HgF_2-assisted Additions to SN and CN Triple Bonds

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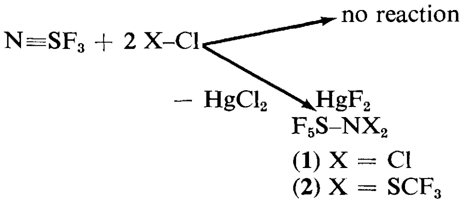
Formal additions of ClF to the SN triple bond in NSF_3 and to the CN triple bond in CF_3CN and $(CN)_2$ are achieved by the system Cl_2–HgF_2; *N*-bromo-amines and -imines are isolated from R_fCN–Br_2–HgF_2·NSF_3 and CF_3SCl–HgF_2 gives $SF_5N(SCF_3)_2$ in high yield.

Polar fluorides X–F (X = H or Cl) readily add to the SN triple bond of NSF_3, mainly with formation of pentafluoro-λ^6-sulphanylamines [reaction (1)].[1–3] The addition of ClF is rather hazardous, and only under very carefully controlled conditions can the formation of large amounts of decomposition products (SF_6 and N_2) and violent explosions be avoided. We have found that, although chlorides [reaction (2a)] do not attack the SN triple bond, in the presence of a stoicheiometric amount of HgF_2, the formal addition of X–F (X = Cl or SCF_3) may be achieved in quantitative yield [reaction (2b)], with decomposition products not being observed. These HgF_2-assisted reactions seem to be much safer, and explosions were not observed; (**1**) itself might tend to decompose violently.

$$N{\equiv}SF_3 + 2\ X{-}F \longrightarrow F_5S{-}NX_2 \qquad (1)$$



$$N{\equiv}SF_3 + 2\ X{-}Cl \longrightarrow \text{no reaction} \qquad (2a)$$

$$N{\equiv}SF_3 + 2\ X{-}Cl \xrightarrow[-\,HgCl_2]{HgF_2} F_5S{-}NX_2 \qquad (2b)$$

(**1**) X = Cl
(**2**) X = SCF_3

The pentafluorosulphanylamines (**1**) and (**2**) were characterized by their spectroscopic properties and by elemental analysis of (**2**). The n.m.r. data for (**1**) agree with literature data,[2] and compound (**2**) is a pale green liquid, b.p. 100.5 °C.†

The HgF_2-assisted addition of sulphenyl chlorides to nitriles is quite complicated [we identified $CF_3CF_2N{=}S(F)CF_3$ and $CF_3CFClN(SCF_3)_2$ spectroscopically in the reaction of $CF_3C{\equiv}N$ with CF_3SCl], but we observed the formation of the dichloroamines (**3a**),[4,5] (**3b**), (**3c**),[6] and (**3d**)[7] [reactions (3) and (4)] from nitriles in HgF_2-assisted additions with excess of Cl_2. Formal additions of ClF to nitriles using metal fluoride–Cl_2 systems have been described,[4] but higher temperatures were applied, and the yields were low.

The reaction of cyanogen with HgF_2[9] and AgF_2[10] at higher temperatures (240—250 and 105—115 °C, respectively) was reported to lead to disruption of the NCCN-chain {with formation of $Hg[N(CF_3)_2]_2$} or to the formation of $\overline{CF_2{-}N{=}N{-}CF_2}$ (probably *via* radical- or nitrene-type intermediates). Although we did not observe the addition of HgF_2 to $(CN)_2$ at room temperature, with excess of chlorine (**4**) was formed slowly [reaction (5)] in quantitative yield; with excess of $(CN)_2$, (**5**) was also isolated. When (**4**) was heated with excess of $(CN)_2$ the dichlorodifluorodiazabutadiene (**6**) was

$$\begin{array}{c} R{-}CN + 2\ Cl_2 + HgF_2 \\ \Big\downarrow \text{room temp.} \\ R{-}CF_2{-}NCl_2 + HgCl_2 \end{array} \qquad (3)$$

(**3a**) R=CF_3 (94% yield)
(**3b**) R=Ph (lower yield, not quantified)

$$\begin{array}{c} Cl{-}CN + 2\ Cl_2 + HgF_2\ (\text{excess}) \\ \Big\downarrow \begin{array}{l} 0\ ^\circ C, \\ 2\ \text{days}, \\ -HgCl_2 \end{array} \\ CF_3NCl_2 + CF_2ClNCl_2 \end{array} \qquad (4)$$

(**3c**) (**3d**)
(3 : 1; 90% overall)

$$\underset{}{(CN)_2} + Cl_2 + \underset{(\text{excess})}{HgF_2} \xrightarrow[\text{temp.}]{\text{room}} \underset{(\mathbf{4})\quad(100\%)}{(CF_2NCl_2)_2} + HgCl_2 \qquad (5)$$

$$(\mathbf{4}) + (CN)_2 \xrightarrow{\text{Heat}} \underset{(\mathbf{5})}{ClN{=}CF{-}CF_2NCl_2} + \underset{(\mathbf{6})}{ClN{=}CF{-}CF{=}NCl} \qquad (6)$$

isolated in 22% yield [reaction (6)], as a colourless solid, m.p. 42 °C. Its structure was confirmed by i.r.‡ [1661vs (CN), 1162vs (CF), and 678vs (NCl) cm^{-1}] and n.m.r. spectroscopy (Table 1).

