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Six-coordinate NbF_5 and TaF_5 complexes with tertiary mono-phosphine and -arsine ligands

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ABSTRACT

The syntheses of the extremely moisture sensitive, neutral $[MF_5(PR_3)]$ (M = Nb or Ta, R = Me or Ph) and $[MF_5(AsR'_3)]$ (R′ = Me or Et), from reaction of the ligands with MF_5 in anhydrous diethyl ether solution are reported. Attempts to isolate analogous complexes with $SbMe_3$ were unsuccessful. The products are characterised by IR and mutinuclear NMR (^1H, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and ^{93}Nb) spectroscopic studies. These are the first examples of six-coordinate phosphine or arsine complexes of the Group 5 pentafluorides. The ionic species, *trans*-$[MF_4(PMe_3)_2][MF_6]$, are obtained from diethyl ether solution of $[MF_5(PMe_3)]$ containing excess PMe_3 and similarly characterised. All complexes are extremely moisture and oxygen sensitive and decomposed by many common solvents. In solution in toluene the $[MF_5(PMe_3)]$ (M = Nb or Ta) and $[MF_5(AsR'_3)]$ are extensively dissociated at ambient temperatures. The $[MF_5(PPh_3)]$ dissolve in CH_2Cl_2 with decomposition to form $[PPh_3H][MF_6]$. Attempts to isolate phosphine complexes of $NbOF_3$ were unsuccessful.

1. Introduction

Niobium and tantalum pentafluorides are very strong, hard Lewis acids which form complexes with many neutral donor ligands; the commonest stoichiometries are the six-coordinate $[MF_5L]$ (L = monodentate ligand) and the “self ionisation” products $[MF_4L_2][MF_6]$ and $[MF_4L_4][MF_6]$ with six- and eight-coordinate cations, respectively [1]. Both types of complex with O-, N- and S-donor ligands have been well characterised in recent studies [1–4], and we reported very recently [5] the first complexes with neutral bidentate phosphorus or arsenic donor ligands, $[MF_4(\text{diphosphine})_2][MF_6]$ (M = Nb or Ta, diphosphine = o-$C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_2PMe_2$, $Et_2P(CH_2)_2PEt_2$ or o-$C_6H_4(PPh_2)_2$) and the diarsine analogues $[MF_4(o\text{-}C_6H_4(AsMe_2)_2)_2][MF_6]$. These were prepared by reaction of the appropriate MF_5 with the Group 15 donor ligand in anhydrous MeCN, and spectroscopic and X-ray structural data showed that they all contain distorted eight-coordinate cations and regular octahedral anions. Attempts to prepare monodentate tertiary phosphine analogues, e.g. with PMe_3, using a similar method were unsuccessful, since the MeCN preferentially coordinated to the hard metal centres [5]. The complexes $[MF_4(Ph_2PCH_2CH_2PPh_2)_2][MF_6]$ are also known [6]. The formation of a *trans*-$[TaF_4(P^nBu_3)_2]^+$ cation from TaF_5 and P^nBu_3 in CH_2Cl_2 solution, identified only *in situ* by ^{19}F NMR spectroscopy, has been mentioned, but the product was not isolated, and decomposed to phosphine oxide species in a few days [7]. Here we report the successful synthesis of several new complexes of the pentafluorides with PR_3 and AsR_3 ligands, providing the first directly synthesised examples with six-coordinate metal centres containing these soft donor pnictogen ligands.

2. Results and discussion

2.1. $[MF_5(PR_3)]$

The successful preparation of the target complexes is highly dependent upon the choice of solvent (as well as rigorous exclusion of moisture). Initial attempts to make PR_3 (R = Me or Ph) complexes of the pentafluorides using MeCN as solvent failed, as described in the Introduction, since the MeCN, which is present in large excess as solvent, is preferred as a ligand over the tertiary phosphine by the hard MF_5 acceptor. Dichloromethane, which was used successfully as a solvent in the synthesis of thio- or seleno-ether complexes [4], also proved to be unsuitable for the phosphines, leading instead to $[PR_3H][MF_6]$ as the major products, along with several other unidentified species. It seems likely that the CH_2Cl_2 is activated towards reaction with the phosphine by the strong Lewis

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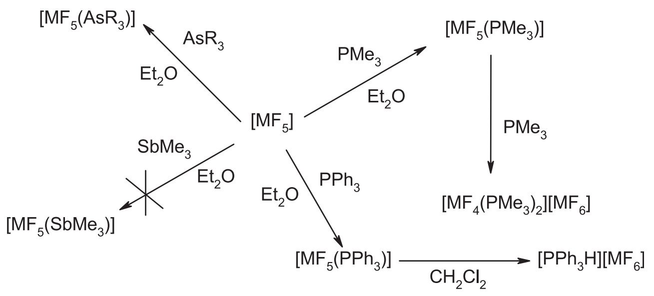

