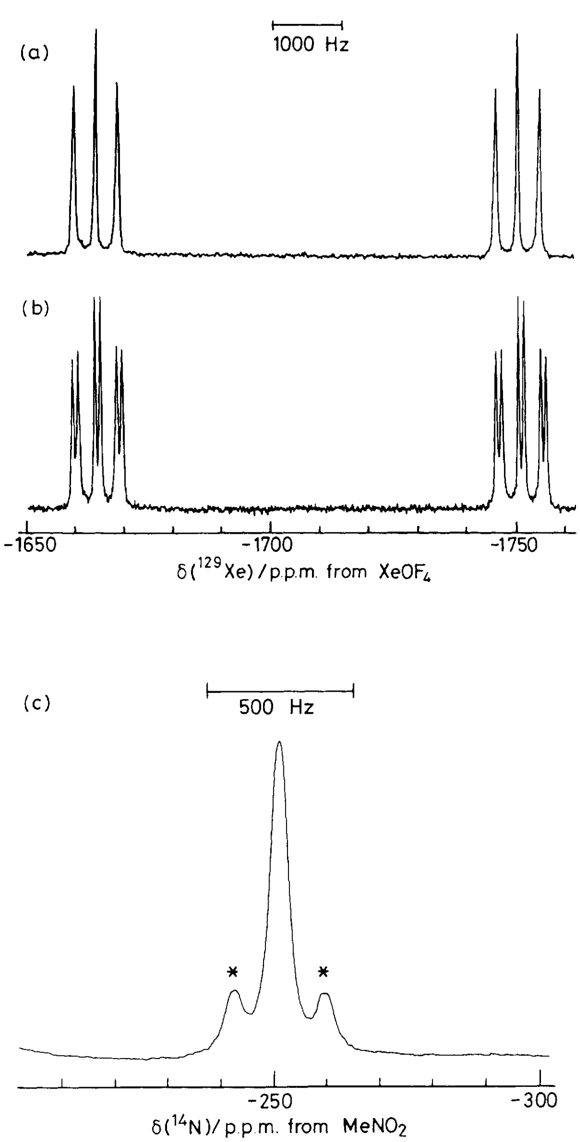

Figure 2. N.m.r. spectra of $CH_3C{\equiv}N{-}XeF^+AsF_6^-$ recorded in HF solvent at −10 °C: (a) and (b) are ^{129}Xe spectra, where (a) is natural abundance and (b) is 99.7% ^{13}C enriched at the 2-carbon; (c) natural abundance ^{14}N spectrum. Asterisks (*) denote ^{129}Xe satellites.

also allow analogous structures to be assigned to the alkyl-, fluoroalkyl- and pentafluorobenzonitrile cations.

The observation of $^1J(^{129}Xe{-}^{14}N)$ in both the ^{14}N and ^{129}Xe spectra is particularly noteworthy and provides conclusive proof that in each case the nitrogen atom is directly bonded to xenon. This is confirmed by comparing their respective reduced coupling constants, $^1K(Xe{-}N)$ (calculated using the expression given in refs. 1—3; (see Table 1), with that of $FXeN(SO_2F)_2$ [$^1J(^{129}Xe{-}^{15}N)$ 307 Hz; $^1K(Xe{-}N)$ 0.913 × 10^{22} NA^{-2} m^{-3}].[1] In addition, the small value of the J-coupling, $^{129}Xe{-}^{13}C$, observed for the ^{13}C enriched sample of $H{-}C{\equiv}N{-}XeF^+$, and a one-bond $^{13}C{-}^1H$ coupling, also confirm that the xenon atom is not bonded to carbon in this species.

