^{19}F NMR Spectroscopy as Useful Tool for Determining the Structure in Solution of Coordination Compounds of MF_5 (M = Nb, Ta)

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Abstract

The salts $[S(NMe_2)_3][MF_6]$ (M = Nb, **2a**; M = Ta, **2b**) and $[S(NMe_2)_3][M_2F_{11}]$ (M = Nb, **2c**; M = Ta, **2d**) have been prepared by reacting MF_5 (M = Nb, **1a**; M = Ta, **1b**) with $[S(NMe_2)_3][SiMe_3F_2]$ (TASF reagent) in the appropriate molar ratio. The solid state structure of **2b** has been ascertained by X ray diffraction. The 1:1 molar ratio reactions of **1a** with a variety of organic compounds (L) give the neutral adducts NbF_5L [L = Me_2CO, **3a**; L = MeCHO, **3b**; L = Ph_2CO, **3c**; L = tetrahydrofuran (thf), **3d**; L = MeOH, **3e**; L = EtOH, **3f**; L = $HOCH_2CH_2OMe$, **3g**; L = Ph_3PO, **3h**; L = NCMe, **3i**] in very good yields. Otherwise, the complexes MF_5L [M = Nb, L = $HCONMe_2$, **3j**; M = Nb, L = $(NMe_2)_2CO$, **3k**; M = Ta, L = $(NMe_2)_2CO$, **3l**; M = Nb, L = $OC(Me)CH{=}CMe_2$, **3m**] have been detected in solution in admixture with other unidentified products, upon 2:1 molar reaction of **1** with the appropriate reagent L. Alternatively, the ionic complexes $[NbF_4(tht)_2][NbF_6]$, **4a**, and $[NbF_4(tht)_2][Nb_2F_{11}]$, **4b**, have been obtained by combination of tetrahydrothiophene (tht) and **1a**, in 1:1 and 2:3 molar ratios, respectively. The treatment of **1** with a two-fold excess of L leads to the species $[MF_4L_4][MF_6]$ [M = Nb, L = $HCONMe_2$, **5a**; M = Ta, L = $HCONMe_2$, **5b**; M = Nb, L = thf, **5c**; M = Ta, L = thf, **5d**; M = Nb, L = OEt_2, **5e**]. The new complexes have been fully characterised by NMR spectroscopy. Moreover, the revised ^{19}F NMR features of the known compounds MF_5L [M = Ta, L = Me_2CO, **3n**; M = Ta, L = Ph_2CO, **3o**; M = Ta, L = MePhCO, **3p**; M = Ta, L = thf, **3q**; M = Nb, L = CH_3CO_2H, **3r**; M = Nb, L = CH_2ClCO_2H, **3s**; M = Ta, L = CH_2ClCO_2H, **3t**], $TaF_4(acac)$, TaF_4(Me-acac) and $[TaF(Me\text{-}acac)_3][TaF_6]$ (Me-acac = methylacetylacetonato anion) are reported.

Keywords: niobium, tantalum, fluoride, ^{19}F-NMR spectroscopy, structural characterization

1. Introduction

The coordination chemistry of niobium and tantalum pentahalides MX_5 (M = Nb, Ta; X = halogen) [1] with oxygen donor ligands was scarcely investigated in the past [2], and recent work by

ourselves has attempted a rationalization in this field [3]. Despite the scarce information available for that chemistry, the use of MCl_5 in catalysis has been progressively grown in the last decade [4]; these highly oxophilic compounds often provide noticeable results in metal-directed organic reactions, moreover they can exhibit unusual behaviour compared to different early transition metal halides in high oxidation state [5].

As far as niobium and tantalum pentafluorides MF_5 (M = Nb, **1a**; M = Ta, **1b**) are concerned, a restricted number of coordination adducts have been described [3a-d, 6] and no X ray structures have been reported hitherto. On the other hand, the fluoro-containing complexes **1** have found application as promoters of a variety of processes [7], including fluorination [8] and alkylation [9] reactions. Recent results have indicated that **1** may be used as efficient catalysts for ring opening polymerisations [10].

A close examination of the literature has shown that most of the reported niobium and tantalum fluoride containing species, including adducts of MF_5 and the $[MF_6]^-$ anion, have not been isolated and their structure has been proposed on the basis of solution NMR spectroscopy (^{93}Nb, ^{19}F) [6a,b,c,e-i, 11]. Unfortunately, the NMR data available in the literature often refer to solvents which react with the metal fluoride (ether, alcohols, nitriles, trifluoroacetic acid, fluorine, hydrogen fluoride), therefore an homogeneous, overall view of the situation is not possible at present.

In order to put some more light in the chemistry of MF_5 (M = Nb, Ta) and with the aim to give a contribution to the development of the use of these interesting compounds in metal-mediated syntheses, we decided to perform a systematic study on the coordination chemistry of **1** with a series of organic substrates, including oxygen-, nitrogen- and sulphur donor ligands. We have found that ^{19}F NMR spectra, recorded at the same temperature and referring to the same solvent, represent a useful tool for detecting the structure in solution of the MF_5 derivatives (M = Nb, Ta). In addition, this characterisation can be coherently supported by electrical conductivity data [12]. The present paper contains the results of our systematic study, which has also allowed to revise some attributions of ^{19}F NMR resonances reported in former reports by ourselves [3a-d].

2. Results and discussion

Our investigation started with the preparation and the full characterization of well defined MF_5 (M = Nb, Ta) derivatives to be used as "standard" for the subsequent analyses. Colourless solutions containing $SiMe_3F$ and $[S(NMe_2)_3][MF_6]$ (M = Nb, **2a**; M = Ta, **2b**), Eq. (1), were obtained by treatment of MF_5 with one equivalent of $[S(NMe_2)_3][SiMe_3F_2]$ (TASF reagent) in CH_2Cl_2. Crystalline compounds could be isolated by layering the solutions with heptane. The compounds **2a-b**, which display a very good solubility in chloroform, have been characterised by ^1H, ^{13}C and ^{19}F NMR spectroscopies, and by X-ray crystallography in the case of M = Ta.

$$[S(NMe_2)_3][SiMe_3F_2] + MF_5 \rightarrow \underset{\textbf{2a-b}}{[S(NMe_2)_3][MF_6]} + SiMe_3F \qquad (1)$$

Similarly, the derivatives $[S(NMe_2)_3][M_2F_{11}]$ (M = Nb, **2c**; M = Ta, **2d**) [11d] were prepared in solution by reacting pure **2a-b** with one equivalent of MF_5, Eq. (2), and characterised by ^{19}F NMR spectroscopy. Alternatively, orange $CDCl_3$ solutions of **2c-d** are obtainable by direct treatment of TASF with an excess of MF_5 (two equivalents or more).

$$\underset{\textbf{2a-b}}{[S(NMe_2)_3][MF_6]} + MF_5 \rightarrow \underset{\textbf{2c-d}}{[S(NMe_2)_3][M_2F_{11}]} \qquad (2)$$

The crystal structure of **2b** (Figure 1 and Table 1) consists in an ionic packing of $[TaF_6]^-$ anions and $[S(NMe_2)_3]^+$ cations. Some short inter-molecular contacts (in the range 2.50-2.66 Å) are present between the fluorine atoms of the anions and the H-methyl protons of the cations (sum of the Van der Waals radii 2.80 Å [13]). The $[TaF_6]^-$ anion displays the expected [14] octahedral geometry with the Ta–F bond distances comprised in a narrow range [1.878(5)-1.904(4) Å; average 1.888(10) Å]. The

structure of the $[S(NMe_2)_3]^+$ cation is in keeping with previous structural determinations reported in the literature [15].