Scheme 1. Reactions of MF_5 with monodentate pnictogen ligands.

acidic metal fluorides. Combining PMe_3 with MF_5 in various substituted aromatic solvents (toluene, fluorobenzene or chlorobenzene) produced brown or purple coloured solutions probably due to the formation of arene radical cations [8]. However, we found that reaction of MF_5 with PMe_3 in anhydrous diethyl ether in a 1:1 molar ratio precipitated white or cream powders with a 1:1 MF_5:PMe_3 composition (Scheme 1).

Although the hard O-donor ether might have been expected to compete for the MF_5, especially when present in excess as solvent, the isolated phosphine complexes showed no diethyl ether present in their ^1H NMR spectra. The [$MF_5(PMe_3)$] complexes are very readily hydrolysed in air and extremely moisture sensitive in solution, a complex mixture of decomposition products identified by their multinuclear NMR signatures include $[PMe_3H]^+$, Me_3PO, $[MF_6]^-$, $[M_2F_{11}]^-$ and complexes of NbF_5 or TaF_5 with Me_3PO [3]. They decompose slowly in the solid state at room temperatures even in sealed containers. As expected, $^{31}P\{^1H\}$ NMR studies show that the complexes are decomposed by MeCN or Me_2CO with liberation of PMe_3, whilst the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra obtained in CH_2Cl_2 solution show decomposition occurs very rapidly to form $[PMe_3H]^+$, $[MF_6]^-$ and $[M_2F_{11}]^-$ and other unidentified products [2(d),4], although resonances of the [$MF_5(PMe_3)$] are also present if the spectra are run immediately. However, the complexes dissolve readily in dry toluene and the spectra of the solutions are unchanged for several hours. The ^1H NMR spectrum of [$TaF_5(PMe_3)$] in d^8-toluene shows a broad singlet at 298 K and this resonance drifts slowly to high frequency on cooling the solution. The $^{19}F\{^1H\}$ NMR spectrum at 298 K shows a very broad feature at $\delta \sim +70$ (s) which sharpens and shifts to low frequency on cooling, then splits <230 K. At 195 K the spectrum contains two broad singlets at $\delta = 82.2$ ([F]) and 43.1 ([4F]) (Fig. 1). The corresponding $^{31}P\{^1H\}$ NMR spectrum at 298 K is a broad singlet ($\delta = -16.4$), which can be compared with the chemical shift of the free phosphine of $\delta = -62$. The resonance shifts to higher frequency on cooling and at 195 K is a singlet at $\delta = +11.0$. These data are consistent with the presence of six-coordinate [$TaF_5(PMe_3)$], which reversibly dissociates PMe_3 at ambient temperatures, but on cooling the exchange slows significantly. This behaviour is broadly similar to that observed in [$TaF_5(SMe_2)$] [4]. In contrast to the spectra of [MF_4(diphosphine)$_2$][MF_6] [5], no ^{31}P–^{19}F coupling was resolved over the temperature range 298–180 K, probably indicating some exchange processes were occurring even at the lowest accessible temperature. The NMR spectra of [$NbF_5(PMe_3)$] show similar behaviour with temperature, although even at 195 K the two resonances in the ^{19}F NMR spectrum are still quite broad; an analogous distorted octahedral structure is therefore proposed. None of the neutral niobium complexes prepared in this work exhibited a ^{93}Nb NMR spectrum, due to fast relaxation in the low symmetry electric fields.

Attempts to produce crystals of either [$MF_5(PMe_3)$] complex were hindered by the limited range of solvents compatible with these unstable complexes, and both species were deposited as fine microcrystalline powders directly from the synthesis solutions. Although a reasonable number of [MF_5L] (L = monodentate ligand) complexes have been reported with N-, O- or S-donor ligands [2–4], the only one that has been characterised crystallographically is the salicylaldimine derivative, [$NbF_5\{\kappa^1\text{-}OC_6H_4CH = NHC_6H_3(CHMe_2)_2\}$]. Here the ligand is O-coordinated to the Nb, although the imine NH is involved in significant H···O and H···F hydrogen bonding [9], which may help to stabilise this complex.

