Synthesis, properties and structures of NbOF₃ complexes and comparisons with NbOCl₃ analogues†

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The first series of complexes of niobium(V) oxide trifluoride, [NbOF₃(OPR₃)₂] (R = Me or Ph), [NbOF₃(dppmO₂)] (dppmO₂ = Ph₂P(O)(CH₂)₂P(O)Ph₂), [NbOF₃(dmso)₂], [NbOF₃(tmeda)] (tmeda = Me₂N-(CH₂)₂NMe₂) and [NbOF₃(diimine)] (diimine = 2,2'-bipy, 1,10-phen) have been prepared, either by direct reaction with the corresponding complexes of NbF₅ and hexamethyldisiloxane (HMDSO) in CH₂Cl₂–MeCN solution, or directly from NbF₅, ligand and HMDSO. They were characterised by IR, ¹H, ³¹P{¹H} and ¹⁹F{¹H} NMR spectroscopy, and X-ray crystal structures are reported for [NbOF₃(OPR₃)₂] (R = Me or Ph) and [NbOF₃(dppmO₂)]. Complexes of NbOCl₃, [NbOCl₃(OPPh₃)₂], [NbOCl₃(dppeO₂)], [NbOCl₃(tmeda)] (dppeO₂ = Ph₂P(O)(CH₂)₂P(O)Ph₂), [NbOCl₃(tmeda)] and [NbOCl₃(diimine)] were made from NbCl₅ and HMDSO in MeCN (which forms [NbOCl₃(MeCN)₂] in situ), followed by addition of the neutral ligand. Their properties are compared with the oxide fluoride analogues. X-ray structures are reported for [NbOCl₃(dppeO₂)], [NbOCl₃(dppeO₂)], [NbOCl₃(tmeda)] and [NbOCl₃(2,2'-bipy)]. The synthesis and spectroscopic characterisation of [MF₃L] (M = Nb or Ta; L = OPR₃, OAsPh₃) and [MF₃(diimine)] [MF₃] are also described, and the key properties of the four series of complexes compared.

Introduction

The fluorides and oxide fluorides of early transition metals in high oxidation states are strong Lewis acids and form a substantial range of complexes with F⁻ and with hard N- or O-donor ligands, whilst their more limited chemistry with soft donor ligands (P, S etc.) sometimes includes redox chemistry at the metal centre and oxidation/fluorination of the heteroatom donor, in addition to adduct formation. The properties of the metal centre are significantly altered by the small very electronegative fluoride ligands, and the chemistry of these fluoride/oxide fluorides is often very different to that of the chloride analogues.

Within Group V, the coordination chemistry of the oxide fluorides VOF₃,²² and VO₂F²⁻³ has been studied in some detail recently, whilst that of VF₅ is completely unexplored. In contrast, an extensive series of complexes of MF₅ (M = Nb or Ta) with both hard N- and O-donor¹⁴ and soft S-donor⁵ ligands are known, but the oxide-fluorides, MOF₃, are intractable and very little studied.⁶⁷ Here we report the synthesis, spectroscopic and structural characterisation of a series of adducts of NbOF₃. Complexes of NbOCl₃ have long been known, originally obtained by adventitious hydrolysis, or O-abstraction from the solvent or ligand in reactions of NbCl₅.⁸ More systematic syntheses used the reaction of NbCl₅ with siloxanes or occasionally direct reaction with the polymeric NbOCl₃,⁹ and selected examples have been re-examined in the present work to provide comparisons with the NbOF₃ complexes. NbOF₃ is obtained by heating NbF₅ with NbO₂F in argon, and has a structure based upon six-coordinate niobium (SnF₄ type), but the O/F disorder is only partially understood. It decomposes on heating above 180 °C, hydrolyses in air in a few hours, and is insoluble in organic solvents, making it completely unsuitable as a synthon to explore the coordination chemistry. TaOF₃, which is formed similarly from TaO₂F and TaF₅, is also disorder and unreactive.⁶