Insert Figure 1 about here
Insert Table 1 about here

The ^1H and ^{13}C NMR spectra of **2a,b** (in $CDCl_3$ solution) display the resonance due to three equivalent methyl groups within the cation [*e.g.* in the case of **2a**: $\delta(^1H)$ = 2.96 ppm, $\delta(^{13}C)$ = 38.4 ppm]. An unique ^{19}F NMR signal accounts for six equivalent fluorines belonging to the anion. More precisely, a singlet at 39.1 ppm is observed in the ^{19}F NMR spectrum of **2b** (in $CDCl_3$), while the ^{19}F NMR resonance related to **2a** appears as a decet centered at 103.5 ppm [6a, 11c,d], see Figure 2, due to coupling of the fluorines with the niobium nucleus, characterized by I = 9/2. The absence of a well resolved octet for the $[TaF_6]^-$ anion (the tantalum nucleus has I = 7/2) is probably due to fast quadrupole relaxation of tantalum causing line broadening, thus affording a single broad peak even at low temperature [6g]. The $[M_2F_{11}]^-$ fluorines in the compounds **2c,d** appear equivalent at room temperature (in $CDCl_3$ solution), as result of fast exchange process. The related ^{19}F NMR resonances have been seen at 135.2 ($[Nb_2F_{11}]^-$) and 77.6 ($[Ta_2F_{11}]^-$) ppm, respectively. Conversely, low temperature NMR experiments (in $CDCl_3$ or CD_2Cl_2) have allowed to distinguish three distinct resonances [*e.g.* for **2d**: δ = 115.8 (2 F, F1), 70.8 (8 F, F2), -73.9 (1 F, F3) ppm, see Figure 3], in accord with what reported previously for the salts $[NBu_4][M_2F_{11}]$ (M = Nb, Ta) [11d].

Insert Figures 2 and 3 about here

The reactions of **1** with equimolar amounts of a variety of organic compounds L, mainly oxygen donors, result in high yield formation of the neutral octahedral adducts $MF_5(L)$, **3a-i,n-t**, see Scheme 1. The analogous species **3j-m** could not be obtained cleanly, however they have been recognised in solution by NMR, upon reaction of **1** with L in 2:1 molar ratio.

Insert Scheme 1 about here

Some of the reactions leading to the compounds **3** have been already described by ourselves [3a,c,d] or by other groups [6c,d]. We decided to repeat these reactions by employing carefully controlled L/M molar ratios, and to report the corresponding ^{19}F-NMR features of the products obtained, in an attempt to generalize the behaviour of MF_5 with Lewis bases. Table 2 also contains the revised ^{19}F NMR characterization of TaF_4(acac), TaF_4(Me-acac) and [TaF(Me-acac)$_3$][TaF_6] (Me-acac = methylacetylacetonato anion) [3a].

The new complexes have been characterised by NMR spectroscopy, elemental analyses and, in some cases, by IR spectroscopy and electrical conductivity.

Insert Table 2 about here

The NMR spectra of **3** (in $CDCl_3$ or CD_2Cl_2 solution) exhibit single sets of resonances, which are typically shifted to high-frequency with respect to what found in the uncoordinated molecule L [*e.g.* in the ^{1}H NMR spectrum of **3d**: δ = 4.46, 2.21 ppm; for free tetrahydrofuran: δ = 3.73, 1.84 ppm]. Furthermore, the ^{19}F NMR spectrum of **3** consists of an unique resonance, accounting for five exchanging fluorines, in accordance with former findings [3d, 16]. Such resonance is in the range 107.1 (**3g**) – 158.9 (**3n**) ppm for the niobium complexes and within 71.8 (**3q**) – 83.3 (**3t**) ppm for the tantalum ones. We have carried out low temperature ^{19}F NMR investigations on complexes **3c,g,i,j,k,l,o,p,r**. We have seen that the exchange process, responsible for the observation of a broad resonance at room temperature, may be frozen enough at low temperature, so to distinguish different fluorine nuclei [16]. This happens at 213 K for the tantalum species **3l,o,p**, whereas the niobium-containing compounds **3c,g,i,k,r** required lower temperatures and the use of CD_2Cl_2 as solvent. In every cases, two resonances have been distinguished at low temperature: these resonances appear as singlets (no F/F or M/F coupling has been observed) and account respectively for the fluorines placed

in *trans* and *cis* position with respect to the oxygen ligand. For instance, the broad peak, observed at room temperature at 81.7 ppm in the ^{19}F NMR spectrum of **3l** (in $CDCl_3$), splits into two signals [121.5 (1 F, *trans*-F), 71.7 (4 F, *cis*-F) ppm] at −60 °C. Similar features were described for the previously reported octahedral adduct $NbF_5(HCO_2Me)$ [16]. The neutral character of the compounds **3a,c,e,f,g,i,p,r** has been corroborated by electrical conductivity measurements in CH_2Cl_2 solution. The values of molar conductivities obtained are well comparable to those reported for analogous neutral, monomeric, MX_5 derivatives (M = Nb, Ta, X = halogen) [16]. According to the present investigation, the adducts of MF_5 with carboxylic acids (**3r-t**) hold neutral structure, and not ionic, as reported incorrectly in a precedent paper [3d].

The synthesis of **3e-g** by reaction of **1** with alcohols deserves some comments. Really the knowledge on the reactivity of **1** with alcohols was limited to NMR studies regarding the behaviour of MF_5 in ethanol solution [6d,h,j]. The complexes **3e-g** are coordination adducts containing the intact alcoholic unit: this result is in contrast with what exhibited by the heavier halides MX_5 (X = Cl, Br, I), which react with alcohols giving vigorous evolution of HX and formation of alcoholato derivatives. The different behaviour shown by MF_5, **1**, with respect to MX_5 (X = Cl, Br) on reacting with alcohols is probably consequence of the increase of the M–X bond energy on decreasing the atomic weight of the halide [17]: in other terms, the high value of the M–F bond energy prevents the formation of HF in the course of the reactions of **1** with alcohols.

The ^1H NMR spectra of **3e,f,g** clearly show a high-frequency resonance due to the hydroxyl proton (*e.g.* at 10.26 ppm for **3f**), and a IR absorption corresponding to the O–H bond is found at *ca.* 3210 cm^{-1}. According to the spectroscopic evidences, 2-methoxyethanol, $MeOCH_2CH_2OH$, in **3g** acts as monodentate ligand through the –OH function (the ^1H NMR resonance related to the methoxy group in **3g** is not shifted significantly with regard to uncoordinated 2-methoxyethanol, indicating that such group does not partecipate to the coordination).

As far as functionalized alcohols are concerned, we have studied the reactivity of NbF_5, **1a**, with propargyl alcohol, $HC{\equiv}CCH_2OH$, a system where the alcoholic moiety is adjacent to a triple carbon-carbon bond. The reaction was performed in $CDCl_3$ inside a NMR tube, and monitored by NMR spectroscopy (see Experimental for details). The addition of $HC{\equiv}CCH_2OH$ to NbF_5 in $CDCl_3$ resulted in a quick darkening of the mixture. After treatment with an excess of water, necessary to make the organic material free from coordination [3d], acetone and 2,2-difluoropropane were detected as main products by NMR and GC-MS, see Scheme 2. This result suggests that the presence of an unsaturation close to the *O*-function may provide halogen transfer from NbF_5, analogously to what seen for the reactivity of **1a** with ethyldiazoacetate [16], thus confirming the potentiality of the use of MF_5 (M = Nb, Ta) in fluorination reactions (see Introduction).