Attempts to isolate complexes with several other phosphines including PMe_2Ph or $PMePh_2$ from Et_2O solution failed to produce solid complexes. The oils or waxes obtained on removing the solvent *in vacuo*, appear from their ^{19}F NMR spectra to be of the [$MF_5(PR_3)$] type, but they could not be purified, and decomposed quite rapidly at ambient temperatures. Solid complexes with PPh_3

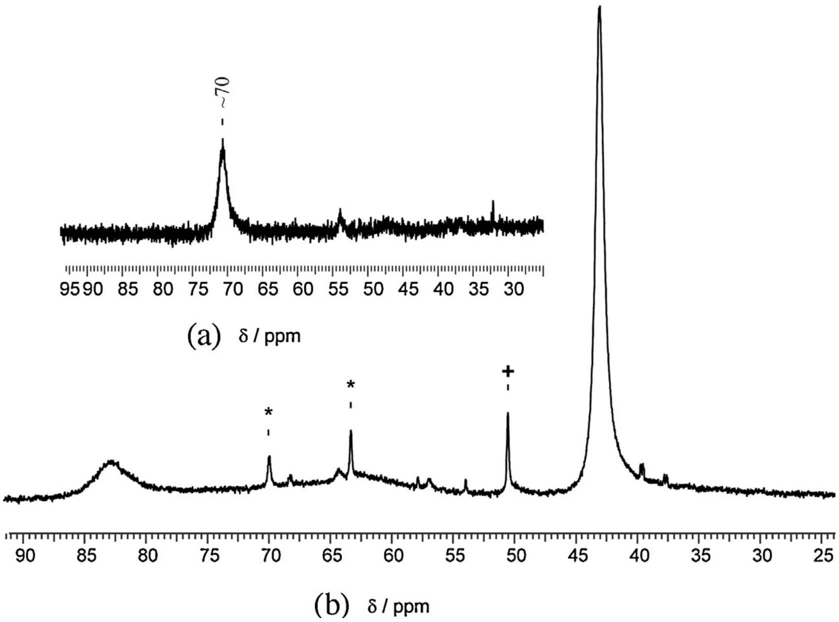

Fig. 1. (a) $^{19}F\{^1H\}$ NMR spectrum (d^8-toluene) of [$TaF_5(PMe_3)$] at 295 K. (b) the spectrum at 195 K. The impurity marked + is due small amounts of the cation $[TaF_4(PMe_3)_2]^+$, the other unidentified minor impurities are marked *.

were obtained from Et_2O solution and the microanalyses and IR spectra are consistent with the presence of a *pseudo*-octahedral metal coordination environment, $[MF_5(PPh_3)]$. However, we were unable to obtain solution NMR data since the complexes are insufficiently soluble in toluene and are decomposed by MeCN or Me_2CO. They dissolve easily in CH_2Cl_2 to give clear solutions initially, but these very rapidly deposit insoluble bluish-white solids, and the supernatant liquid shows $[PPh_3H][MF_6]$ as the only significant species. Crystals of $[PPh_3H][TaF_6]$ were deposited over several days from one such solution.

2.2. $[MF_4(PMe_3)_2][MF_6]$

The reaction of the MF_5 and PMe_3 in Et_2O using a 1:3 molar ratio of metal pentafluoride:PMe_3 was undertaken in an attempt to prepare the self-ionisation products with eight-coordinate cations, $[MF_4(PMe_3)_4][MF_6]$, analogous to the diphosphine complexes described recently [5]. These reactions initially precipitated the neutral $[MF_5(PMe_3)]$ species which were identified by their characteristic NMR spectra. However, if the solutions were stirred for several hours at room temperature, the initial precipitate redissolved and then the solution slowly deposited a white solid. The microanalyses on several batches for both metals were in excellent agreement with expectations for a MF_5 to PR_3 ratio of 1:1, suggesting a $[MF_4(PMe_3)_2][MF_6]$ formulation. Obtaining solution NMR data proved to be challenging due to their decomposition in, or reaction with, most common deuterated solvents. In addition to being extremely moisture sensitive, the complexes were decomposed by CD_3CN, CD_3NO_2 or $(CD_3)_2CO$, and were poorly soluble in d^8-toluene. It proved possible to obtain clean reproducible NMR spectra from *freshly prepared* CD_2Cl_2 solutions with spectra *recorded immediately*; monitoring the solutions over time revealed significant decomposition in ~2 h. This shows that once formed, these ionic complexes are less reactive towards chlorinated solvents than the neutral $[MF_5(PMe_3)]$. This is almost certainly due to the fact that they are much less dissociated into their constituents in solution at ambient temperatures (it is the "free" phosphine which reacts with the chlorinated solvent).

