Preparation of the Nitrenes $ReF_5(NF)$, $ReF_5(NCl)$, and $ReF_5(NBr)$. *X*-Ray Crystal Structures of $ReF_5(NF)$ and $ReF_5(NCl)$ †

John Fawcett, Raymond D. Peacock,* and David R. Russell
Department of Chemistry, University of Leicester, Leicester LE1 7RH

The action of $Si(CH_3)_3(N_3)$ on ReF_6 leads to the nitride fluoride ReF_4N in low yield together with a mixture which appears to contain ReF_3N. Treatment of either of these materials with XeF_2, ClF_3, or BrF_3 as appropriate gives the 'nitrenes' $ReF_5(NF)$, $ReF_5(NCl)$, and $ReF_5(NBr)$; other methods of preparing $ReF_5(NCl)$ and $ReF_5(NBr)$ are also described. From single-crystal measurements it has been shown that in $ReF_5(NF)$ and $ReF_5(NCl)$ the ReNF and ReNCl bonds respectively are nearly linear; the short N–F and N–Cl bond lengths are 1.257(13) and 1.56(2) Å respectively.

In a recent communication we reported brief details of the preparation of the nitride fluoride ReF_4N and of the 'nitrenes' $ReF_5(NF)$ and $ReF_5(NCl)$.[1] Although a number of nitrido- and nitrene derivatives of transition metal halides have been characterised,[2–4] the only fluoro-derivatives other than the present compounds are the anions $[WF_5(NR)]^-$ and the neutral complex $WF_4(NMe)$.[5] In addition, the nitrene halides $VCl_3(NX)$ (X = Cl, Br, or I) have been characterised by Dehnicke and co-workers,[6] and the iodide was shown to have an almost linear M–N–X grouping. Similar linear or nearly linear groupings are common to a number of transition metal complexes involving a $\overset{-}{M}\equiv\overset{+}{N}{-}X$ pattern (X = halide, H, C, N, or Si);[2–4,7] a recent example is $[Mo(NC_6H_4Me\text{-}p)Cl_4(thf)]$ (thf = tetrahydrofuran).[8]

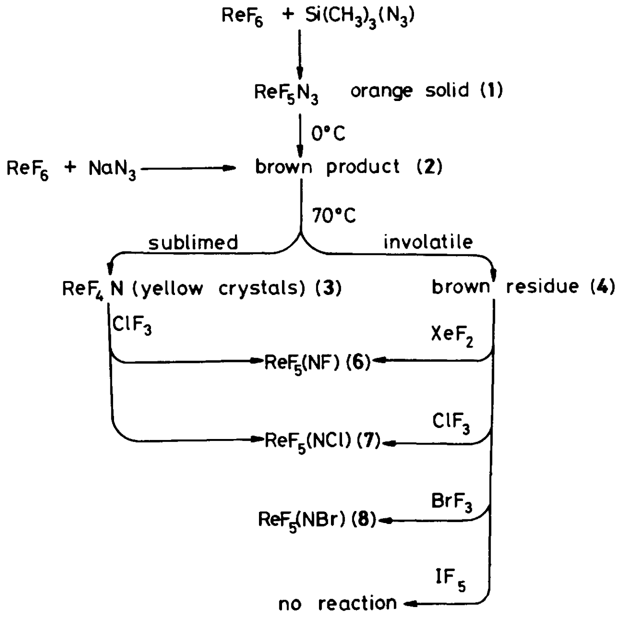
Following our original report, Dehnicke and co-workers[9] have determined the structure of the interesting mixed complex $ReF_4N{\cdot}ReF_5(NCl)$, prepared from the action of fluorine on $ReCl_4N$.

In the present paper we describe more fully the preparation, chemistry, and structures of ReF_4N, $ReF_5(NF)$, and $ReF_5(NCl)$, and report for the first time the isolation of the bromo-derivative $ReF_5(NBr)$.

Discussion

Rhenium hexafluoride reacts with $Si(CH_3)_3(N_3)$ in a complicated manner (Scheme 1). Even in the presence of excess of the hexafluoride the combining ratio of $Si(CH_3)_3(N_3)$ to ReF_6 is greater than 1:1; another feature is the rapid initial rate of reaction at −50 °C but a long completion time (*cf.* ReF_6 with BCl_3).[10] The colour changes suggest that the first product is an azido-derivative (*cf.* WF_5N_3)[11] which undergoes decomposition or further reaction with $Si(CH_3)_3(N_3)$ as the temperature rises. ReF_4N is formed in small yield (*ca.* 10%) by a process which must involve oxidation of Re^{VI} to Re^{VII}, but the greater proportion of the final product is a dark brown or black amorphous powder whose properties suggest the presence of a mixture including a lower nitride fluoride such as ReF_3N and undecomposed azide. It should be noted that the replacement of ReF_6 in the original reaction mixture by ReF_7 does not increase the yield of ReF_4N.