Insert Scheme 2 about here

The reaction of NbF_5 with limited amounts of tetrahydrothiophene (tht) does not produce any neutral product analogous to **3**, even when the organic substrate is made reacted in molar defect respect to the metal (see below). Thus, the ionic $[NbF_4(tht)_2][NbF_6]$, **4a**, resulting from self-ionisation of niobium pentafluoride, has been isolated cleanly by the 1:1 molar ratio reaction. The ^{19}F NMR spectrum of this compound clearly shows two resonances at 159.1 and 111.6 ppm, ascribable respectively to the $[MF_4]^+$ and $[MF_6]^-$ units. In addition, the ionic character is supported by solution conductivity data (see Experimental). Alternatively, the reaction of NbF_5 with a defect of tetrahydrothiophene, performed in a NMR tube, has allowed to identify the probable, prevalent, presence in solution of the ionic compound $[NbF_4(tht)_2][Nb_2F_{11}]$, **4b,**. The two resonances observed in the ^{19}F NMR spectrum fall respectively at 158.5 and 144.0 ppm. The former accounts for the $[NbF_4]^+$ moiety and does not shift significantly from that observed in **4a**, whereas the latter is ascribable to the $[Nb_2F_{11}]^-$ anion, on the basis of the characterisation carried out on **2c**. Unfortunately, low temperature NMR investigations on **4a,b**, with the aim to collect more information about the

structure of the cation, were not possible due to the low solubility exhibited by these compounds. The formation of ionic species by addition of a neutral ligand to MX_5 (M = Nb, Ta; X = halogen), occurring *via* self-ionisation, is not novel, since it has been described about the compound $[TaBr_4\{OC(NMe_2)_2\}_2][TaBr_6]$, characterised by X ray diffraction [3c].

It has to be stated that the synthesis of compounds **3j-m** is not straightforward: the latter have been recognised in $CDCl_3$ solution by means of NMR spectroscopy, upon reacting **1** with the appropriate ligand, L, in 2:1 ratio (NMR data related to **3j-m** are reported in the Experimental Section). Minor unidentified products, containing either the $[M_2F_{11}]^-$ or the $[MF_6]^-$ anion, have been detected by ^{19}F NMR. It is noteworthy that the possibility of formation of neutral species by reacting NbF_5 with dmf was ruled out by former findings. Interestingly, the use of equimolar amounts of **1** and L (L = dimethylformamide, tetramethylurea, mesityl oxide) does produce mixtures of not clearly identifiable ionic species (the characterisation of the complex $[NbF_4(OC(Me)CH{=}CMe_2)][NbF_6]$ has been recently reported by ourselves [16]). In other words, the formation of ionic derivatives seems to be favoured by increasing the L/M molar ratio. In order to investigate this point in more detail, we decided to study the reactions of **1** with a molar excess of organic compounds, L.

Hence, we have found that the addition of two equivalents of L to **1**, or alternatively the treatment of the isolated 1:1 precursors MF_5L (M = Nb, L = thf, **3d**; M = Ta, L =thf, **3q**; M = Nb, L = Et_2O [16]), with one further equivalent of L, results in complete consumption of the organic material and consequential formation of ionic complexes bearing probably octacoordinated cations, *i.e.* $[MF_4L_4][MF_6]$, **5a-e**, see Scheme 3. Clear detection of the $[MF_6]^-$ anion has been possible by ^{19}F analysis: more precisely, the ^{19}F NMR spectra of **5** display two peaks, one attributed to the $[MF_4]^+$ unit and the other one due to $[MF_6]^-$ [*e.g.* in the case of **5d**: $\delta(TaF_4^+)$ = 80.0 ppm; $\delta(TaF_6^-)$ = 39.6 ppm]. The decet structure of the $[NbF_6]^-$ ion in **5c** came clearly discernible only at 213 K. Also the ^{19}F NMR spectra of compounds **5a,b** have been recorded at low temperature (213 K, $CDCl_3$ solution), in order to see eventual variations in the pattern of the resonance related to $[MF_4]^+$.

However, the latter does not change significantly (no peak splittings or evidences for F-F or F-Nb couplings have been observed). Solution conductivity data for **5a-d** are comparable to those found for **2a,b** (see Experimental), thus confirming the ionic nature of the former.

Insert Scheme 3 about here

The formation of ionic species comprising the ion $[MF_4L_4]^+$, upon treatment of MF_5 with potential neutral ligands, was formerly hypothesised [6e,k]. Moreover, we have recently found that bidentate oxygen donors (*O*-*O*) promptly react with **1** in 1:1 ratio to afford complexes of formula $[MF_4(O\text{-}O)_2][MF_6]$, which include octacoordinated cations [16, 18]. The formation of compounds **5**, which occurs *via* self-ionisation of MF_5 into $[MF_4^+]$ and $[MF_6^-]$, appears privileged with respect to the alternative formation of the hypothetical, hepta-coordinated species $[MF_5L_2]$ (not detected). This is not surprising taking into account the exceptional stability of the $[MF_6^-]$ ions, which have revealed to be able to stabilise very unusual organic cations [3,16].

The formation of ionic adducts upon treatment of **1** with excess L is not limited to **5a-e**: indeed ^{19}F NMR experiments have indicated that the addition of 2÷5 equivalents of Me_2CO, MePhCO or CH_3CO_2H to NbF_5, in $CDCl_3$, results in generation of the $[NbF_6^-]$ ion. However, no other detectable species containing fluorine could be observed in these cases, in the ^{19}F NMR spectra, even at 213 K. According to former reports, the absence of ^{19}F resonances attributable to MF_5 descending cations might be the consequence of short relaxation times and/or fast fluorine exchange [6e].

Furthermore, by using ROH/M = 2, the reactions of **1a** with ROH (R = Me, Et) gave oily products different from **3j-l** [19]. Such products have not been characterised undoubtedly, however, according to ^{19}F NMR data, they probably bear ionic structure; in particular, the self-ionization of NbF_5 into $[NbF_4]^+[NbF_6]^-$ in solution of dry ethanol has been formerly proposed [6g,h,j].

Otherwise, we have seen that the addition of a large excess of chloroacetic acid to NbF_5 (up to 3 equivalents), in CD_2Cl_2 after 10 hours, affords uniquely the 1:1 adduct **3s**.

Finally, in order to evaluate the possibility of some solvent-effect in the reactivity of **1** with simple oxygen donors, we tried the reaction of NbF_5, **1a**, with dimethylformamide, dmf, in CD_3CN (see Experimental for details). Indeed the high polarity of acetonitrile may favour in principle the stabilisation of ionic products. Nevertheless, when dmf was added to a colourless solution of **1a** in CD_3CN, containing presumably the adduct $NbF_5(CD_3CN)$, progressive turning to light yellow was observed. The NMR analyses evidenced the presence of a neutral compound, *i.e.* NbF_5(dmf), see Experimental. According to these features, solvent polarity does not appear to play a key role in determining the formation of ionic, rather than neutral, derivatives of **1**.

3. Conclusion

This paper intends to give a "homogeneous" view of the coordination chemistry of niobium and tantalum pentafluorides with small molecules (oxygen-, nitrogen- and sulphur donors), a topic already discussed by different authors for some metal/ligand combinations. The unambiguous ^{19}F NMR detection of the $[MF_6]^-$ anions in chlorinated solvents, based on the full characterization of the crystalline salts $[S(NMe_2)_3][MF_6]$, has made possible the clear understanding of the room temperature ^{19}F NMR spectra of MF_5 derivatives, in $CDCl_3$ or CD_2Cl_2.

By regulating the ligand to metal molar ratio (L/M = 0.5 ÷ 1, according to the cases), it is possible to obtain a large variety of monomeric, neutral coordination compounds, for which a broad resonance (^{19}F NMR spectrum) is observed in solution at room temperature. The increasing of the ligand to metal molar ratio favours the formation of ionic derivatives: some compounds of general formula $[MF_4L_4][MF_6]$, comprising octacoordinated cations, have been identified upon reaction of MF_5 with a two-fold excess of the appropriate L. The possibility for the metal to host up to four organic ligands is made possible by self-ionization of $[MF_5]$ into $[MF_4]^+$ and $[MF_6]^-$, which, in turn, is consequence of the high stability of the MF_6^- anion.

Since $[MF_4(thf)_4][MF_6]$ (M = Nb, Ta) are yielded by combining MF_5 and thf in 1:2 molar ratio, the MF_5-directed polymerisation reaction of tetrahydrofuran probably occurs *via* ionic intermediates, in contrast with our previous hypothesis [10].