Assuming that the Xe–N spin-spin couplings in xenon–nitrogen compounds are dominated by the Fermi contact term, a comparison of $^1K(Xe{-}N)$ values for $R{-}C{\equiv}N{-}XeF^+$ with that of the trigonal planar sp^2-hybridised nitrogen atom in $FXeN(SO_2F)_2$[1] allows assessment of the relative degrees of hybridisation for the nitrogen orbitals used in bonding to xenon. The ratios of $[^1K(Xe{-}N)]_{sp}$ to $[^1K(Xe{-}N)]_{sp^2}$ are 1.42—1.53 for the cations listed in Table 1, in excellent agreement with the theoretical ratio, 1.50, calculated from the predicted fractional s-characters of the nitrogen orbitals used in bonding to xenon.

In the case of the perfluoroalkyl derivatives (R = C_2F_5 and C_3F_7), the Xe–N bonds are found to be labile on the n.m.r. time scale in HF solvent at temperatures down to −30 °C as a result of a decrease in base strength for $RC{\equiv}N$: with increasing fluorine substitution at C-2.

The salts $HC{\equiv}N{-}XeF^+AsF_6^-$ and $CH_3C{\equiv}N{-}XeF^+AsF_6^-$ were isolated from HF solvent by pumping the solutions under vacuum at −50 to −30 °C to give white solids whose Raman spectra were recorded at −196 °C (514.5 nm excitation). The Raman spectrum of $HC{\equiv}N{-}XeF^+AsF_6^-$ was assigned in detail while only key frequencies of $CH_3C{\equiv}N{-}XeF^+AsF_6^-$ have presently been assigned. In addition to the three Raman active

Table 1. N.m.r. parameters[a] for $RC{\equiv}N{-}XeF^+$ cations.

Chemical shifts[b]

R	$\delta(^{129}Xe)$	$\delta(^{19}F)$[c]	$\delta(^{14}N)$	$\delta(^{13}C)$	$\delta(^{1}H)$
H[d]	−1552 −1569[e]	−198.4	−235.4	104.1	6.01 5.67[f]
CH_2F	−1541	−198.4 (XeF) −241.7 (CF)	−229.2		5.44
CH_3	−1708	−185.5	−251.1	115.3 (CN)[g] 0.6 (CH_3)[h]	2.41
C_2H_5	−1717	−184.6	−251.9		1.29 (CH_3) 2.80 (CH_2)
C_6F_5[i]	−1426				

Coupling Constants[j]

	$HC{\equiv}N{-}XeF^{+}$[c]	$CH_2FC{\equiv}N{-}XeF^+$	$CH_3C{\equiv}N{-}XeF^+$[f,g]	$C_2H_5C{\equiv}N{-}XeF^+$	$C_6F_5C{\equiv}N{-}XeF^+$
$^1J(^{129}Xe{-}^{14}N)$	334	333	313	311	
$^1J(^{129}Xe{-}^{19}F)$	6150 (6181)[e]	6163	6020	6017	6610
$^1J(^{14}N{-}^{13}C)$	22				
$^1J(^{13}C{-}^{1}H)$	308		141		
$^2J(^{129}Xe{-}^{13}C)$	84		79		
$^2J(^{19}F{-}^{1}H)$		44			
$^2J(^{19}F{-}^{14}N)$			18		
$^3J(^{129}Xe{-}^{1}H)$	26.8				
$^3J(^{19}F{-}^{13}C)$	18		19		
$^3J(^{1}H{-}^{1}H)$				7.5	
$^4J(^{19}F{-}^{1}H)$	2.6				
^1K(Xe–N)	1.393×10^{22}	1.389×10^{22}	1.305×10^{22}	1.297×10^{22}	