Rhenium tetrafluoride nitride, ReF_4N, is the only fluoride nitride of a transition element which has been positively identified; the related chloride $ReCl_4N$ was characterised several years ago.[12] That the compound is ReF_4N and not $ReF_3(NF)$ is indicated by its breakdown pattern in the mass spectrometer (Scheme 2). The yellow crystals are too easily deformed to give an *X*-ray pattern sufficiently good to define the space group, but the volume of the apparently orthorhombic unit cell indicates a very clear parallel with the structures of WF_4O and ReF_4O[13] in terms of the packing of atoms. The appearance of a dimeric fragment in the mass spectrum also suggests a bridged structure, perhaps with bridging fluorine atoms, and the absorption at 1 110 cm^{-1} in the i.r. spectrum would support a formulation with terminal nitrogen atoms; however, other features of the spectrum, and especially the absorption at 1 030 and 950 cm^{-1}, remain to be explained.



Scheme 1.

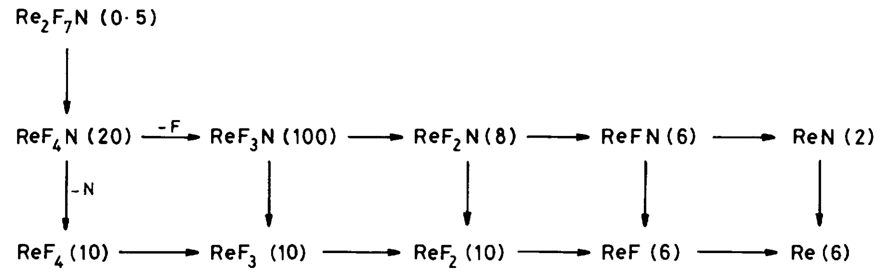
Rhenium hexafluoride reacts readily with $Si(CH_3)_3(NCO)$ (Scheme 3). The product, which seems to be almost insoluble in any solvent with which it does not also react chemically, appears, from analysis, to be impure $ReF_5(NCO)$, and is hence a Re^{VI} compound of a type similar to $WF_5(NCO)$[14] and WF_5N_3.[11]

Treatment of ReF_4N or of the ReF_3N mixture with XeF_2, ClF_3, or BrF_3 as described in the Experimental section leads to the nitrene fluorides $ReF_5(NX)$ (X = F, Cl, or Br), together with varying proportions of ReF_6. With ReF_7 as fluorinating

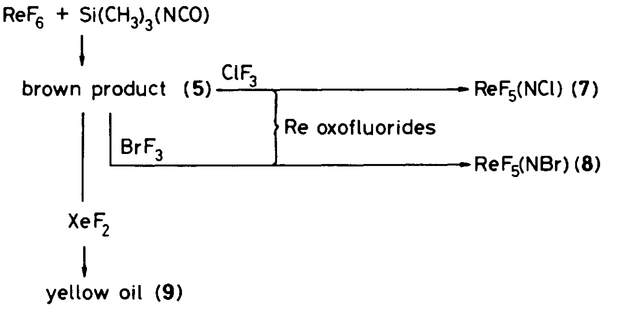
---

† Fluoroimidorhenium and chloroimidorhenium pentafluorides respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme 2. Mass spectroscopic fragmentation pattern of ReF_4N (percentage intensities in parentheses throughout)



Scheme 3.

agent, only ReF_6 is formed (see below). $ReF_5(NCl)$ is also formed by the action of ClF_3 on $ReF_5(NCO)$ and on an uncharacterised rhenium fluoride isonitrile, and by the action of XeF_2 and $ReCl_3N$. From the preparative point of view $ReF_5(NCO)$ is less suitable than the other Re compounds as a starting material because oxygen-containing products are also formed, presumably by oxygen abstraction from the isocyanate group. The formation of $ReF_5(NBr)$ by treatment of ReF_6 with $[Si(CH_3)_3]_2NBr$ followed by oxidation with BrF_3 illustrates the direct formation of a metal–NBr link by exchange.