4. Experimental

4.1. General

All manipulations of air and/or moisture sensitive compounds were performed under atmosphere of pre-purified argon using standard Schlenk techniques. The reaction vessels were oven dried at 150°C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. MF_5 (M = Nb, **1a**; M = Ta, **1b**) and $[S(NMe_2)_3][SiMe_3F_2]$ (TASF) were commercial products (Aldrich) of the highest purity available, stored under Argon atmosphere as received. Me_2CO, MeCHO, MePhCO, Ph_2CO, CH_3CO_2H, CH_2ClCO_2H, MeOH, EtOH, $HO(CH_2)_2OMe$, Ph_3PO, $HCO(NMe_2)$, $(NMe_2)_2CO$, Et_2O, tetrahydrofuran (thf), MeCN and tetrahydrothiophene (tht) were commercial products (Aldrich) of the highest purity available. CH_2Cl_2, $CDCl_3$ and $CHCl_3$ were distilled before use under Argon atmosphere from P_4O_{10}, while pentane and heptane were distilled from $LiAlH_4$. Compounds **3k,l** [3c], **3m** [16], **3n-p** [3a], **3q** [3b], **3r-t** [3d] were prepared according to the literature. Infrared spectra were recorded at 293 K on a FT IR Spectrum One Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR measurements were recorded on Varian Gemini 200BB instrument at 293 K, unless otherwise specified. The chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent, while the chemical shifts for ^{19}F NMR spectra were referenced to $CFCl_3$. The line-widths ($\Delta\nu_{1/2}$) of ^{19}F NMR resonances were measured at half-height. Molar conductivities (Λ_M) were calculated on the basis of resistance measurements performed by a Metrohm AG Konduktometer E382 Instrument (cell constant = 0.815 cm^{-1}) on dichloromethane solutions *ca.* 0.010 M of the distinct compounds [12]. C, H, N elemental analyses were performed at the Dipartimento di Chimica Farmaceutica of the University of Pisa on a Carlo Erba mod. 1106

instrument, paying particular attention to the more sensitive compounds which were weighed and directly introduced into the analyzer. The halide content was determined by the Volhard method [20] after exhaustive hydrolysis of the sample. The metal was analyzed as M_2O_5 obtained by hydrolysis of the sample followed by calcination in a platinum crucible. Reproducibility was checked by repeating the metal analyses twice.

*4.2. Preparation of $[S(NMe_2)_3][MF_6]$ (M = Nb, **2a**; M = Ta, **2b**).*

The synthesis of $[S(NMe_2)_3][NbF_6]$, **2a**, is described in detail, compound **2b** being prepared in a similar way. A suspension of NbF_5 (**1a**; 0.160 g, 0.852 mmol), in CH_2Cl_2 (12 ml), was treated with $[S(NMe_2)_3][SiMe_3F_2]$ (0.240 g, 0.871 mmol). The mixture was stirred for 90 minutes, during which progressive dissolution of the solid was noticed. The volatile materials were removed in vacuo, and the residue was washed with heptane (2 × 5 mL). Crystallization from CH_2Cl_2/heptane gave **2a** as a colourless microcrystalline solid. Yield: 0.272 g, 86 % yield. Anal. Calcd. for $C_6H_{18}F_6N_3NbS$: C, 19.41; H, 4.89; N, 11.32; Nb, 25.03. Found: C, 19.32; H, 4.95; N, 11.15; Nb, 24.82 %. IR (solid state, cm^{-1}): 2972w, 2921w, 1467m-sh, 1451m, 1415w-m, 1271m, 1200m-s, 1153m, 1055m, 1032m, 946vs, 908vs, 717s, 690m. ^1H NMR ($CDCl_3$): δ 2.96 (s, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 38.4 (Me) ppm. ^{19}F NMR ($CDCl_3$): δ 103.5 (decet, 6 F, $^1J_{Nb-F} \approx 340$ Hz) ppm. $\Lambda_M(CH_2Cl_2, 293\ K) = 2.5\ S\cdot cm^2\cdot mol^{-1}$.

$[S(NMe_2)_3][TaF_6]$, ***2b***. Colourless, 88 % yield from TaF_5 (0.200 g, 0.725 mmol) and $[S(NMe_2)_3][SiMe_3F_2]$ (0.200 g, 0.726 mmol). Anal. Calcd. for $C_6H_{18}F_6N_3STa$: C, 15.69; H, 3.95; N, 9.15; Ta, 39.40. Found: C, 15.50; H, 4.03; N, 9.01; Ta, 39.11 %. ^1H NMR ($CDCl_3$): δ 2.97 (s, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 38.6 (Me) ppm. ^{19}F NMR ($CDCl_3$): δ 39.1 (s, $\Delta\nu_{1/2}$ = 97 Hz, 6 F) ppm. $\Lambda_M(CH_2Cl_2, 293\ K) = 2.5\ S\cdot cm^2\cdot mol^{-1}$.

The addition of $[S(NMe_2)_3][SiMe_3F_2]$ (0.25 mmol) to MF_5 (M = Nb, Ta, 0.25 mmol), in $CDCl_3$ (0.60 mL) / CH_2Cl_2 (0.25 mmol) inside a NMR tube, gave a solution analyzed by ^1H and ^{19}F NMR: $[S(NMe_2)_3][MF_6]$, $SiMe_3F$ and CH_2Cl_2 were recognised in 1:1:1 ratio.

*4.3. NMR characterisation of $[S(NMe_2)_3][M_2F_{11}]$ (M = Nb, **2c**; M = Ta, **2d**).*

The preparation of $[S(NMe_2)_3][Nb_2F_{11}]$, **2c**, is described in detail, compound **2d** being obtained in a similar way. A solution of $[S(NMe_2)_3][NbF_6]$ (**2a**; 0.135 g, 0.350 mmol), in $CDCl_3$ (0.85 ml), was treated with NbF_5 (0.068 g, 0.36 mmol). The tube was sealed and dissolution of added NbF_5 was completed after 2 hours, giving a light-orange solution. ^{19}F NMR ($CDCl_3$): δ 135.2 (s, $\Delta\nu_{½}$ = 660 Hz, 11 F) ppm. ^{19}F NMR (CD_2Cl_2): δ 128.3 (s, $\Delta\nu_{½}$ = 341 Hz, 11 F) ppm. ^{19}F NMR (CD_2Cl_2, 183 K): δ 190.4 (m, $\Delta\nu_{½}$ = 365 Hz, 2 F), 144.8 (s, $\Delta\nu_{½}$ = 112 Hz, 8 F), –56.5 (m, $\Delta\nu_{½}$ = 412 Hz, 1 F) ppm.

*$[S(NMe_2)_3][Ta_2F_{11}]$, **2d***. Light-orange solution from $[S(NMe_2)_3][TaF_6]$ (0.30 mmol) and TaF_5 (0.35 mmol). ^{19}F NMR ($CDCl_3$): δ 77.6 (s, $\Delta\nu_{½}$ = 930 Hz, 11 F) ppm. ^{19}F NMR ($CDCl_3$, 213 K): δ 115.8 (s, $\Delta\nu_{½}$ = 62 Hz, 2 F), 70.8 (m, $\Delta\nu_{½}$ = 230 Hz, 8 F), -73.9 (m, $\Delta\nu_{½}$ = 625 Hz, 1 F) ppm.