We describe here a convenient alternative route to NbOF₃ complexes involving F/O exchange from the corresponding NbF₅ adducts, using hexamethyldisiloxane (HMDSO). Similar halogen/oxygen exchange has proved to be a useful route for the preparation of complexes of polymeric oxide halides, including, for example, MOₓX₂ (M = Mo or W; X = Cl or Br),¹⁰ although it has rarely been used for oxide fluoride complexes.¹
The reaction of NbF₅ with 2,2'-bipyridyl or 1,10-phenanthroline in CH₂Cl₂ solution gave very poorly soluble complexes with a 1:1 NbF₅:diimine composition, originally assumed to be seven-coordinate monomers. We found them to be sufficiently soluble in CD₂Cl₂ solution to obtain ¹H and ¹⁹F NMR spectra after long accumulations, which show equivalent pyridyl rings and two ¹⁹F resonances with intensity ratio of 2:3. The more intense resonance is the characteristic 10 line multiplet of [NbF₅]⁻, leading to the revised formulation, [NbF₅(diimine)]⁺[NbF₆]⁻, with an eight-coordinate cation, as found in other adducts with chelating bidentate ligands. The [TaF₅(diimine)]⁺[TaF₆]⁻ were made similarly and were even less soluble. Eight-coordination is also found in the diimine complexes of Zr and Hf (M=Zr, Hf). The very poor solubility of the isolated [M═(diimine)]⁻[MF₆]⁺ complexes made them unsuitable as synthons for the O/F exchange reactions, and hence studies were switched to using in situ syntheses, although the data on the isolated MF₅ adducts are useful for comparison purposes (Table 1).

### NbOF₃ complexes

Treatment of an anhydrous CH₂Cl₂ solution of [NbF₅(OPPh₃)] with one mol. equivalent of OPPh₃, followed by one mol. equivalent of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. Subsequently, we found that “one-pot” syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF₅ and two mol. equivalents of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF₅ and two mol. equivalents of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF₅ and two mol. equivalents of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF₅ and two mol. equivalents of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF₅ and two mol. equivalents of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF₅ and two mol. equivalents of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF₅ and two mol. equivalents of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1). The addition of NbF₅ and two mol. equivalents of HMDSO, resulted in slow formation of a white precipitate, identified as [NbOF₃(OPPh₃)]. We subsequently found that "one-pot" syntheses were possible and more convenient, although the sequence of addition of the reactants and the time-scales are key to obtaining pure complexes (Scheme 1).
which was stirred for 20 min. and then one mol. equivalent of HMDSO and a small amount of MeCN were added. After 24 h the mixture, now containing much white precipitate, was concentrated *in vacuo*, and the \([\text{NbOF}_3(\text{OPPh}_3)_2]\) isolated. If the HMDSO was added before, or simultaneously with, the OPPh$_3$, very impure products resulted, and several hours seem necessary to complete the O/F exchange. The role of the MeCN is not entirely clear, but its presence seems necessary to obtain pure preparations. In the syntheses of \([\text{WO}_2\text{Cl}_2\{\text{RS(CH}_2)_2\text{SR}\}]\) from WCl$_6$ or WOCl$_4$, RS(CH$_2$)$_2$SR and HMDSO, use of MeCN–CH$_2$Cl$_2$ as solvent prevents the precipitation of polymeric WO$_2$Cl$_2$, by forming the nitrile adduct *in situ*. While a similar role may be present in the niobium systems, we note that attempts to isolate nitrile complexes failed (see below). The complexes \([\text{NbOF}_3(\text{OPMe}_3)_2]\) and \([\text{NbOF}_3(\text{dppmO}_2)]\) were prepared similarly to \([\text{NbOF}_3(\text{OPPh}_3)_2]\), but all attempts to obtain \([\text{NbOF}_3(\text{OAsPh}_3)_2]\) gave mixtures containing \([\text{NbF}_5(\text{OAsPh}_3)_2]\), \([\text{NbF}_5^-]\) and Ph$_3\text{AsF}_2$ (identified based upon *in situ* $^1$H and $^{93}$Nb NMR spectra). \([\text{NbOF}_3(\text{OAsPh}_3)]\) was originally reported to be formed from adding OAsPh$_3$ to a solution of NbO$_3$ in conc. aqueous HF, although identified only by an IR spectrum. Using a 4 : 2 : 1 molar ratio of OPPh$_3$ : HMDSO : Nb$_5$ in CH$_2$Cl$_2$–MeCN resulted only in isolation of \([\text{NbOF}_3(\text{OPPh}_3)_2]\), further O/F exchange did not occur. The complex \([\text{NbOF}_3(\text{dmso})_2]\) was also isolated in high yield from reaction of NbF$_5$, dms and HMDSO. As noted above, the very poor solubility of \([\text{NbF}_5(\text{diimine})_2]\)[NbF$_6$] made it impossible to redissolve them in CH$_2$Cl$_2$ for conversion to oxide-fluoride complexes. However, combination of the diimine and Nb$_5$ in a large volume of CH$_2$Cl$_2$ (which gave a opalescent solution), followed by addition of HMDSO, did give \([\text{NbOF}_3(\text{diimine})]\). The \([\text{NbOF}_3(\text{tmeda})]\) was made in high yield as an air-stable white powder by sequential reaction of NbF$_5$, tmeda and HMDSO also failed. Ester, nitrile and thioether adducts of Nb$_5$ are well characterised, but it seems that these ligands are too weakly bound to the “NbOF$_5$” to prevent polymerisation and precipitation of ligand-free NbOF$_3$. Similar behaviour was observed with VO$_2$F, and the niobium system seems to be a further example of the metal centre preferring to form oxide/fluoride bridges rather than coordinate to weak, neutral donor groups. Thus far, attempts to isolate TaOF$_3$ complexes from TaF$_5$, ligand (ligand = OP$_5$$_3$, dmso or 2,2′-bipy) and HMDSO under similar reaction conditions, have been unsuccessful.

