

The Nitrenes, $\text{ReF}_5(\text{NCl})$ and $\text{ReF}_5(\text{NF})$

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The nitride fluoride ReNF_4 has been isolated from the action of Me_3SiN_3 on ReF_6 ; subsequent reactions with ClF_3 yield the nitrenes $\text{ReF}_5(\text{NCl})$ and $\text{ReF}_5(\text{NF})$, characterized by X -ray structure determinations.

Although a number of nitrido- and nitrene-derivatives of transition metal halides have been isolated,¹⁻³ the only fluorides to be identified are the anions $[\text{MoNF}_4]^-$,⁴ $[\text{WF}_5(\text{NR})]^-$ ⁵ and the neutral complex $\text{WF}_4(\text{NMe})$.⁵ The nitrene compound $\text{VCl}_3(\text{NCl})$ has been isolated and fully characterised.⁶ We report the isolation, in very small yield, and identification of the nitrido-complex ReNF_4 , and the isolation and characterisation of the nitrene derivatives $\text{ReF}_5(\text{NCl})$ and $\text{ReF}_5(\text{NF})$ by X -ray crystallography.

Azidotrimethylsilane, Me_3SiN_3 , reacts with ReF_6 at -50°C in Genetron 113 (1,1,2-trichlorotrifluoroethane) solution according to Scheme 1. The reaction is violent (CAUTION) and detonation is possible even if maximum control is exercised by repeated cooling with liquid nitrogen. On allowing to warm to 0°C the initially orange solid (1) and solution darken, and nitrogen is evolved; this stage of the reaction is also hazardous. After the solvent has been removed, warming of the residue (2) to 70°C *in vacuo* allows the sublimation of a very reactive pale yellow crystalline solid (3). Mass spectroscopy of (3) (Scheme 2) shows ReF_4N^+ to be important, though traces of a dimeric ion $\text{Re}_2\text{F}_7\text{N}^+$ also appear. Preliminary X -ray study suggests an orthorhombic unit cell having the approximate dimensions $a = 5.64$, $b = 14.76$, $c = 4.26$ Å, $Z = 4$, but the crystals are too poorly defined for structure determination. There is an i.r. absorption frequency at $1110(\text{m})$ cm^{-1} characteristic of $\nu(\text{Re}=\text{N})$; other absorptions occur at $1030(\text{ms})$, $950(\text{m})$, $715(\text{m})$, and $665(\text{m})$ cm^{-1} . Compound (3) dissolves in dilute alkali with the evolution of NH_3 and the formation of a colourless solution containing ReO_4^- and F^- ions. This evidence is sufficient to

identify compound (3) as the new nitride fluoride ReF_4N .

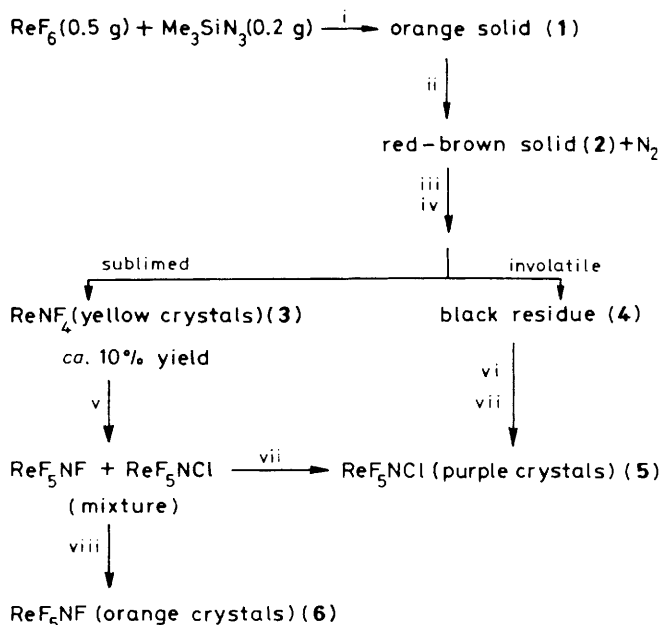
Fluorination of the black residue (4) by ClF_3 (Scheme 1) leads to formation of a purple crystalline solid (5) in good yield which may be readily sublimed at 70°C *in vacuo*. A single crystal structure determination of (5) shows it to be the nitrene $\text{ReF}_5(\text{NCl})$.

Crystal data: ClF_5NRe , $M = 330.65$, monoclinic, $a = 4.964(1)$, $b = 8.359(1)$, $c = 7.728(7)$ Å, $\beta = 124.8(1)^\circ$, $U = 263.25$ Å³, $Z = 2$, $D_c = 4.17$ g cm^{-3} , $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, space group $P2_1/m$. 662 Intensities, measured by a Stoe STADI-2 Weissenberg diffractometer, having $I > 3\sigma(I)$ have been refined by least squares to $R = 0.058$ ($R_w = 0.058$).†