These nitrenes, $ReF_5(NX)$, show colours which range from orange ($X = F$) to pink ($X = Cl$) to purple ($X = Br$); the colours are presumably associated with charge-transfer transitions. However, the recently isolated $OsF_5(NCl)$ is nearly colourless.[15] The ^{19}F n.m.r. spectra show the expected doublets (Experimental section), but the quintets, when observed at all, are very poorly resolved. In $ReF_5(NF)$ the doublet is split by the F(N), but the F(N) signal has not been observed because of the low solubility of the compound in ClF_3.

The compounds $ReF_5(NF)$ and $ReF_5(NCl)$ are similar in molecular geometry (Figure, Table 1). The Re–N–X units are linear, and the *trans* Re–F bond lengths show that the NF and NCl groups have a small *trans* influence, though this is even less than in the related ion $[WCl_5(NC_2Cl_5)]^-$ reported by Dehnicke and co-workers.[16] However, the Re–N distances in both compounds are significantly larger than the W–N distance in $[WCl_5(NC_2Cl_5)]^-$ (1.684 Å),[16] a feature which is also reflected in the observed $\nu(\overset{-}{M}\equiv\overset{+}{N}X)$ i.r. stretching frequencies: 1 268 cm^{-1} in $[WCl_5(NC_2Cl_5)]^-$ and 1 205 cm^{-1} in $ReF_5(NCl)$. The N–F bond in $ReF_5(NF)$ is shorter than that in the fluoroimide compound $SF_4(NF)$ [1.357(8) Å],[17] which has a non-linear S–N–F unit [118(1)°]. The N–Cl bond in $ReF_5(NCl)$, is, as expected, shorter than that in $HNCl_2$ (1.75 Å).[18]

The i.r. spectra of the three nitrenes are complex, and show features, particularly in the 900—1 050 cm^{-1} region which have not yet been reliably assigned.

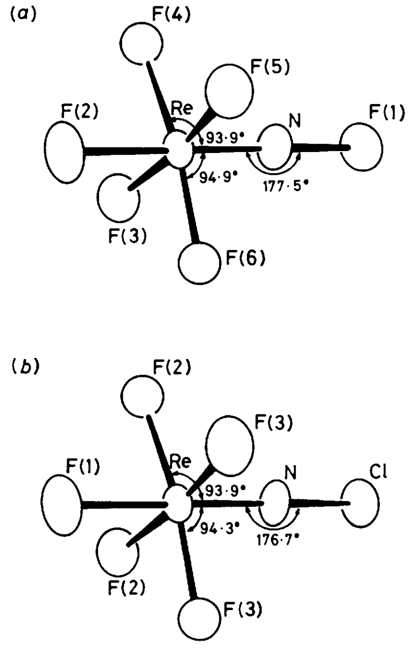


Figure. Molecular structures of (*a*) $ReF_5(NF)$ and (*b*) $ReF_5(NCl)$

Table 1. Selected bond distances (Å) and angles (°)

(*a*) $ReF_5(NF)$ (**6**)			
Re–F(2)	1.860(8)	F(2)–Re–F(3)	83.9(4)
Re–F(3)	1.816(8)	F(2)–Re–F(4)	85.7(4)
Re–F(4)	1.831(9)	F(2)–Re–F(5)	86.3(4)
Re–F(5)	1.829(9)	F(2)–Re–F(6)	85.5(5)
Re–F(6)	1.834(9)	N–Re–F(3)	94.1(5)
Re–N	1.717(11)	N–Re–F(4)	93.9(5)
N–F(1)	1.257(13)	N–Re–F(5)	95.8(5)
		N–Re–F(6)	94.9(5)
		Re–N–F(1)	177.5(11)
(*b*) $ReF_5(NCl)$ (**7**)			
Re–F(1)	1.87(2)	F(1)–Re–F(2)	85.9(8)
Re–F(2)	1.82(1)	F(1)–Re–F(3)	85.8(8)
Re–F(3)	1.82(1)	F(2)–Re–N	93.9(6)
Re–N	1.73(2)	F(3)–Re–N	94.3(6)
N–Cl	1.56(2)	Re–N–Cl	176.7(14)

The enthalpy of formation of $ReF_5(NCl)$ has been estimated from calorimetric measurements of the enthalpy of alkaline hydrolysis to be $-1\,195 \pm 5$ kJ mol^{-1}.[19] From this figure, and using reasonable values for the enthalpies of sublimation and for differences in N–Cl and N–F bond strengths, ΔH_f-$[ReF_5(NF)$ (s)] is calculated to be *ca.* $-1\,260$ kJ mol^{-1}. This figure compares with $-1\,366$ kJ mol^{-1} for the enthalpy of formation of ReF_6 (g),[20] and it is not therefore surprising to find that rhenium hexafluoride is formed as well as or instead of

$ReF_5(NF)$ during the fluorination of ReF_4N or the ReF_3N mixture.