The solid \([\text{NbOF}_3(\text{OPPh}_3)_2]\), \([\text{NbOF}_3(\text{dmso})_2]\) and \([\text{NbOF}_3(\text{dppmO}_2)]\) complexes are white powders, relatively air-stable in the solid state (some appear hygroscopic on prolonged exposure), although hydrolysed by wet solvents. They are easily soluble in CH$_2$Cl$_2$, whereas the \([\text{NbOF}_3(\text{diimine})]\) are very poorly soluble, and \([\text{NbOF}_3(\text{tmeda})]\) is insoluble. The $^1$H and $^{31}$P($^1$H) NMR spectra (Table 1) of \([\text{NbOF}_3(\text{OPMe}_3)_2]\) show two phosphine oxide environments, and the $^{13}$F($^1$H) NMR spectrum contains two singlets with integrals in the ratio 1 : 2, which is consistent with mer-fluorines and one OPM$_3$ trans to O and one trans to F. Attempts to record a $^{93}$Nb NMR spectrum were unsuccessful (an effect observed for all the NbOF$_3$ adducts), contrasting with the ready observation of resonances from the NbF$_5$ adducts described above. The low symmetry at the niobium centre will result in a large electric field gradient, and unobservably broad lines due to fast quadrupolar relaxation. The different *trans*-influences of Nb–F and Nb–O groups in these complexes are also shown by the difference in $^{31}$P chemical shifts for the *trans* disposed OPM$_3$ ligands (∼14 ppm), and similar differences are seen in the $\nu$(PO) frequencies in the IR spectra which differ by >50 cm$^{-1}$. A strong band in the range 970–920 cm$^{-1}$ is assignable to the terminal Nb=O vibrations.

Confirmation of the geometry of \([\text{NbOF}_3(\text{OPMe}_3)_2]\) comes from the X-ray crystal structure (Fig. 1).

There is no evidence in this molecule for O/F disorder in plane, which is a common problem in this area of chemistry (cf. \([\text{VOF}_3(\text{OPPh}_3)_2]\)). The niobium is in a distorted octahedral environment with the axial F–Nb–F unit bent away from the
the solvent molecule are omitted for clarity. The second Nb2 centred molecule is similar with the third (Nb3) being disordered. Selected bond lengths (Å) and angles (°): Nb1–O1 = 1.773(2), Nb1–F1 = 1.850(3), Nb1–F2 = 2.104(2), Nb1–O2 = 1.532(4), O1–Nb1–F2 = 98.63(9), F2–Nb1–F3 = 87.90(8), F3–Nb1–O3 = 84.76(9), F1–Nb1–O3 = 82.46(9), O2–Nb1–O3 = 81.80(8).

oxido-ligand. The Nb–F trans F are longer than Nb–F trans O by ~0.06 Å and the Nb–O = 1.773(2) Å is consistent with the expected multiple bond character. The Nb–O(P) trans F distances of 2.104(2) Å and Nb–O(P) trans O = 2.085(2) Å show the disparate effects of the trans donor and parallel the spectroscopic evidence. Curiously, d(P–O) in the two phosphine oxide ligands are only slightly different. The spectroscopic data on [NbOF3(OPMe3)2] (Table 1) are very similar to those of the OPMe3 complex discussed, but in this case the X-ray structure (Fig. 2) shows F/O disorder trans to OPMe3, and the bond length and angle data are correspondingly unreliable, although the identity of the complex is confirmed.