*4.4. Synthesis and isolation of $NbF_5(L)$ [L = Me_2CO, **3a**; L = MeCHO, **3b**; L = Ph_2CO, **3c**; L = thf, **3d**; L = MeOH, **3e**; L = EtOH, **3f**; L = $HOCH_2CH_2OMe$, **3g**; L = Ph_3PO, **3h**; L = NCMe, **3i**], detection in solution of $MF_5(L)$ [M = Nb, L = $HCONMe_2$, **3j**; M = Nb, L = $(NMe_2)_2CO$, **3k**; M = Ta, L = $(NMe_2)_2CO$, **3l**; M = Nb, L = $OC(Me)CH=CMe_2$, **3m**] and spectroscopic data of $MF_5(L)$ [M = Ta, L = Me_2CO, **3n**; M = Ta, L = Ph_2CO, **3o**; M = Ta, L = MePhCO, **3p**; M = Ta, L = thf, **3q**; M = Nb, L = CH_3CO_2H, **3r**; M = Nb, L = CH_2ClCO_2H, **3s**; M = Ta, L = CH_2ClCO_2H, **3t**].*

The synthesis of $NbF_5(Me_2CO)$, **3a**, is described in detail, those of the other new compounds have been performed in a similar way. Acetone (0.048 mL, 0.65 mmol) was added to a stirred suspension of NbF_5 (**1a**; 0.120 g, 0.639 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 2 hours, then the volatile materials were removed in vacuo. Crystallization of the residue from

CH_2Cl_2/pentane gave **3a** as a yellow microcrystalline solid. Yield: 0.129 g, 82 % yield. Anal. Calcd. for $C_3H_6F_5NbO$: C, 14.65; H, 2.46; Nb, 37.77. Found: C, 14.57; H, 2.53; Nb, 37.60. ^{1}H NMR ($CDCl_3$): δ 2.66 (s, Me) ppm. ^{19}F NMR ($CDCl_3$): δ 114.4 (s, $\Delta\nu_{½}$ = 1.20 KHz, 5 F) ppm. Λ_M(CH_2Cl_2, 293 K) = 0.66 S·cm^2·mol^{-1}.

NbF_5(MeCHO), ***3b***. Orange solid, 79 % yield from NbF_5 (0.100 g, 0.532 mmol) and MeCHO (0.55 mmol). Anal. Calcd. for $C_2H_4F_5NbO$: C, 10.36; H, 1.74; Nb, 40.05. Found: C, 10.27; H, 1.68; Nb, 39.85. ^{1}H NMR ($CDCl_3$): δ 9.32 (d, 1 H, $^3J_{HH}$ = 9 Hz, CH), 2.49 (d, 3 H, $^3J_{HH}$ = 9 Hz, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 205.9 (CO), 22.9 (CH_3) ppm. ^{19}F NMR ($CDCl_3$): δ 133.8 (s, $\Delta\nu_{½}$ = 2.12 KHz, 5 F) ppm.

NbF_5(Ph_2CO), ***3c***. Orange solid, 81 % yield from NbF_5 (0.100 g, 0.532 mmol) and Ph_2C=O (0.56 mmol). Anal. Calcd. for $C_{13}H_{10}F_5NbO$: C, 42.19; H, 2.72; Nb, 25.10. Found: C, 42.08; H, 2.66; Nb, 25.17. IR (solid state, cm^{-1}): 2890w-m, 1593vs ($\nu_{C=O}$), 1497s, 1484m, 1457s, 1398vs, 1335w-m, 1315w, 1224m-s, 1189m, 1168m, 998w, 921m, 847w, 806w, 770w-m, 706vs, 685s. ^{1}H NMR ($CDCl_3$): δ 8.11÷7.70 (Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 179.6 (CO), 139.4 (*ipso*-C), 135.7, 130.1 (Ph) ppm. ^{19}F NMR ($CDCl_3$): δ 142.6 (s, $\Delta\nu_{½}$ = 3.20 KHz, 5 F) ppm. ^{19}F NMR (CD_2Cl_2) δ = 144.0 (s, $\Delta\nu_{½}$ = 2.55 KHz, 5 F) ppm. ^{19}F NMR (CD_2Cl_2, 183 K) δ = 171.8 (s, $\Delta\nu_{½}$ = 270 Hz, 1 F, *trans*-F), 137.9 (s, $\Delta\nu_{½}$ = 1.18 KHz, 4 F, *cis*-F) ppm. Λ_M(CH_2Cl_2, 293 K) = 0.22 S·cm^2·mol^{-1}.

NbF_5(thf), ***3d***. Colorless solid, 83 % yield from NbF_5 (0.090 g, 0.48 mmol) and thf (0.49 mmol). Anal. Calcd. for $C_4H_8F_5NbO$: C, 18.48; H, 3.10; Nb, 35.73. Found: C, 18.40; H, 3.19; Nb, 35.60. ^{1}H NMR ($CDCl_3$): δ 4.46 (m, 4 H, OCH_2), 2.21 (m, 4 H, OCH_2CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 75.5 (OCH_2), 25.7 (OCH_2CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ 156.3 (s, $\Delta\nu_{½}$ = 1.83 KHz, 5 F) ppm.

NbF_5(MeOH), ***3e***. Colourless crystalline solid, 88 % yield from NbF_5 (0.095 g, 0.51 mmol) and methanol (0.51 mmol). Anal. Calc. for CH_4F_5NbO: C, 5.46; H, 1.83; Nb, 42.24. Found C, 5.34; H, 1.79; Nb, 42.11. IR (solid state, cm^{-1}): 3206m (ν_{O-H}), 2952m, 1634 m, 1464w-m, 1391w, 1115m,

1054m, 845vs. ^{1}H NMR ($CDCl_3$) δ = 10.40 (br, 1 H, OH), 5.10 (s, 3 H, Me) ppm. ^{19}F NMR ($CDCl_3$) δ = 128.1 (s, $\Delta\nu_{½}$ = 3.62 KHz, 5 F) ppm. Λ_M(CH_2Cl_2, 293 K) = 0.30 S·cm^2·mol^{-1}.

NbF_5(EtOH), ***3f***. Colourless crystalline solid, 89 % yield from NbF_5 (0.095 g, 0.51 mmol) and ethanol (0.53 mmol). Anal. Calc. for $C_2H_6F_5NbO$: C, 10.27; H, 2.58; Nb, 39.71. Found C, 10.33; H, 2.46, Nb, 39.60. ^{1}H NMR ($CDCl_3$) δ = 10.26 (s br, 1 H, OH), 4.91 (br, 2 H, CH_2), 1.61 (t, $^{3}J_{HH}$ = 7.33 Hz, 3 H, Me) ppm. ^{19}F NMR ($CDCl_3$) δ = 136.9 (s, $\Delta\nu_{½}$ = 4.75 KHz, 5 F) ppm. Λ_M(CH_2Cl_2, 293 K) = 0.18 S·cm^2·mol^{-1}.

NbF_5($HOCH_2CH_2OMe$), ***3g***. Colourless crystalline solid, 83 % yield from NbF_5 (0.105 g, 0.559 mmol) and 2-methoxyethanol (0.57 mmol). Anal. Calc. for $C_3H_8F_5NbO_2$: C, 13.65; H, 3.05; Nb, 35.19. Found C, 13.52; H, 2.99; Nb, 35.25. IR (solid state, cm^{-1}): 3210w-m ($\nu_{O\text{-}H}$), 2981w-m, 2891w, 1463w-m, 1380w, 1348w, 1262w, 1231w, 1196w, 1081s, 1006s, 938m-s, 771vs, 717vs cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 9.18 (s, 1 H, OH), 4.41 (t, $^{3}J_{HH}$ = 3.66 Hz, 2 H, C*H*$_2$OH), 3.78 (t, $^{3}J_{HH}$ = 3.66 Hz, 2 H, C*H*$_2$OMe), 3.52 (s, 3 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 72.7, 68.9 (CH_2), 59.5 (Me) ppm. ^{19}F NMR ($CDCl_3$) δ = 107.1 (s, $\Delta\nu_{½}$ = 1.75 KHz, 5 F) ppm. ^{19}F NMR (CD_2Cl_2) δ = 109.9 (s, $\Delta\nu_{½}$ = 1.35 KHz, 5 F) ppm. ^{19}F NMR (CD_2Cl_2, 183 K) δ = 154.0 (s, $\Delta\nu_{½}$ = 380 Hz, 1 F, *trans*-F), 102.6 (s, $\Delta\nu_{½}$ = 1.25 KHz, 4 F, *cis*-F) ppm. Λ_M(CH_2Cl_2, 293 K) = 0.11 S·cm^2·mol^{-1}.