The ^1H and $^{31}P\{^1H\}$ NMR spectra are rather uninformative, other than showing a single environment for the coordinated PMe_3, but the $^{19}F\{^1H\}$ NMR spectrum of $[NbF_4(PMe_3)_2][NbF_6]$ at 295 K (Fig. 2a) showed a singlet at $\delta = 118.5$ ([4F]), together with a very broad resonance at $\delta = 103.4$ ([6F]). The chemical shifts were little changed on cooling the solution to 193 K, but the latter feature resolved into the characteristic 10 line pattern of $[NbF_6]^-$ ($^1J_{NbF} = 334$ Hz) (Fig. 2b) [4]. The $^{19}F\{^1H\}$ NMR spectra of $[TaF_4(PMe_3)_2][TaF_6]$ (Section 4.8) are similar, showing at ambient temperatures the $[TaF_6]^-$ anion and a broad singlet for the cation. It should be noted that the NMR data are quite different to those of $[MF_5(PMe_3)]$, and clearly establish there are four equivalent fluorides in the cation (compared to six in the familiar hexafluoride anions), but do not distinguish between $[MF_4(PMe_3)_2]^+$ and $[MF_4(PMe_3)_4]^+$ formulations.

The former was indicated by the microanalytical data, and confirmation that the cations were six-coordinate came from the low temperature (178 K) $^{19}F\{^1H\}$ NMR spectrum of $[TaF_4(PMe_3)_2][TaF_6]$ which showed a 1:2:1 triplet ($^2J_{PF} = 70$ Hz) confirming the presence of two phosphines as the *trans* isomer (Fig. 3). Coupling was only clearly resolved for the tantalum cation at low temperatures and from dilute solutions. The cation resonance of the niobium analogue was a broad singlet over the temperature range 295–178 K and we were unable to resolve any coupling. As with the $[MF_5(PR_3)]$ complexes, solution instability prevented the growth of X-ray quality crystals of the $[MF_4(PMe_3)_2][MF_6]$ salts.

2.3. Attempts to prepare $[NbOF_3(PMe_3)_2]$

Attempts to prepare $[NbOF_3(PMe_3)_2]$ from reaction of $[NbF_5(PMe_3)]$, PMe_3 and $O(SiMe_3)_2$ in a 1:1:1 molar ratio in Et_2O, produced only a white insoluble powder, most likely $NbOF_3$ based on its IR spectrum [10]. Complexes including $[NbOF_3(OPR_3)_2]$ (R = Me or Ph), $[NbOF_3(dmso)_2]$ and $[NbOF_3(diimine)]$ are obtained from reaction of NbF_5, the appropriate ligand and $O(SiMe_3)_2$ in MeCN solution, although complexes containing weaker donor ligands (MeCN, ethers or thioethers) did not form [3]. Since the $[NbF_5(PMe_3)]$ is extensively dissociated in solution at room temperature (NMR evidence above), it is likely that the $O(SiMe_3)_2$ reacts with the uncoordinated NbF_5 present to form $NbOF_3$, which then polymerises, making it unavailable for coordination to the phosphine.

2.4. $[MF_5(AsR_3)]$

The reaction of $AsMe_3$ with MF_5 in anhydrous Et_2O gave white (M = Ta) or cream (M = Nb) powders of composition $[MF_5(AsMe_3)]$. In contrast, the reaction of MF_5 with $AsEt_3$ in Et_2O did not lead to the precipitation of solid complexes. However, upon removal of the solvent *in vacuo*, clear fawn oils remained, which darken to a