The structural parameters of [NbOF3(dppmO2)] are generally similar to those already discussed above, and this complex seems free of O/F disorder (Fig. 3).

The [NbOF3(tmeda)] is insoluble in non-coordinating solvents and MeCN, and is partially decomposed by dmf or dmso which prevented solution measurements. However, the [NbOF3(diimine)], although very poorly soluble in chloro carbons or MeCN (a property shared with the NbF5 analogues above, and also the ZrF4, HfF4, VO4F, and VO2F diimine complexes), gave 1H NMR spectra showing inequivalent pyridyl rings, and hence that the diimine was trans to O/F. The 19F(1H) NMR spectrum of [NbOF3(2,2′-bipy)] (Table 1) shows two resonances in the ratio 1 : 2 consistent with a mer arrangement of the fluorines, and the chemical shifts are ~100 ppm to low frequency of those observed for the [NbF5(diimine)].

The [NbOF3(1,10-phen)] was very poorly soluble in weakly coordinating solvents and a convincing 19F(1H) NMR spectrum was not obtained. The diimine complexes are readily hydrolysed in solution in CH2Cl2 or MeCN forming [NbF6]2− ions, based upon 19F NMR evidence and also shown by attempts to obtain crystals of [NbOF3(2,2′-bipy)] for an X-ray study which produced a few poor quality crystals of [2,2′-bipy]2[NbF6]. The solids also hydrolyse slowly on exposure to the atmosphere.
Solid NbOCl₃ contains dimeric [Cl₂Nb(O)(μ-Cl)₂Nb(O)Cl₂] units linked into chains via unsymmetrical oxide bridges, giving six-coordinate niobium.¹⁴ The syntheses of the [NbOCl₃(L–L)] (L–L = 2,2′-bipy, 1,10-phen, dppme₂, dppeO₂, tmeda and 2 × OPPh₃) were carried out in anhydrous MeCN solution, with the reversed order of reagent addition to that used for the oxide-fluoride syntheses, i.e. reacting NbCl₅ with HMDSO to form ‘NbOCl₅’ in situ, followed by addition of the neutral ligand (Scheme 2). The initially yellow solution of NbCl₅ in MeCN rapidly pales on addition of HMDSO, indicating formation of [NbOCl₃(MeCN)₂] upon addition of the neutral ligand. Once isolated, the [NbOCl₃(tmeda)] is essentially insoluble in non-coordinating solvents, although crystals were grown adventitiously from the reaction filtrate. The other complexes are soluble in CH₂Cl₂ or MeCN. The IR spectra of [NbOCl₃(L–L)] upon addition of the neutral ligand (Scheme 2) show strong ν(Nb=O) vibrations for the phosphine oxide groups trans to Cl and cis to O. In solution, the ³¹P{¹H} NMR spectra of [NbOCl₃(L–L)] (L–L = dppmO₂, dppeO₂, 2 × OPPh₃) show the expected inequivalence of the neutral donor groups, but attempts to record ⁹³Nb spectra were unsuccessful; as with the oxide-fluorides this is attributed to fast quadrupolar relaxation in the low symmetry electric fields.

X-Ray crystal structures were obtained for five of the complexes. The structure of [NbOCl₃(OPPh₃)₂] has been reported previously and shows₁⁶ mer-chlorines, and cis OPPh₃ groups, with O/Cl disorder trans to OPPh₃. The crystal structures of the two diphosphine dioxide complexes (Fig. 4 and 5) show d(Nb=O) slightly shorter by 0.04 Å compared to the oxide-fluoride complexes, but with similarly disparate d(Nb–O(P)) suggesting the trans influence of F and Cl are similar in these complexes. The d(Nb=O) and d(Nb–Cl) distances in a range of NbOCl₃ adducts cover quite a narrow range,⁹,¹⁵,¹⁶ suggesting that these are the dominant bonding interactions, with the neutral ligands completing the coordination sphere, but having little influence on the Nb=O and Nb–Cl bonds.