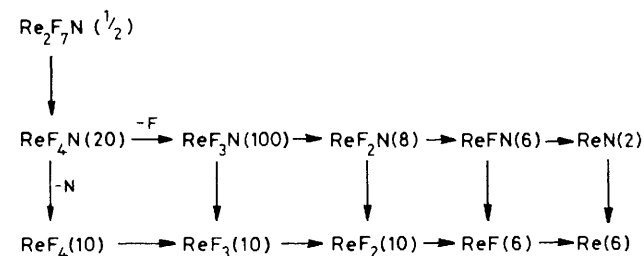
The molecular geometry is shown in Figure 1. The Re, N, Cl, and *trans*-F atoms lie on a crystallographic mirror plane. The Re-N-Cl unit is linear [176.6° (1.4)] and the equatorial fluorine atoms are bent away with an average N-Re-F angle of 94.15° . The *trans*-Re-F bond length demonstrates that (NCl) has a small *trans*-influence although the difference of about 0.05 Å between axial and equatorial Re-F bond lengths is less than the value of 0.10 Å found⁷ in $[\text{WCl}_5(\text{NC}_2\text{Cl}_5)]^-$. The Re-N distance is significantly longer than the W-N distance in $[\text{WCl}_5(\text{NC}_2\text{Cl}_5)]^-$, 1.684 Å, and is reflected in the observed $\nu(\text{M}=\text{N})$ i.r. stretching frequencies; 1268 cm^{-1} in $[\text{WCl}_5(\text{NC}_2\text{Cl}_5)]^-$ and 1205 cm^{-1} in $\text{ReF}_5(\text{NCl})$. Further i.r. absorptions are found at 1053(mw), 1012(s), and 963(vs) cm^{-1} . The mass spectrum of (5) shows the parent ion to be present. The ¹⁹F n.m.r. spectrum of (5), obtained at -10°C in ClF_3 solution shows a well resolved doublet (90 Hz, +180.4 p.p.m.) and a quintet (+163.5 p.p.m.) relative to CFCl_3 .

Fluorination of ReNF_4 (3) by ClF_3 (Scheme 1) leads to a mixture of $\text{ReF}_5(\text{NCl})$ and of orange crystals (6), which may be separated by fractional sublimation. A single-crystal X -ray determination of (6) shows it to be the nitrene $\text{ReF}_5(\text{NF})$.

Crystal data: F_6NRe , $M = 314.20$, monoclinic, $a = 5.298(2)$, $b = 9.286(3)$, $c = 9.979(6)$ Å, $\beta = 109.4(0.2)^\circ$, $U = 463.21$ Å³, $Z = 4$, $D_c = 4.507$ g cm^{-3} , $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, space group $P2_1/c$ No. 14. 1182 unique intensities, measured by a Stoe STADI-2 Weissenberg diffractometer, having $I > 3\sigma(I)$ have been refined by least squares to $R = 0.0569$.†



Scheme 1. i, $\text{CF}_2(\text{Cl})\text{CFCl}_2$, -50°C ; ii, warm to 0°C ; iii, remove solvent; iv, 70°C , *in vacuo*; v, ClF_3 , 0°C ; vi, ClF_3 , 0°C ; vii, sublime, 70°C , *in vacuo*; viii, sublime, 40°C , *in vacuo*.



Scheme 2. Mass spectroscopic fragmentation pattern of ReNF_4 (intensities in brackets).

† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

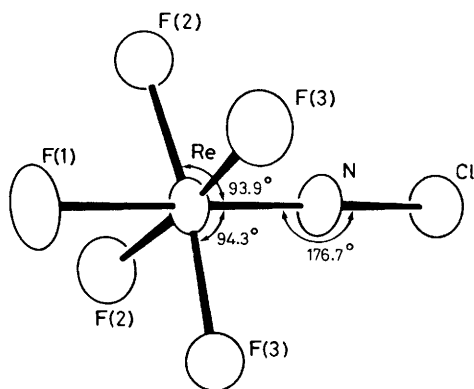


Figure 1. Molecular structure of $\text{ReF}_5(\text{NCl})$. Bond lengths are: $\text{Re-F}(1)$ 1.881(16), $\text{Re-F}(2)$ 1.828(11), $\text{Re-F}(3)$ 1.825(11), Re-N 1.731(19), and N-Cl 1.558(18) Å. For $\text{ReF}_5(\text{NF})$ bond lengths are: $\text{Re-F}(1)$ 1.860(8), equatorial Re-F 1.816(9), 1.831(9), 1.829(9), and 1.834(9), Re-N 1.717(11), and N-F 1.257(13) Å. The Re-N-F angle is $177.5(1.1)^\circ$, N-Re-F equatorial angles average to 94.7° .

The molecular geometry is very similar to that of $\text{ReF}_5(\text{NCl})$ (see Figure 1). The Re-N-F unit is linear, and NF appears to exert a smaller *trans*-influence than NCl . The N-F bond length in this fluoronitrene complex is markedly shorter than that recently found in the fluoro-imido-complex SF_4NF [1.357(8) Å],⁸ which has a non-linear S-N-F unit [$118(1)^\circ$]. The mass spectrum of (6) includes the parent ion.

The reaction between Me_3SiN_3 and ReF_6 is clearly complex. Even in the presence of an excess of ReF_6 more azide is consumed than is required for the formation of a mono-azido-derivative (contrast WF_5N_3)⁸ so that the orange solid (1) is probably a mixture. Decomposition to (2) involves oxidation of Re^{VI} to Re^{VII} rather than disproportionation, since a typical analysis of the residue (4) indicates approximate ratios $\text{Re}:\text{F}:$

N (by difference) 1:4.35:1.25 The nitride ReNF_4 appears only in small and variable yield from necessarily small-scale experiments; the oxidation by ClF_3 to a mixture of the two nitrenes provides an independent confirmation of the formula. ReNF_4 has been synthesised independently by Professor Dehnicke and his colleagues from the reaction between ReNCl_4 and fluorine.^{10,11}

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