Experimental

Reagents and Apparatus.—Rhenium hexafluoride was prepared by heating an excess of rhenium metal powder with fluorine for 4 h at 390 ± 10 °C. Azidotrimethylsilane (P.C.R. Inc.) and trimethylsilyl isocyanate (Lancaster Synthesis) were vacuum distilled, rejecting the first and last fractions. Genetron 113 (1,1,2-trichlorotrifluoroethane, $C_2Cl_3F_3$) (Fluka A.G.) was purified by trap-to-trap distillation and dried over P_2O_5. Experiments were performed in FEP tubes fitted with Teflon valves (Production Techniques, Fleet, Hants.). The reaction vessels were pretreated with chlorine trifluoride and pumped to high vacuum before use. Volatile materials were manipulated in a Monel vacuum line fitted with high-pressure valves (Autoclave Engineers), and non-volatile products were handled in an inert atmosphere glove-box (Vacuum Atmospheres Co.). Infrared spectra were recorded using a Perkin-Elmer 580B spectrophotometer, with KBr plates and Nujol mull suspension. Attack on the plates was not observed provided the spectra were run rapidly. Mass spectra were recorded on a VG micromass 16B instrument, and ^{19}F n.m.r. spectra obtained using a JEOL PS100 n.m.r. spectrometer.

CAUTION: Reactions involving azides and heavy metal fluorides, or nitrogen-containing species and halogen fluorides, are hazardous, and all experiments were executed on a small scale (*ca.* 1 mmol) behind safety screens. The FEP reaction tubes, whilst primarily employed for their chemical resistance to higher metal fluorides, fluorine, and halogen fluorides, were found to deform and rupture relatively easily in the event of a detonation.

Reaction of ReF_6 *with* $Si(CH_3)_3(N_3)$.—In a typical experiment Genetron solvent (0.5 cm^3) was added by vacuum distillation to an FEP tube containing azidotrimethylsilane (1.23 mmol). The Genetron was condensed at the top of the tube and allowed to wash all traces of $Si(CH_3)_3(N_3)$ from the walls. An excess of rhenium hexafluoride (1.29 mmol) was then vacuum distilled into the tube at −196 °C. [**CAUTION**: At any stage of warming the reaction can become extremely vigorous and detonate, even if maximum control is exercised by repeated cooling with liquid nitrogen.] Upon warming to −50 °C an orange-red mixture (**1**) was obtained (see Scheme 1). With further warming to 0 °C the initial orange solid and red solution darkened and nitrogen was evolved. After standing at 20 °C for several hours a pale yellow solution remained over a dark solid (**2**). After the removal of solvent and volatile products, the solid product was warmed *in vacuo*. At 70 °C approximately 10% of the material sublimed as a very reactive pale yellow crystalline solid (**3**), identified as ReF_4N. The bulk of the material remained as a dark brown residue (**4**), identified as a mixture of ReF_3N with other materials.

Rhenium Tetrafluoride Nitride, ReF_4N (**3**).—This forms poorly defined yellow crystals, m.p. 85 °C, which oscillation and Weissenberg photographs show to be orthorhombic with dimensions $a = 5.64, b = 14.76, c = 4.26$ Å, and $U = 354.6$ Å^3. The mass spectrum, taken at 50 °C (Scheme 2) shows a principal peak due to ReF_4N^+, though a peak of low intensity due to a dimeric ion, $Re_2F_7N^+$, also appears. The i.r. spectrum shows an absorption at 1 110m cm^{-1}, characteristic of ν(Re≡N), and further absorption bands at 1 030ms, 950m, 715m, and 665m cm^{-1}. The yellow crystals are extremely moisture sensitive, and dissolve in dilute alkali with the evolution of NH_3 and the formation of F^- and ReO_4^- ions.

The compound ReF_4N is also formed during the reaction of the ReF_3N mixture (**4**) with XeF_2.

Brown Residue (**4**).—The dark brown, involatile, insoluble residue (decomp. without melting >200 °C) gave an analysis of Re, 65.0; F, 28.9%; Re:F = 1:4.34. The material did not give an i.r. spectrum. It dissolved in dilute alkali evolving ammonia and forming a brown precipitate ($ReO_2 \cdot nH_2O$) which was rapidly oxidised in air. The above observations, together with the fact that (**4**) reacts with XeF_2 giving first ReF_4N, then $ReF_5(NF)$, and with ClF_3 to give $ReF_5(NCl)$ suggest that (**4**) is a mixture containing ReF_3N and perhaps ReF_5N_3.