The structure of [NbOCl₃(tmeda)] (Fig. 6) shows the same features as those of the oxygen donor complexes, although the carbon atoms about N₂ show some disorder; there is no evidence for O/Cl disorder. The dimensions in the structure of [NbOCl₃(2,2′-bipy)] (Fig. 7) are also unexceptional, although the octahedron about the niobium is more distorted due to the small chelate bite of the 2,2′-bipyridyl (N₁–Nb–N₂ = 69.52(21)°).

Attempts to obtain a complex of NbOCl₃ with 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃-tacn) gave a mixture of products. Recrystallisation of the mixture from MeCN gave a few crystals identified as [(Me₃-tacn)H]₂[NbOCl₃]. The anion
has been structurally characterised with a variety of cations, but often the niobium is on a high symmetry site which results in O/Cl disorder.\textsuperscript{17} In the present case the structure appears to free of such disorder and the data are presented as ESL.\textsuperscript{†}

**Comparisons of NbF\textsubscript{5}, NbOF\textsubscript{3} and NbOCl\textsubscript{3} complexes**

Comparisons of the spectroscopic data in Table 1 for [NbF\textsubscript{5}(OPR\textsubscript{3})\textsubscript{n}] and [NbOF\textsubscript{3}(OPR\textsubscript{3})\textsubscript{n}] shows very significant differences due to replacement of two fluoride ligands by the oxo-group. The \(19\text{F}\) and \(31\text{P}\) chemical shifts are very different, with those of [NbF\textsubscript{5}(OPR\textsubscript{3})\textsubscript{n}] at much higher frequency for each nucleus. Similar differences are apparent in the \(19\text{F}\) chemical shifts for the two series of N-donor complexes. The data demonstrate that the presence of the strong \(\pi\)-donating oxo-group significantly changes the electron density at the Nb(v) centre, making it much less electron poor, and hence a weaker Lewis acid. Within the NbOF\textsubscript{3} complexes there is also a large \textit{trans} influence of the oxo-group which results in significantly longer bonds to the \textit{trans} ligand than for those groups \textit{trans} to fluorine. The \(d(P\equiv O)\) show very small differences, although the relative \textit{trans} influence is clear in the \(\nu(P\equiv O)\) vibrations in the IR spectra. Comparing the structural and spectroscopic data on corresponding NbOF\textsubscript{3} and NbOCl\textsubscript{3} complexes reveals rather small differences. The \(d(Nb\equiv O)\) in these and in literature examples of the oxide chloride complexes\textsuperscript{6,9,15,16} show they occur in a narrow range, \(\sim 1.7\)–\(1.8\) Å, irrespective of the halide or neutral co-ligands present. Similarly, \(d(Nb\equiv Cl)\)\textit{trans} 1 is relatively insensitive to the nature of L (the ligand types are too restricted to make a similar comparison for the fluoride).

The bond angles about the niobium centres also show significant deviations from those expected for a regular octahedral geometry. The factors determining the geometry adopted by ML\textsubscript{n} complexes of transition metals as a function of ligand types (\(\sigma\)-donor only, or \(\sigma\) and \(\pi\) donor), \(d^0\) count and ligand architecture have been discussed in several articles,\textsuperscript{18} and the fact that \([MF\textsubscript{n}L\textsuperscript{\textit{\pi}}\textsuperscript{\textit{\pi}}]^-\) species are Os\textsubscript{n} and [M(CH\textsubscript{3})\textsubscript{n}L\textsuperscript{\textit{\pi}}\textsuperscript{\textit{\pi}}]^- (\(n = 1\))
The niobium oxide halide structures discussed in the present work (12e, d? complexes) are based upon distorted octahedral geometries, as would be expected, given the presence of dominant ? and ? donor ligands. As observed in many early transition metal complexes containing M=O bonds, the angles involving the latter, O=M=L and O=M=X are larger than X=M=X, X=M=L, or L=M=L, in effect the electron rich multiply bonded M=O unit occupies more space about the metal centre. Superimposed upon this are smaller effects arising from the steric demands of the X and L groups and constraints of neutral ligand geometries, such as chelate bites in the bidentates. In the cis-MOX2L2 unit the axial X=M=X group bends away from the M=O and towards the neutral co-ligands.2,3,5,8