[a] Spectra were recorded in anhydrous HF at −10 °C using 9 mm o.d. FEP sample tubes at 5.8719 T, and spectrometer frequencies (MHz): ^{129}Xe 69.563, ^{19}F 235.361, ^{14}N 18.075, ^{13}C 62.915, ^{1}H 250.132. [b] Samples were referenced externally at 24 °C with respect to the neat liquid references: $XeOF_4$ (^{129}Xe), $CFCl_3$ (^{19}F), CH_3NO_2 (^{14}N), $SiMe_4$ (^{13}C and ^{1}H). A positive chemical shift denotes a resonance occurring to high frequency of the reference compound. [c] All ^{19}F spectra displayed a broad saddle-shaped feature at *ca.* −68 p.p.m. arising from the partially quadrupole collapsed ^{75}As–^{19}F coupling of the octahedral AsF_6^- anion. [d] Sample prepared from 99.2% ^{13}C enriched $H^{13}CN$. [e] Measured in BrF_5 solvent at −58 °C; the $^1J(^{129}Xe{-}^{14}N)$ coupling was found to be completely quadrupole collapsed under these conditions. The sample was prepared by redissolving solid $HC{\equiv}N{-}XeF^+AsF_6^-$, prepared in HF solvent, in BrF_5 at −50 °C. [f] Measured in a 5 mm o.d. precision glass tube in BrF_5 solvent at −58 °C, at 80.022 MHz (1.8790 T) for ^{1}H. The sample was prepared by redissolving solid $HC{\equiv}N{-}XeF^+AsF_6^-$, prepared in HF solvent, in BrF_5 at −50 °C. [g] Sample prepared from 99% ^{13}C enriched $CH_3{}^{13}CN$. [h] Sample prepared from 99.7% ^{13}C enriched $^{13}CH_3CN$. [i] Decomposition occurred at −10 to −20 °C, preventing fuller characterisation. [j] *J* values in Hz; K values in $NA^{-2}m^{-3}$.

modes consistent with an octahedral AsF_6^- anion at 679(50), $\nu_1(a_{1g})$; 581(13), $\nu_2(e_g)$; 371(15), $\nu_5(t_{2g})$ cm^{-1}; and the formally Raman inactive modes $\nu_3(t_{1u})$ at 692(12) and $\nu_4(t_{1u})$ at 244(1), 269(6), 280(14) cm^{-1}; the most prominent features of the linear $HC{\equiv}N{-}XeF^+$ cation spectrum are the factor-group-split C≡N stretch at 2159(41) and 2163(18) cm^{-1} and a pair of intense lines at 559(100) and 569(94) cm^{-1} assigned to the factor-group-split Xe–F stretch. ^{13}C enrichment (99.2%) confirms the assignment of ν(C≡N) (isotopic shift, 31.6 cm^{-1}) and the split, doubly degenerate bend δ(C≡N–Xe) at 327(4), 334(2) cm^{-1} (isotopic shift, 5.5 cm^{-1}; also *cf.* the N≡C–I bend in ICN at 304 cm^{-1}).[4] A low-frequency shoulder on ν_5 of the anion at 368 cm^{-1} was tentatively assigned to the Xe–N stretch (*cf.* ν(Xe–N) of $FXeN(SO_2F)_2$ at 422 cm^{-1})[1] and a weak band at 3141(4) cm^{-1} was assigned to ν(C–H) (*cf.* the C–H stretching frequency of gaseous HC≡N, 3311 cm^{-1}.)[5] The remaining features were assigned to the doubly degenerate bends δ(F–Xe–N) [116(33), 133(10), 157(5), 180(2) cm^{-1}] and δ(H–C≡N) [706(1) cm^{-1}]. Preliminary assignments of some key frequencies for the $CH_3C{\equiv}N{-}XeF^+$ cation spectrum were made by comparison with those of $CH_3C{\equiv}N$[6] and $HC{\equiv}N{-}XeF^+$: $\nu_{asym}(CH_3)$, 3013(6), 3021(7), 3027(4) cm^{-1}; $\nu_{sym}(CH_3)$, 2944(19), 2949(19) cm^{-1}; $\nu_{asym}(CH_3)$, 2335(16) cm^{-1}; ν(XeF), 559(100), 570(74), 571(34) cm^{-1}; δ(F–Xe–N), 160(7), 170(6) cm^{-1}.

Additional examples of nitriles and other inorganic and organic nitrogen bases are under active investigation as potential electron-pair donors towards noble gas-cations, as well as representative *X*-ray crystal structures containing the $RC{\equiv}N{-}XeF^+$ cations.

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