Reaction between ReF_6 *and* $Si(CH_3)_3(NCO)$.—Isocyanatotrimethylsilane (1.52 mmol) suspended in Genetron 113 (0.5 cm^3) was cooled to −150 °C under vacuum and ReF_6 in slight excess (1.66 mmol) was added by distillation/sublimation. The mixture was allowed to warm up; at −50 °C it became red (*cf.* the azido-reaction), and at 25 °C a pale yellow solution (excess of ReF_6) over a brownish purple solid was formed. After the excess of solvent and other volatiles had been pumped off a brownish purple solid (**5**) remained [Found: C, 5.05; F, 30.55; N, 5.35. Calc. for $ReF_5(NCO)$: C, 3.70; F, 29.4; N, 4.30%]. The i.r. spectrum of (**5**) showed absorptions at 2 260 (sh), 2 230vs, and 2 210 (sh) cm^{-1} attributable to $\nu_{asym}(NCO)$, at 1 290vs cm^{-1} attributable to $\nu_5(NCO)$, and at 670vs cm^{-1} (Re–F). The air-sensitive material decomposed without melting at 200—230 °C.

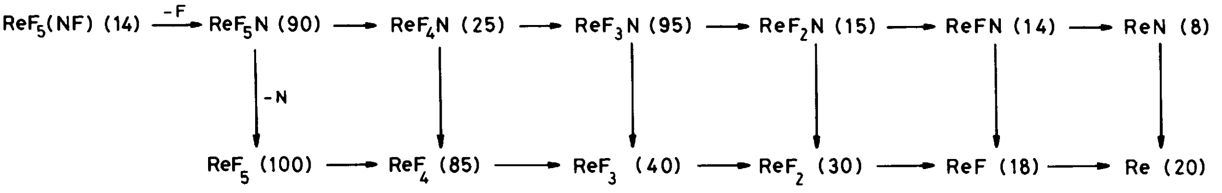
Reaction of ReF_3N *Mixture* (**4**) *with* XeF_2.—An excess of XeF_2 (*ca.* 0.6 mmol) was added to (**4**) (*ca.* 0.5 mmol) in a dry-box. The brown solid became uniformly yellow (at this stage ReF_4N could be identified when the solid was sublimed in a vacuum). Addition of Genetron 113 resulted in an orange-yellow solution. After 1 h, the solvent was pumped off leaving an apparently homogeneous amber solid; on heating in a dynamic vacuum this yielded a colourless sublimate of XeF_2 at 40 °C, and orange crystals at 60 °C, identified as $ReF_5(NF)$ (**6**).

Reaction of ReF_4N *with* ClF_3.—Addition of a large excess of liquid ClF_3 to ReF_4N resulted immediately in the formation of a deep purple solution. After removal of the solvent by distillation and pumping, a purple solid remained which was separated into two constituents upon pumping under a dynamic vacuum. At 60 °C pale orange crystals, identified as $ReF_5(NF)$ (**6**), sublimed, followed at 70 °C by purple crystals, identified as $ReF_5(NCl)$ (**7**), in an approximately equivalent amount.

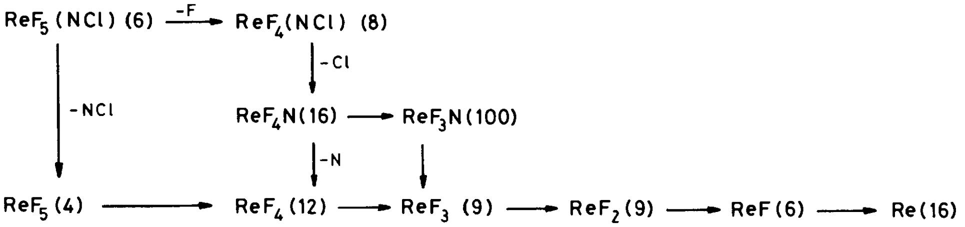
Reaction of ReF_3N *Mixture* (**4**) *with* ClF_3.—The mixture (**4**) (*ca.* 0.2 g) was treated with successive aliquots of ClF_3 *vapour* (*ca.* 1.33 × 10^4Pa mm) until reaction was clearly as complete as possible. At this stage successive small quantities (*ca.* 0.05 cm^3) of *liquid* ClF_3 were condensed on the reaction mixture until sufficient was present to dissolve the solid. (This procedure minimises the possibility of explosion.) After removal of the ClF_3 by distillation and pumping a purple solid remained which sublimed completely at 70 °C in a dynamic vacuum. This was identified as $ReF_5(NCl)$ (**7**).