The differences between NbOF3 and NbOCl3 as acceptors towards weaker donor ligands such as ethers or nitriles, where the latter forms complexes with thf, MeO(CH2)2OMe, MeCN, etc. 4,9,15 but attempts to isolate analogous with NbOF3 result in intractable, ligand-free products (NbOF3 polymer). This can be ascribed to the preference of the niobium centre to form fluoride bridges over weak Nb-L bonds, and is seen in other fluoride and oxide fluoride systems.1

Finally, these niobium complexes can be compared with those of the 3d analogue, vanadium. VO3 forms similar phosphine oxide, diimine and diamine complexes to NbOF3, but also complexes with ethers, thioethers and nitriles.2 The differences are again readily rationalised by the niobium’s preference for fluorne bridges; NbOF3 is an inert, very strongly bridged polymer (above), whereas VO3 although (weakly) F-bridged in the solid,30 easily vapourises as a monomer on heating and dissolves in most organic solvents. The complexes of VOCI3 with neutral ligands are thermally and often photo-labile, and extremely readily hydrolysed and reduced (often spontaneously) to V(IV) or V(III) compounds,31 whereas the NbOCl3 adducts remain pentavalent, unless specifically treated with reducing agents.

Conclusions

The O/F exchange reaction between complexes of the binary fluoride NbF2 and a siloxane have been shown to produce complexes of the otherwise intractable oxide-fluoride, NbOF3, in good yield. However, further O/F exchange to form derivatives of NbO2F did not occur under similar conditions. Comparison of the spectroscopic properties of the NbF2 and NbOF3 complexes demonstrates the substantial effect on the metal centre of replacing two fluoride by the stronger ? donor oxido-group.

Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm–1. 1H, 19F{1H}, 31P{1H} and 93Nb NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to the protio resonance of the solvent, external CFCl3, 85% H3PO4, and [NEt4][NbCl6] in CD3CN, respectively. Microanalyses were undertaken by Medac Ltd or London Metropolitan University. Solvents were dried prior to use: THF, Et2O and MeOCH2CH2OMe by distillation from sodium benzophenone ketyl, MeCN and CH2Cl2 from CaH2. OPEt3 was sublimed in vacuo, OPPh3, OAsPh3, 2,2′-bipy, 1,10-phen were heated in vacuo, and temda distilled from BaO. All preparations were undertaken using standard Schlenk techniques under a N2 atmosphere.

[NbF6(OPPh3)]: A solution of OPPh3 (0.262 g, 1.0 mmol) in CH2Cl2 (20 mL) was added to finely powdered NbF3 (0.188 g, 1.0 mmol), and vigorously stirred to give a clear solution. This was filtered to remove any residual solid and concentrated in vacuo to ~5 mL. On standing a white powder separated, which was filtered off and dried in vacuo. Yield 0.40 g, 85%. Anal: required for C18H15F5NBOP (466.2): C, 46.4; H, 3.2. Found: C, 46.9; H, 3.6%. 1H NMR (CD2Cl2, 293 K): 1.9 (s, 2JHH = 15 Hz). 19F{1H} NMR (CD2Cl2, 293 K): +157.6 (s, [F]), 134.5 (s, [4F]); +134.7 (s, [4F]). 31P{1H} NMR (CD2Cl2, 293 K): +161.8 (s, [F]), +128.6 (s, [4F]); +128.6 (s, [4F]).

[NbF6(OPEt3)]: Made similarly to the OPPh3 adduct. Yield 75%. Anal: required for C18H15F5NBOP (466.2): C, 46.9; H, 3.2. Found: C, 13.2; H, 3.5%. 1H NMR (CD2Cl2, 293 K): 1.9 (d, 2JHH = 15 Hz). 19F{1H} NMR (CD2Cl2, 293 K): +157.6 (s, [F]), 134.5 (s, [4F]); +134.5 (s, [4F]); +134.5 (s, [4F]). 31P{1H} NMR (CD2Cl2, 293 K): +157.6 (s, [F]), +128.6 (s, [4F]); +128.6 (s, [4F]).