NbF_5(Ph_3PO), ***3h***. Colourless crystalline solid, 84 % yield from NbF_5 (0.100 g, 0.532 mmol) and O=PPh_3 (0.55 mmol). Anal. Calc. for $C_{18}H_{15}F_5NbOP$: C, 46.38; H, 3.24; Nb, 19.93. Found C, 46.44; H, 3.19; Nb, 19.80. ^{1}H NMR ($CDCl_3$) δ = 7.81÷7.54 (Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 135.1, 133.1, 130.0, 128.2 (Ph), 125.7, 123.5 (*ipso*-Ph) ppm. ^{19}F NMR ($CDCl_3$) δ = 128.2 (s, $\Delta\nu_{½}$ = 1.17 KHz, 5 F) ppm.

NbF_5(MeCN), ***3i***. Light yellow solid, 81 % yield from NbF_5 (0.110 g, 0.585 mmol) and acetonitrile (0.61 mmol). Anal. Calcd. for $C_2H_3F_5NNb$: C, 10.49; H, 1.32; N, 6.12; Nb, 40.58. Found: C, 10.37; H, 1.38; N, 6.06; Nb, 40.67. ^{1}H NMR ($CDCl_3$): δ 2.45 (s, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 101.2 (N*C*Me), 2.3 (Me) ppm. ^{19}F NMR ($CDCl_3$): δ 158.9 (s, $\Delta\nu_{½}$ = 280 Hz, 5 F, NbF_5) ppm. ^{19}F

NMR (CD_2Cl_2): δ 164.0 (s, $\Delta\nu_{½}$ = 123 Hz, 5 F, NbF_5) ppm. ^{19}F NMR (CD_2Cl_2, 183 K) δ = 182.3 (s, $\Delta\nu_{½}$ = 95 Hz, 1 F, *trans*-F), 154.9 (s, $\Delta\nu_{½}$ = 730 Hz, 4 F, *cis*-F) ppm. Λ_M(CH_2Cl_2, 293 K) = 0.13 $S \cdot cm^2 \cdot mol^{-1}$.

$NbF_5(HCONMe_2)$, ***3j***. ^1H NMR ($CDCl_3$): δ 8.94 (s, 1 H, CH), 3.91, 3.78 (s, 6 H, NMe_2) ppm. ^{19}F NMR ($CDCl_3$): δ 149.7 (s, $\Delta\nu_{½}$ = 935 Hz, 5 F, NbF_5) ppm. ^{19}F NMR ($CDCl_3$, 213 K) δ = 175.5 (br, $\Delta\nu_{½}$ = 450 Hz, 1 F, *trans*-F), 143.3 (s, $\Delta\nu_{½}$ = 1.38 KHz, 4 F, *cis*-F) ppm. ^1H NMR ($CDCl_3$): δ 8.80 (s, 1 H, CH), 3.68, 3.56 (s, 6 H, NMe_2) ppm. ^{19}F NMR (CD_3CN): δ 135.0 (s, $\Delta\nu_{½}$ = 750 Hz, 5 F, NbF_5) ppm.

$NbF_5[(NMe_2)_2CO]$, ***3k***. ^1H NMR (CD_2Cl_2): δ 3.07 (s, NMe_2) ppm. ^{19}F NMR (CD_2Cl_2): δ 126.8 (s, $\Delta\nu_{½}$ = 1.85 KHz, 5 F, NbF_5) ppm. ^{19}F NMR (CD_2Cl_3): δ 124.5 (s, $\Delta\nu_{½}$ = 1.90 KHz, 5 F, NbF_5) ppm. ^{19}F NMR (CD_2Cl_2, 183 K) δ = 148.2 (br, $\Delta\nu_{½}$ = 650 Hz, 1 F, *trans*-F), 121.5 (s, $\Delta\nu_{½}$ = 395 KHz, 4 F, *cis*-F) ppm.

$TaF_5[(NMe_2)_2CO]$, ***3l***. Colorless solid. ^1H NMR ($CDCl_3$): δ 3.15 (s, NMe_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 161.1 (CO), 40.2 (NMe_2) ppm. ^{19}F NMR ($CDCl_3$): δ 81.7 (s, $\Delta\nu_{½}$ = 825 Hz, 5 F, TaF_5) ppm. ^{19}F NMR ($CDCl_3$, 213 K) δ = 121.5 (br, $\Delta\nu_{½}$ = 450 Hz, 1 F, *trans*-F), 71.7 (s, $\Delta\nu_{½}$ = 1.58 KHz, 4 F, *cis*-F) ppm.

$NbF_5[OC(Me)CH=CMe_2]$, ***3m***. ^{19}F NMR ($CDCl_3$, yellow solution): δ 152.7 (s, W½ = 1.25 KHz, 5 F) ppm.

$TaF_5(Me_2CO)$, ***3n***. Light yellow solid. IR (CH_2Cl_2, cm^{-1}): 1661s ($\nu_{C=O}$). ^1H NMR ($CDCl_3$): δ 2.78 (s, Me) ppm. ^{19}F NMR ($CDCl_3$): δ 78.4 (s, W½ = 1.55 KHz, 5 F) ppm.

$TaF_5(Ph_2CO)$, ***3o***. Orange solid. ^1H NMR ($CDCl_3$): δ 7.90÷7.49 (Ph) ppm. ^{13}C NMR ($CDCl_3$): δ 179.8 (CO), 136.2÷128.8 (Ph) ppm. ^{19}F NMR ($CDCl_3$): δ 72.2 (s, $\Delta\nu_{½}$ = 1.40 KHz, 5 F) ppm. ^{19}F NMR ($CDCl_3$, 213 K) δ = 98.8 (s, $\Delta\nu_{½}$ = 250 Hz, 1 F, *trans*-F), 65.1 (s, $\Delta\nu_{½}$ = 1.10 KHz, 4 F, *cis*-F) ppm.

$TaF_5(MePhCO)$, ***3p***. Light orange solid. IR (solid state, cm^{-1}): 3069vw, 1593m ($\nu_{C=O}$), 1557s, 1497m, 1470s, 1450m, 1426m, 1360m-s, 1311s, 1292vs, 1234vs, 1193m, 1165w-m, 1098m, 1019m, 1006m-s, 979s, 875vs, 817s, 765s, 735vs. ^{1}H NMR ($CDCl_3$): δ 8.30, 7.94, 7.67 (5 H, Ph), 3.16 (s, 3 H, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 190.1 (CO), 140.4, 132.9, 130.2 (Ph), 25.6 (Me) ppm. ^{19}F NMR ($CDCl_3$): δ 78.6 (s, $\Delta\nu_{½}$ = 635 Hz, 5 F, TaF_5) ppm. ^{19}F NMR ($CDCl_3$, 213 K) δ = 104.5 (br, $\Delta\nu_{½}$ = 906 Hz, 1 F, *trans*-F), 71.4 (s, $\Delta\nu_{½}$ = 1.64 KHz, 4 F, *cis*-F) ppm. Λ_M(CH_2Cl_2, 293 K) = 0.080 $S\cdot cm^2\cdot mol^{-1}$.

$TaF_5(thf)$, ***3q***. Colorless solid. ^{1}H NMR ($CDCl_3$): δ 4.60 (m, 4 H, OCH_2), 2.25 (m, 4 H, OCH_2CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ 77.3 (OCH_2), 25.6 (OCH_2CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ 71.8 (s, $\Delta\nu_{½}$ = 1.33 KHz, 5 F) ppm.

$NbF_5(CH_3CO_2H)$, ***3r***. Orange solid. IR (solid state, cm^{-1}): 3186w ($\nu_{O–H}$), 2944m, 2795m, 2519w-m, 1616vs ($\nu_{C=O}$), 1555vs, 1407w, 1370w, 1247m, 1053w, 918m, 852m-s. ^{1}H NMR (CD_2Cl_2): δ 11.78 (s, 1 H, OH), 2.56 (s, 3 H, Me) ppm. ^{19}F NMR (CD_2Cl_2): δ 153.6 (s, $\Delta\nu_{½}$ = 210 Hz, 5 F, NbF_5) ppm. ^{19}F NMR ($CDCl_3$): δ 151.8 (s, $\Delta\nu_{½}$ = 380 Hz, 5 F, NbF_5) ppm. ^{19}F NMR (CD_2Cl_2, 183 K) δ = 206.4 (s, $\Delta\nu_{½}$ = 213 Hz, 1 F, *trans*-F), 141.6 (s, $\Delta\nu_{½}$ = 980 Hz, 4 F, *cis*-F) ppm. Λ_M(CH_2Cl_2, 293 K) = 0.12 $S\cdot cm^2\cdot mol^{-1}$.