Reaction of $ReF_5(NCO)$ (**5**) *with* ClF_3.—After treatment with ClF_3 as described immediately above a purple solid remained, from which $ReF_5(NCl)$ (**7**) was sublimed in a dynamic vacuum at 70 °C. A green residue remained (decomp. 160—240 °C) which gave i.r. absorption frequencies at 1 021 and 955 cm^{-1} (probably Re–O) and at 601 cm^{-1} (Re–F); this is believed to be a mixture of oxide fluorides formed through abstraction of oxygen from the NCO group by the Re.

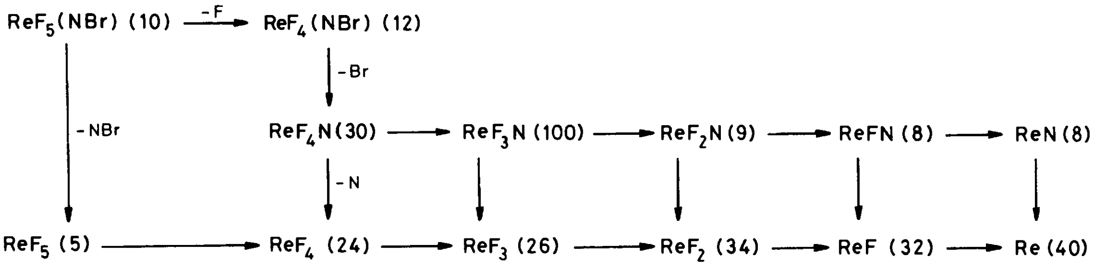
Fluoroimidorhenium Pentafluoride, $ReF_5(NF)$.—This compound forms very reactive orange crystals, m.p. *ca.* 80 °C. The



Scheme 4. Mass spectroscopic fragmentation pattern of $ReF_5(NF)$



Scheme 5. Mass spectroscopic fragmentation pattern of $ReF_5(NCl)$



Scheme 6. Mass spectroscopic fragmentation pattern of $ReF_5(NBr)$

mass spectrum, obtained at 45 °C (Scheme 4), shows $ReF_5(NF)^+$ as the parent ion, with strong peaks for ReF_5^+ and ReF_5N^+. The i.r. spectrum shows absorptions at 2 375m, 1 200w, 1 010m, 962m, 661m, 637m, 596w, 582vw, and 542mw cm^{-1}.

The ^{19}F n.m.r. spectrum of $ReF_5(NF)$, obtained in ClF_3 solution at -10 °C shows, because of very limited solubility, only a very poorly defined doublet associated with the four equatorial fluorines; this is split by F(N) (*J* 90 MHz, $+187.5$ p.p.m. relative to $CFCl_3$). Attempts to obtain spectra from solutions in anhydrous HF were unsuccessful.

Chloroimidorhenium Pentafluoride, $ReF_5(NCl)$.—This was obtained as reactive purple crystals, m.p. *ca.* 80 °C. The mass spectrum, obtained at 110 °C (Scheme 5), shows the parent ion, $ReF_5(NCl)^+$, the species $ReF_4(NCl)^+$ and the fluoro ions ReF_5^+ to ReF^+ (Re–O species formed by decomposition in the mass spectrometer were also present). The i.r. spectrum has absorptions at 2 384mw, 2 350vw, 2 310w, 1 200s, 1 009ms, 960s, 704s, 655s, 580s, 494m, 438ms, and 390w cm^{-1}; upon partial hydrolysis a new absorption at 900 cm^{-1} appeared (Re–O) although the remaining absorptions maintained the same relative intensities.

The ^{19}F n.m.r. spectrum, obtained at -10 °C in ClF_3 solution, shows a well resolved doublet (*J* 90 Hz, $+180.4$ p.p.m.) and a very poorly resolved quintet ($+163.5$ p.p.m.) relative to $CFCl_3$.

Reaction of the ReF_3N *Mixture* (**4**) *with* BrF_3.—The addition of successive very small quantities of BrF_3 (*ca.* 0.1 mol each) to the mixture (**4**) (0.1 g) led to the appearance of a purple solid which dissolved in excess of BrF_3. This reaction was much less vigorous than that with ClF_3 described above, and was only completed by warming to 50 °C. After the solvent had been pumped off, sublimation of the purple residue in a dynamic vacuum at 150 °C yielded $ReF_5(NBr)$ (**8**) as deep purple crystals. The isocyanate $ReF_5(NCO)$ (**5**) behaved similarly towards bromine trifluoride.