[NbF6(OAsPh3)]: Prepared as for the OPPh3 analogue except that the complex was prepared in ice-bath and solution stirred for 5 min. It was then concentrated in vacuo and the precipitated solid isolated immediately. If the solid is left in solution a yellow and then brown colour develops and in situ NMR data shows formation of Ph3AsF2, [NbF6]− and other unidentified impurities. The pure solid seems stable for some weeks in a freezer. Yield 55%. Anal: required for C18H15F5NBOP (466.2): C, 42.4; H, 3.0. Found: C, 42.4; H, 3.0%. 1H NMR (CD2Cl2, 293 K): 7.2–7.6 (m). 19F{1H} NMR (CD2Cl2, 293 K): +145.0 (s, [F]), +110.5 (s, [4F]). 93Nb NMR (CD2Cl2, 293 K): −1511 (br, s). IR (Nujol/cm–1): 1092 (vs) PO, 615 (vs, br). NbF3.

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[\text{NbF}_5(2,2'\text{-bipy})][\text{NbF}_6\text{]:} \text{NbF}_5 (0.188 g, 1.0 mmol) was added to CH_2Cl_2 (20 mL) and vigorously stirred, whilst a solution of 2,2'-bipy (0.16 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added, resulting in rapid precipitation of a fine white powder. After 2 h the solid was isolated by filtration, rinsed with diethyl ether (5 mL) and dried in \textit{vacuo}. Yield 0.30 g, 86%. Anal: required for C_{20}H_{16}F_{10}N_{4}Nb_{2} (688.2): C, 34.9; H, 2.3; N, 8.1. Found: C, 34.7; H, 2.2, N, 8.1%. \textsuperscript{1}H NMR (CD_2Cl_2, 293 K): 9.34 (d, [H], J = 9 Hz), 8.63 (d, [H], J = 9 Hz), 8.40 (m, [2H]), 7.78 (m, [2H]). \textsuperscript{19}F{^1}H NMR (CD_2Cl_2, 293 K): +139.7 (s, [F]), +103.2 (10 lines, J = 13 Hz). IR (Nujol/cm\textsuperscript{-1}): 3659, 3649, 3580, 3439, 2931, 1761, 1610, 1570, 1493, 1445, 1414, 1373, 1278, 1156, 1088, 1044, 959, 920, 693, 608, 582, 507, 490, 428 s, [19F, 2F]. IR (Nujol/cm\textsuperscript{-1}): 959 s [NbO, 612 vs, 579 s NbF).}

[\text{NOBF}_5(1,10\text{-phen})][\text{NbF}_6\text{]:} \text{NbF}_5 (0.19 g, 1 mmol) was dissolved in CH_2Cl_2 (200 mL) and dry 1,10-phen (0.18 g, 1 mmol) in CH_2Cl_2 (10 mL) added with stirring, producing some fine white precipitate. After 5 min hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred for 48 h at room temperature, producing a dense white precipitate. The precipitate was filtered off, rinsed with diethyl ether (10 mL) and dried in \textit{vacuo}. Yield 0.30 g, 86%. Anal: required for C_{32}H_{16}F_{20}N_{4}O_{2}Nb (692.2): C, 37.0; H, 2.3; N, 8.1. Found: C, 34.7; H, 2.3; N, 8.1%. \textsuperscript{1}H NMR (CD_2Cl_2, 293 K): 9.36 (s, [H]), 9.28 (s, [H]), 8.77 (m, [H]), 8.56 (m, [H]), 8.19 (s, [H]), 8.13 (s, [H]), 8.02 (s, [H]), 7.90 (s, [H]). \textsuperscript{19}F{^1}H NMR (CD_2Cl_2, 293 K): insufficiently soluble. IR (Nujol/cm\textsuperscript{-1}): 970 s (NbO), 610 sh, 594 s, 583 s NbF).}

[\text{NOBF}_5(\text{OPPh}_3)][\text{NbF}_6\text{]:} \text{NbF}_5 (0.19 g, 1 mmol) and OPPh\textsubscript{3} (0.56 g, 2 mmol) were added to dry CH_2Cl_2 (25 mL) and the mixture stirred for 20 min. Hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred overnight at room temperature. The solvents were removed in \textit{vacuo} leaving a slightly sticky cream powder which was extracted with CH_2Cl_2 (20 mL), filtered to remove some undissolved solid, and concentrated to ~5 mL. Dry diethyl ether (10 mL) was added slowly and the cream precipitate filtered off and dried in \textit{vacuo}. Yield 0.34 g, 45%. Refrigeration of the filtrate for 5 d. gave crystals suitable for the X-ray data collection. Anal: required for C_{25}H_{32}F_{2}NbO_{2}P_{2} (582.3): C, 51.6; H, 3.8. Found: C, 51.5; H, 3.9%. \textsuperscript{1}H NMR (CD_2Cl_2, 293 K): 7.82–7.15 (m, [10H], 3.70 (m, [H], J = 13 Hz). \textsuperscript{19}F{^1}H NMR (CD_2Cl_2, 293 K): 9.28 (s, [F]), 6.10 (s, [F]), 6.10 (s, [F]). \textsuperscript{31}P{^1}H NMR (CD_2Cl_2, 293 K): 46.4 (d, [P], J_{pp} = 17 Hz), 36.8 (s, [P], J_{pp} = 17 Hz). IR (Nujol/cm\textsuperscript{-1}): 1156 s, 1088 s (PO), 944 s NbO, 608 vs, 582 s NbF).}