$NbF_5(CH_2ClCO_2H)$, ***3s***. Orange solid. IR (solid state, cm^{-1}): 3228w-br ($\nu_{O–H}$), 2956w, 1661vs ($\nu_{C=O}$), 1551m, 1432m, 1395m-s, 1275m, 1203m-br, 906vs, 797vs. ^{1}H NMR ($CDCl_3$): δ 11.61 (s, 1 H, OH), 4.38 (s, 2 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ 176.8 (CO), 40.8 (CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ 156.0 (s, $\Delta\nu_{½}$ = 1.60 KHz, 5 F) ppm.

$TaF_5(CH_2ClCO_2H)$, ***3t***. Pale-yellow solid. IR (solid state, cm^{-1}): 3225m-br ($\nu_{O–H}$), 2958w, 1630vs ($\nu_{C=O}$), 1555m, 1450m, 1390m-s, 1270m, 1170m, 923s, 903s, 850m-s, 804s, 712m-s. ^{1}H NMR ($CDCl_3$): δ 11.59 (s, 1 H, OH), 4.34 (s, 2 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ 176.1 (CO), 40.9 (CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ 83.3 (s, $\Delta\nu_{½}$ = 975 Hz, 5 F) ppm.

4.5. Reactivity of NbF_5 with propargyl alcohol, $HC{\equiv}CCH_2OH$.

A suspension of NbF_5 (0.085 g, 0.45 mmol) in $CDCl_3$ (0.85 mL) was treated first with dichloromethane (0.029 mL, 0.45 mmol) and then with $HC{\equiv}CCH_2OH$ (0.026 mL, 0.45 mmol). The solution turned dark red in one hour, and formation of an oily precipitate was noticed. The tube was opened and a large excess of water (0.20 mL, 11 mmol) was added. A colourless solution was separated from a dark precipitate and analyzed by GC/MS and ^1H and ^{13}C NMR: dichloromethane, acetone and 2,2-difluoropropane were found in 8:3:2 ratio.

*4.6. Preparation of $[NbF_4(tht)_2][NbF_6]$, **4a**, and detection in solution of $[NbF_4(tht)_2][Nb_2F_{11}]$, **4b**.*

A CH_2Cl_2 suspension of NbF_5 [0.110 g (0.585 mmol) in 12 mL] was treated with tetrahydrothiophene, tht (0.070 mL, 0.60 mmol). After stirring for 3 hours at room temperature, the volatiles were removed in vacuo. Crystallization of the residue from CH_2Cl_2/heptane gave **4a** as a yellow oily-solid (0.131 g, 81 % yield). Anal. Calcd. for $C_8H_{16}F_{10}Nb_2S_2$: C, 17.40; H, 2.92; Nb, 33.65. Found: C, 17.27; H, 3.00; Nb, 33.20. ^1H NMR ($CDCl_3$): δ 3.44 (s, 4 H, SCH_2), 2.40 (s, 4 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 32.9 (SCH_2), 28.9 (CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ 159.1 (br, $\Delta\nu_{½}$ = 740 Hz, 4 F, NbF_4), 111.6 (m-br, $\Delta\nu_{½}$ = 3.80 KHz, 6 F, NbF_6) ppm. Λ_M(CH_2Cl_2, 293 K) = 2.66 $S{\cdot}cm^2{\cdot}mol^{-1}$. In a different experiment, tht (0.11 mmol) was added to a suspension of NbF_5 (0.230 mmol), in $CDCl_3$ (0.70 mL), inside a NMR tube. Then, the tube was sealed and the resulting mixture underwent NMR analysis after 24 hours. ^1H NMR ($CDCl_3$): δ 3.34 (s, 4 H, SCH_2), 2.16 (s, 4 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 37.6 (SCH_2), 30.6 (CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ 158.5 (s-br, $\Delta\nu_{½}$ = 630 Hz, 4 F, NbF_4), 144.0 (s-br, $\Delta\nu_{½}$ = 880 Hz, 11 F, Nb_2F_{11}) ppm.

*4.7. Preparation of $[MF_4L_4][MF_6]$ [M = Nb, L = dmf, **5a**; M = Ta, L = dmf, **5b**; M = Nb, L = thf, **5c**; M = Ta, L = thf, **5d**; M = Nb, L = OEt_2, **5e**].*

The synthesis of $[NbF_4(dmf)_4][NbF_6]$, **5a**, is described in detail, those of compounds **5b-e** being performed in a similar way. NbF_5 (0.110 g, 0.585 mmol), suspended in $CHCl_3$ (10 mL), was treated with dimethylformamide (1.10 mmol). After 3 hours stirring at room temperature, volatiles were removed in vacuo. Crystallization of the residue from CH_2Cl_2/heptane gave **5a** as a colorless solid (0.160 g, 82 % yield). Anal. Calcd. for $C_{12}H_{28}F_{10}N_4Nb_2O_4$: C, 21.57; H, 4.22; N, 8.39; Nb, 27.81. Found: C, 22.04; H, 4.12; N, 8.48; Nb, 27.55. ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 1 H, CH), 3.34, 3.23 (s, 6 H, Me) ppm. ^{19}F NMR ($CDCl_3$): δ 144.1 (br, $\Delta\nu_{½}$ = 2.35 KHz, 4 F, NbF_4), 103.7 (decet, 6 F, $^1J_{Nb–F} \approx$ 335 Hz, NbF_6) ppm. Λ_M(CH_2Cl_2, 293 K) = 2.8 S·cm^2·mol^{-1}.

$[TaF_4(dmf)_4][TaF_6]$, ***5b***. White solid, 79 % yield from TaF_5 (0.150 g, 0.544 mmol) and dimethylformamide (1.15 mmol). Anal. Calcd. for $C_{12}H_{28}F_{10}N_4O_4Ta_2$: C, 17.07; H, 3.34; N, 6.64; Ta, 42.87. Found: C, 17.22; H, 3.19; N, 6.58; Ta, 42.61. ^{1}H NMR ($CDCl_3$): δ 8.02 (s, 1 H, CH), 3.32, 3.19 (s, 6 H, Me) ppm. ^{19}F NMR ($CDCl_3$): δ 64.9 (br, $\Delta\nu_{½}$ = 1.24 KHz, 4 F, TaF_4), 39.6 (s, $\Delta\nu_{½}$ = 205 Hz, 6 F, TaF_6) ppm. Λ_M(CH_2Cl_2, 293 K) = 2.8 S·cm^2·mol^{-1}.

$[NbF_4(thf)_4][NbF_6]$, ***5c***. Light-yellow solid, 86 % yield from NbF_5 (0.110 g, 0.585 mmol) and tetrahydrofuran (1.30 mmol). Anal. Calcd. for $C_{16}H_{32}F_{10}Nb_2O_4$: C, 28.93; H, 4.86; Nb, 27.97. Found: C, 28.81; H, 4.70; Nb, 27.81. ^{1}H NMR ($CDCl_3$): δ 4.22 (m, 4 H, OCH_2), 2.10 (m, 4 H, OCH_2CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 72.3 (OCH_2), 25.6 (OCH_2CH_2) ppm. ^{19}F NMR ($CDCl_3$, 213K): δ 180.1 (s, $\Delta\nu_{½}$ = 330 Hz, 4 F, NbF_4), 103.1 (decet, 6 F, $^1J_{Nb–F} \approx$ 340 Hz, NbF_6) ppm. Λ_M(CH_2Cl_2, 293 K) = 3.1 S·cm^2·mol^{-1}.