Bromoimidorhenium Pentafluoride, $ReF_5(NBr)$.—This compound forms deep purple crystals, m.p. 140 °C, which decompose rapidly in air. The crystals were unsuitable for *X*-ray investigation. The mass spectrum, obtained at 140 °C (Scheme 6) shows the parent ion $ReF_5(NBr)^+$ as well as $ReF_4(NBr)^+$; the pattern resembles that from $ReF_5(NCl)$. The i.r. spectrum shows absorptions at 2 322mw, 2 220w, 1 300mw, 1 202vw, 1 153w, 1 121mw, 989s, 953s, 721ms, 704w, 663s, 610m, 543s, and 479m cm^{-1}.

Reaction of $ReF_5(NCO)$ (**5**) *with* XeF_2.—To a suspension of (**5**) (0.1 g) in Genetron 113 (0.5 cm^3) was added a slight excess of XeF_2 in the form of small crystals. The liquid became strongly yellow in colour; reaction was deemed to be complete when gas evolution ceased. When all volatile materials had been pumped off a yellow oil (**9**) remained.

The i.r. spectrum of (**9**) showed strong peaks at 1 895 and 1 520 cm^{-1}, 1 180 cm^{-1} (Re–N), 1 105, 1 058, and 1 010 cm^{-1}, and absorptions at 770 and 660 cm^{-1} associated with Re–F stretches. The mass spectrum of the oil, obtained at 35 °C, showed the complete fragmentation pattern of $ReF_5(NF)$, including the

Table 2. Final fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) $ReF_5(NF)$ (**6**)			
Re	0.313 59(9)	0.109 39(5)	0.215 79(5)
F(1)	−0.057(2)	0.316 4(12)	0.019 2(10)
F(2)	0.560 7(19)	−0.013 2(10)	0.339 4(10)
F(3)	0.609 3(17)	0.196 1(10)	0.199 5(11)
F(4)	0.335(2)	0.214 3(11)	0.374 4(9)
F(5)	0.056 4(19)	−0.002 5(11)	0.248 8(13)
F(6)	0.319(2)	−0.018 3(11)	0.076 6(11)
N	0.095(2)	0.226 8(13)	0.101 8(11)
(*b*) $ReF_5(NCl)$ (**7**)			
Re	0.235 3(2)	0.250 00	0.205 03(14)
Cl	0.188 3(18)	0.250 00	−0.236 7(9)
F(1)	0.272(7)	0.250 00	0.461(4)
F(2)	−0.079(4)	0.097 3(15)	0.120(2)
F(3)	0.546(4)	0.093 0(16)	0.323(2)
N	0.199(5)	0.250 00	−0.032(3)

parent ion (313/315), but in addition pairs of peaks at *m*/*e* 344/346 and 363/365 appeared, indicating the presence of material(s) with CF_n groups. There are a number of intriguing possibilities for the nature of the yellow oil, including $ReF_5[N(F)CF_2]$, $ReF_5(NCF_3)$ and $[ReF_5(NF)]_2CF_2$.

Single-crystal Examination of $ReF_5(NF)$ (**6**).—Crystals of (**6**) were transferred in a glove-box into preseasoned Pyrex capillaries.

Crystal data. F_6NRe, $M = 314.20$, orange monoclinic crystals, $a = 5.298(2)$, $b = 9.286(3)$, $c = 9.979(6)$ Å, $\beta = 109.4(2)°$, $U = 463.21$ Å^3, $Z = 4$, $D_c = 4.507$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 251.9$ cm^{-1}, $F(000) = 543.8$, space group $P2_1/c$.

The cell dimensions were determined from an oscillation photograph about the *c* axis of an irregular parallelepiped crystal and from its optimized counter angles for zero and upper layer reflections on a Weissenberg diffractometer. The intensities of 1 206 unique reflections with $0.08 < (\sin\theta/\lambda) < 0.7$ Å^{-1} were collected at 20 °C, using a Stoe STADI-2 Weissenberg diffractometer and ω-scan technique.