[\text{NOBF}_5(\text{dmso})_2][\text{NbF}_6\text{]:} \text{NbF}_5 (0.19 g, 1 mmol) was added to dry CH_2Cl_2 (25 mL) followed by dry dmso (0.5 mL) and the mixture stirred for 20 min. producing a clear colourless solution. Hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred for 6 h at room temperature, during which a fine microcrystalline solid was deposited. The solid was filtered off, rinsed with diethyl ether (5 mL) and dried in \textit{vacuo}. Yield 0.25 g, 78%. Anal: required for C_{33}H_{18}F_{2}NbO_{2}S_{2} (522.2): C, 49.5; H, 3.8. Found: C, 49.5; H, 3.9%. \textsuperscript{1}H NMR (CD_2Cl_2, 293 K): 1140 (m, 1087 s (PO), 958 s, NbO, 614 s, 555 s NbF).}

[\text{NOBF}_5(\text{OPMe}_3)_2][\text{NbF}_6\text{]:} \text{NbF}_5 (0.19 g, 1 mmol) and OPMe\textsubscript{3} (0.56 g, 2 mmol) were added to dry CH_2Cl_2 (25 mL) and the mixture stirred for 20 min. producing a clear colourless solution. Hexamethyldisiloxane (0.16 g, 1 mmol) and MeCN (0.5 mL) were added and the mixture stirred for 6 h at room temperature, during which a fine microcrystalline solid was deposited. The solid was filtered off, rinsed with diethyl ether (5 mL) and dried in \textit{vacuo}. Yield 0.25 g, 78%. Anal: required for C_{32}H_{16}F_{2}NbO_{2}S_{2} (522.2): C, 44.9; H, 3.8. Found: C, 45.1; H, 3.9%. \textsuperscript{1}H NMR (CD_2Cl_2, 293 K): 2.65 (br); (253 K): 2.59 ([6H]). 19F{^1}H NMR (CD_2Cl_2, 293 K): 50.4 (s, [F]), 38.0 (s, [2F]). \textsuperscript{31}P{^1}H NMR (CD_2Cl_2, 293 K): 46.4 (d, [P], J_{pp} = 17 Hz), 36.8 (s, [P], J_{pp} = 17 Hz). IR (Nujol/cm\textsuperscript{-1}): 1156 s, 1088 s (PO), 944 s NbO, 608 vs, 582 s NbF).
[**[NbOCl₄]**]: was made similarly to [**[NbOCl₄]**]. Yield 67%. Crystals of [**[NbOCl₄]**] were grown from a saturated dichloromethane solution in the freezer. Anal: required for C₃H₇Cl₃N₂O₈ (371.4): C, 32.3; H, 2.2; N, 7.5%. IR (Nujol/cm⁻¹): 943 (s) NbO, 338 (s) NbCl.

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Details of the crystallographic data collection and refinement parameters are given in Table 2. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (100 μm focus) with the crystal held at 100 K (N2 cryostream). Structure solution and refinement were straightforward, except as detailed below, with H atoms bonded to C being placed in calculated positions using the default C–H distance. Several cases of O/X disorder have been discussed in the text. Three of the carbon atoms in [NbOCl3(tmeda)], C4, C5 and C6 were elongated, suggesting some disorder, but attempts to split these over two positions were unsuccessful. For [NbOCl3(2,2′-bipy)] Nb2 was initially placed on the two-fold axis but showed a very elongated ellipsoid with two large Q peaks close to Nb2. A subsequent model displaced Nb2 by a few tenths of an Å from the axis and this gave a better fit to the data, R1 reduced from ~0.08 to ~0.05.

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