$[TaF_4(thf)_4][TaF_6]$, ***5d***. Colorless solid, 88 % yield from TaF_5 (0.170 g, 0.616 mmol) and tetrahydrofuran (1.40 mmol). Anal. Calcd. for $C_{16}H_{32}F_{10}O_4Ta_2$: C, 22.87; H, 3.84; Ta, 43.07. Found: C, 22.66; H, 3.71; Ta, 42.95. ^{1}H NMR ($CDCl_3$): δ 4.44 (m, 4 H, OCH_2), 2.19 (m, 4 H, OCH_2CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 75.7 (OCH_2), 25.1 (OCH_2CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ 80.0 (s, $\Delta\nu_{½}$ = 722 Hz, 4 F, TaF_4), 39.6 (s, $\Delta\nu_{½}$ = 515 Hz, 6 F, TaF_6) ppm. Λ_M(CH_2Cl_2, 293 K) = 2.5 S·cm^2·mol^{-1}.

$[NbF_4(OEt_2)_4][NbF_6]$, ***5e***. Light-pink solid, 79 % yield from NbF_5 (0.110 g, 0.585 mmol) and diethyl ether (1.50 mmol). Anal. Calcd. for $C_{16}H_{40}F_{10}Nb_2O_4$: C, 28.58; H, 6.00; Nb, 27.64. Found: C, 28.43; H, 6.05; Nb, 27.38. ^{1}H NMR ($CDCl_3$): δ 3.85 (q, 2 H, $^3J_{HH}$ = 7 Hz, CH_2), 1.31 (t, 3 H, $^3J_{HH}$ = 7 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 68.6 (CH_2), 14.4 (CH_3) ppm. ^{19}F NMR ($CDCl_3$): δ 158.9 (br, $\Delta\nu_{½}$ = 215 Hz, 4 F, NbF_4), 104.4 (decet, 6 F, $^1J_{Nb-F} \approx$ 340 Hz, NbF_6) ppm.

*4.8. Crystal structure solution and refinement of compound $[S(NMe_2)_3][TaF_6]$, **2b**.*

Crystal data and collection details for $[S(NMe_2)_3][TaF_6]$, **2b**, are reported in Table 3. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using *Mo-Kα* radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [21]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [22]. Hydrogen atoms bonded to C-atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystal is racemically twinned with a refined Flack parameter of 0.422(13) [23] and it was, therefore, refined using the TWIN refinement routine of SHELXTL.

Table 3 about here

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 736702, $[S(NMe_2)_3][TaF_6]$, **2b**. Copies of the crystallographic data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-123-336033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

6. Acknowledgments

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Captions for Figures

Figure 1. View of the structure of $[S(NMe_2)_3][TaF_6]$, **2b**. Displacement ellipsoids are at 50% probability level.

Figure 2. The ^{19}F NMR spectrum of $[S(NMe_2)_3][NbF_6]$ (298 K, $CDCl_3$, $CFCl_3$ as external standard).

Figure 3. Schematic drawing of the $[M_2F_{11}]^-$ (M = Nb, **2c**; M = Ta, **2d**) anion with fluorine numbering scheme.

Tables

Table 1
Selected bond distances (Å) and angles (deg) of $[S(NMe_2)_3][TaF_6]$, **2b**.

F(1)–Ta(1)	1.888(4)	F(2)–Ta(1)	1.904(4)
F(3)–Ta(1)	1.895(4)	F(4)–Ta(1)	1.878(5)
F(5)–Ta(1)	1.884(4)	F(6)–Ta(1)	1.882(4)
N(1)–S(1)	1.693(4)	N(2)–S(1)	1.614(6)
N(3)–S(1)	1.626(6)		
C(1)–N(1)	1.484(9)	C(2)–N(1)	1.493(10)
C(3)–N(2)	1.464(8)	C(4)–N(2)	1.472(8)
C(5)–N(3)	1.462(9)	C(6)–N(3)	1.468(9)
N(2)–S(1)–N(3)	116.5(3)	N(2)–S(1)–N(1)	100.2(3)
N(3)–S(1)–N(1)	98.3(3)	C(1)–N(1)–C(2)	110.9(4)
C(1)–N(1)–S(1)	112.5(4)	C(2)–N(1)–S(1)	110.7(5)
C(3)–N(2)–C(4)	116.3(5)	C(3)–N(2)–S(1)	116.2(5)
C(4)–N(2)–S(1)	122.6(4)	C(5)–N(3)–C(6)	114.6(5)
C(5)–N(3)–S(1)	114.2(5)	C(6)–N(3)–S(1)	122.9(5)

Table 2
^{19}F NMR data for compounds **2-5** (298 K, $CDCl_3$, δ-values referred to $CFCl_3$ as external standard).

	MF_5	$[MF_4]^+$	$[MF_6]^-$	$[M_2F_{11}]^-$
2a			103.5	
2b			39.1	
2c				135.2
2d				77.6
3a	114.4			
3b	133.8			
3c	142.6			
3d	156.3			
3e	128.1			
3f	136.9			
3g	107.1			
3h	128.2			
3i	158.9			
3j	149.7			
3k	124.5			
3l	81.7			
3m	152.7			
3n	78.4			
3o	72.2			
3p	78.6			
3q	71.8			
3r	151.8			
3s	156.0			
3t	83.3			
4a		159.1	111.6	
4b		118.5	144.0	
5a		144.1	103.7	
5b		64.9	39.6	
5c		180.1	103.1	
5d		80.0	39.6	
5e		158.9	104.4	
TaF_4(acac)		99.7		
TaF_4(Me-acac) [a]		96.2		
$[TaF(Me\text{-}acac)_3][TaF_6]$ [a,b]			39.5	

[a] Me-acac = methylacetylacetonato anion
[b] δ(TaF) =86.0 ppm

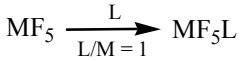
Table 3
Crystal data and experimental details for **2b**.

Complex	**2b**
Formula	$C_6H_{18}F_6N_3STa$
Fw	459.24

T, K	100(2)
λ, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a, Å	6.4050(16)
b, Å	11.099(3)
c, Å	9.685(2)
α, (deg)	90
β, (deg)	97.991(2)
γ, (deg)	90
Cell Volume, Å^3	681.8(3)
Z	2
D_c, g cm^{-3}	2.237
μ, mm^{-1}	8.267
F(000)	436
Crystal size, mm	0.18×0.15×0.12
θ limits, (deg)	2.12–25.99
Reflections collected	5067
Independent reflections	2604 [R_{int} = 0.0342]
Data / restraints /parameters	2604 / 1 / 155
Goodness on fit on F^2	1.031
R_1 ($I > 2\sigma(I)$)	0.0255
wR_2 (all data)	0.0655
Largest diff. peak and hole, eÅ^{-3}	1.786 / –1.821

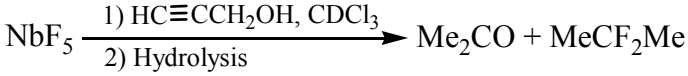
Schemes

Scheme 1



M	L	
Nb	Me_2CO	**3a**
Nb	MeCHO	**3b**
Nb	Ph_2CO	**3c**
Nb	thf	**3d**
Nb	MeOH	**3e**
Nb	EtOH	**3f**
Nb	$HOCH_2CH2OMe$	**3g**
Nb	Ph_3PO	**3h**
Nb	NCMe	**3i**
Nb	$HCONMe_2$ (dmf)	**3j**
Nb	$(NMe_2)_2CO$	**3k**
Ta	$(NMe_2)_2CO$	**3l**
Nb	$OC(Me)CH=CMe_2$	**3m**
Ta	Me_2CO	**3n**
Ta	Ph_2CO	**3o**
Ta	MePhCO	**3p**
Ta	thf	**3q**
Nb	CH_3CO_2H	**3r**
Nb	CH_2ClCO_2H	**3s**
Ta	CH_2ClCO_2H	**3t**

Scheme 2



Scheme 3