We also found that the formal addition of BrF to nitriles is possible by this method [reactions (7) and (8)]. After 1 week at 0 °C small amounts of the *N*-bromoimide (**8**)[4] were formed [reaction (7)], and the dibromoamine (**7**)§ was isolated in 90%

$$CF_3CN + \underset{(\text{excess})}{Br_2} \xrightarrow[-\,HgBr_2]{HgF_2} \underset{(\mathbf{7})}{CF_3CF_2NBr_2} + \underset{(\mathbf{8})}{CF_3CF{=}NBr} \qquad (7)$$

$$(CN)_2 + Br_2 \xrightarrow[-\,HgBr_2]{HgF_2} \underset{(\mathbf{9})}{BrN{=}CFCF{=}NBr} + \underset{(\mathbf{10})}{BrN{=}CFCF_2NBr_2} + \underset{(\mathbf{11})}{Br_2NCF_2CF_2NBr_2} \qquad (8)$$

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† (**1**): ^{19}F n.m.r., δ 61.68 (F^A) and 52.66 p.p.m. (F^B), J_{AB} 150.2 Hz; (**2**): ^{19}F n.m.r., δ 67.28 (SF^A), 56.97 ($SF^B{}_4$), and −52.18 p.p.m. (CF_3); J_{AB} 152.8, J (F^A . . . . . CF_3) 0.55, J (F^B . . . . . CF_3) 5.63 Hz; i.r. (gas), 1200sh, 1182vs, 1118vs, 942s, 901vs, 859vs, 804w, 758w, 701w, 605m, 593w, and 461w cm^{-1}; m/z (70 eV) 343 (M^+, 12%), 242 (M^+-SCF_3, 35%), and 216 (M^+-SF_5, 100%).

‡ Spectra were recorded in the gas phase with AgCl windows.

§ (**8**): i.r. (gas), 1340m, 1238vs, 1185s, 1148s, 1023s, 756w, 685w, and 536w cm^{-1}; m/z (70 eV, cold source) 293 (M^+, 25%), 224 (M^+-CF_3, 40%), 192 (M^+-Br, 67%) 124 (27%), and 69 (100%).

Table 1. ^{19}F and ^{13}C n.m.r. data for the *N*-chloro- and *N*-bromo-amino- and -imino-ethanes.

	^{19}F N.m.r.				^{13}C N.m.r.					
	δ, p.p.m.			J_{FF} /Hz	δ, p.p.m.				$^1J_{FC}$ /Hz	$^2J_{FC}$ /Hz
	CF	CF$_2$	CF$_3$		CF	CF$_2$	CF$_3$			
(4)	—	−92.12	—	—	—	117.35	—		284.5	32.7
(5)	−35.07	−90.6	—	7.25	152.25	116.18	—	F^A	358.1	43.7
								F^B	272.3	34.9
(6)	−37.08	—	—	—	150.62	—	—		339.4	43.3
(7)	—	−91.83	−77.0	1.3	—	116.15	115.48	F^A	277.1	40.4
								F^B	288.9	38.9
(8)	−26.9	—	−71.6	5·45	—	—	—		—	—
(9)	−20.07	—	—	—	149.65	—	—		339.4	47.9
(10)	−19.9	−81.0	—	7.2	150.98	115.85	—	F^A	358.0	46.6
								F^B	271.3	31.2
(11)	—	−80.2	—	—	—	115.95	—		283.6	33.8

yield, as a reddish liquid (m.p. < -78 °C) which was separated from (**8**) and excess of Br_2 by fractional condensation under high vacuum at −50 °C.

Under similar conditions cyanogen and excess of bromine gave compound (**9**) [reaction (8)], as colourless crystals, m.p. 58 °C, the i.r. spectrum‡ of which [1660vs (CN), 1140s (CF), and 570m (NBr) cm^{-1}] is very similar to that of (**6**). The presence also of (**10**) and (**11**) was confirmed by mass and n.m.r. spectroscopy (Table 1), but the pure compounds could not be isolated. The total yield of (**9**) and (**10**) was >85%.

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