The 1 182 reflections with $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarization effects. Subsequent computations were carried out using the computer program SHELX.[21] Scattering factors for neutral atoms were taken from ref. 22 with full correction for anomalous scattering and the structure solved by conventional Patterson and difference Fourier techniques. Full-matrix least-squares refinement of positional and isotropic thermal parameters for all atoms reduced *R* to 0.14. An absorption correction was applied to the data, with maximum and minimum transmission factors of 0.148 and 0.015 respectively. Final cycles of refinement used anisotropic thermal parameters for all atoms and employed a weighting parameter *g* (0.001 44): $w = 1/[\sigma^2(F_o) + g(F_o)^2]$. The final residual indices were $R\,[= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|] = 0.0569$ and $R'\,\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.0564$. A final difference Fourier map was featureless except for two residual peaks (3 e Å^{-3}) at <0.9 Å from the rhenium atom. An analysis of the weighting scheme over $|F_o|$ and $\sin\theta/\lambda$ was satisfactory.

Single-crystal Examination of $ReF_5(NCl)$ (**7**).—Crystals of (**7**) were obtained by vacuum sublimation at 75 °C.

Crystal data. ClF_5NRe, $M = 330.65$, purple monoclinic crystals, $a = 4.964(1)$, $b = 8.359(1)$, $c = 7.728(7)$ Å, $\beta = 124.8(1)°$, $U = 263.25$ Å^3, $Z = 2$, $D_c = 4.17$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 226.1$ cm^{-1}, $F(000) = 287.9$, space group $P2_1/m$.

The details of data collection and structure solution were identical to those for $ReF_5(NF)$ (**6**) except for the following. The intensities of 711 unique reflections were measured, of these 662 reflections had $I \geqslant 3\sigma(I)$. An absorption correction was applied to the data with maximum and minimum transmission factors of 0.139 and 0.025. The weighting parameter employed in final cycles of refinement was $g = 0.006\,36$, and the final residual indices were $R = 0.0577$ and $R' = 0.0579$. The only significant feature of the final difference Fourier map was a residual peak (3 e Å^{-3}) at *ca.* 1.2 Å from the rhenium atom.

Final atomic co-ordinates for both structures are given in Table 2.

Mass Spectra.—There was no certain evidence for metastable ions. The fragmentation patterns and the origins of the fragment ions are those assumed to be the most reasonable.

References

1 J. Fawcett, R. D. Peacock, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1982, 958.
2 K. Dehnicke and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 413.
3 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.
4 W. P. Griffiths, *Coord. Chem. Rev.*, 1972, **8**, 369.
5 O. R. Chambers, M. E. Harman, D. S. Rycroft, D. W. A. Sharp, and J. M. Winfield, *J. Chem. Res.*, 1977, (*S*) 150, (*M*) 1849.
6 J. Strähle and K. Dehnicke, *Z. Anorg. Chem.*, 1965, **338**, 287; K. Dehnicke and W. Liebett, *ibid.*, 1979, **453**, 9.
7 W. A. Nugent and R. L. Harlow, *J. Am. Chem. Soc.*, 1980, **102**, 1759.
8 C. Y. Chou, J. C. Huffman, and E. A. Maatta, *J. Chem. Soc., Chem. Commun.*, 1984, 1184.
9 W. Kafitz, K. Dehnicke, E. Schweda, and J. Strähle, *Z. Naturforsch., Teil B*, 1984, **39**, 1114.
10 J. Burgess, C. J. W. Fraser, I. Haigh, and R. D. Peacock, *J. Chem. Soc., Dalton Trans.*, 1973, 501.
11 J. Fawcett, R. D. Peacock, and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1980, 2294.
12 W. Liese, K. Dehnicke, I. Wallace, and J. Strähle, *Z. Naturforsch., Teil B*, 1979, **34**, 693.
13 A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1968, 2074, 2511.
14 J. Fawcett, G. Griffith, and R. D. Peacock, unpublished work, 1984.
15 R. Cockman and R. D. Peacock, unpublished work, 1984.
16 U. Wesher, K. Dehnicke, and D. Fenske, *Z. Anorg. Chem.*, 1979, **457**, 105.
17 D. D. Desmarteau, H. H. Eysel, H. Oberhammer, and H. Gunther, *Inorg. Chem.*, 1982, **21**, 1607.
18 J. D. Richards, in 'Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry. Nitrogen,' Longmans, London, 1967, vol. 8, Suppl. II, Part II, Sect. XXXIII, p. 409 *et seq.*
19 J. Burgess, J. Fawcett, and R. D. Peacock, *J. Fluorine Chem.*, 1984, **24**, 341.
20 J. Burgess, J. Fawcett, N. Morton, and R. D. Peacock, *J. Chem. Soc., Dalton Trans.*, 1977, 2149.
21 G. M. Sheldrick SHELX 76 Program for Crystal Structure Determination, University of Cambridge, 1976.
22 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—100, 149—150.

Received 9*th June* 1986; *Paper* 6/1156