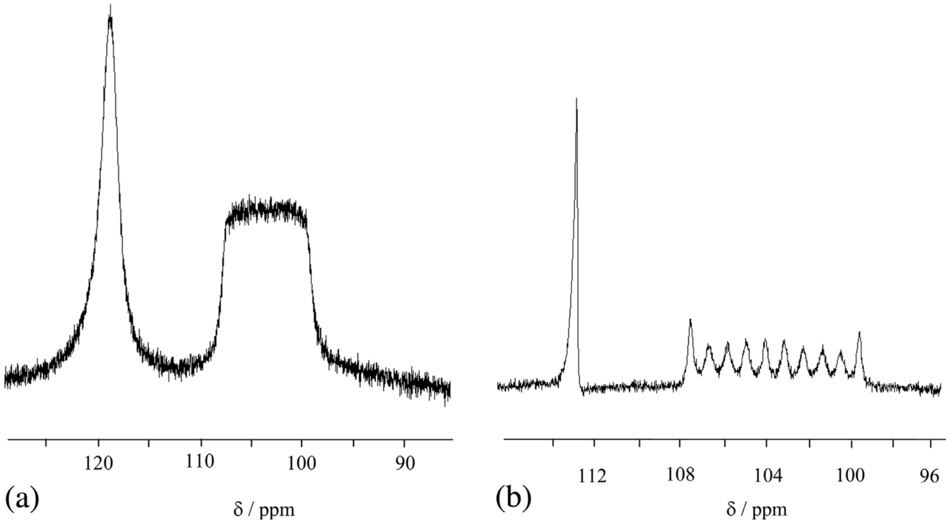

Fig. 2. $^{19}F\{^1H\}$ NMR spectrum of $[NbF_4(PMe_3)_2][NbF_6]$ in CD_2Cl_2 (a) at 295 K; (b) at 193 K.

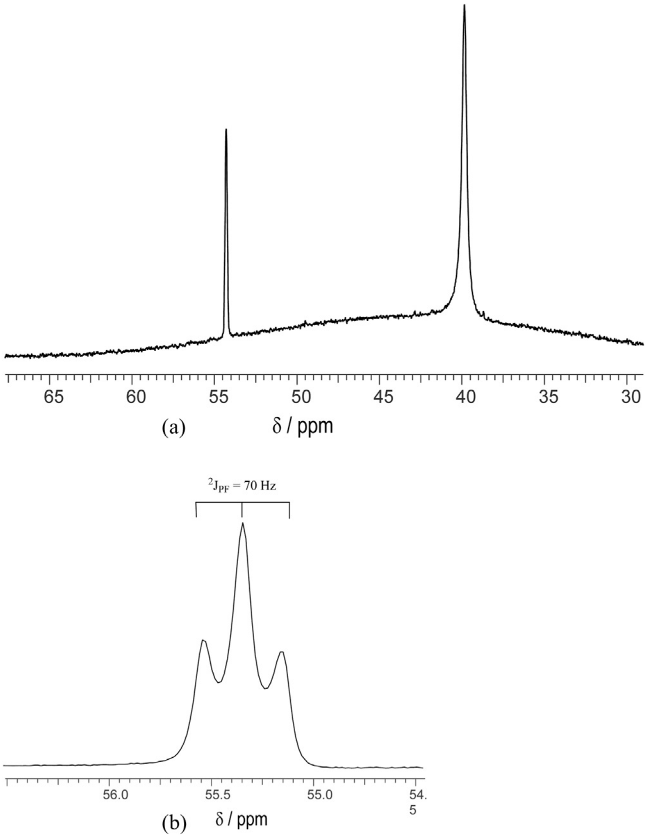

Fig. 3. (a) The $^{19}F\{^1H\}$ NMR spectrum of $[TaF_4(PMe_3)_2][TaF_6]$ at 220 K; (b) expansion of the cation resonance at 178 K.

blue-grey colour over ~24 h at room temperature. The oils solidified to waxes on cooling in an ice-bath, but melted upon re-warming. Notably, the $[MF_5(SEt_2)]$ are also oils which solidify below room temperature [4,11]. The $[MF_5(AsMe_3)]$ complexes were very poorly soluble in d^8-toluene or CD_2Cl_2, but their NMR spectra were similar to those of the readily soluble $[MF_5(AsEt_3)]$. In toluene solution the $[MF_5(AsR_3)]$ complexes did not exhibit $^{19}F\{^1H\}$ NMR spectra at 293 K, but upon cooling the solutions, very broad resonances appeared which gradually sharpened and at 195 K the tantalum complex of $AsEt_3$ showed two singlets at $\delta = 69.2$ ([F]) and 34.6 ([4F]), consistent with the presence of $[TaF_5(AsEt_3)]$ (Fig. 4). These spectral changes are reversible on warming. The behaviour of $[NbF_5(AsEt_3)]$ was similar, although even at 195 K the resonances in the $^{19}F\{^1H\}$ NMR spectrum were still very broad, indicating some exchange was still occurring on the NMR time-scale. The diarsine species, $[MF_4(o\text{-}C_6H_4(AsMe_2)_2)_2][MF_6]$ [5], were less stable than the diphosphine anlogues, and it is therefore not surprising that the $[MF_5(AsR_3)]$ appear to be substantially dissociated in solution at room temperature, although the low temperature $^{19}F\{^1H\}$ NMR spectra seem good evidence for the identity of the complexes. Using a higher AsR_3: MF_5 ratio resulted only in isolation of the $[MF_5(AsR_3)]$; in contrast to the PMe_3 systems, ionic products were not observed.

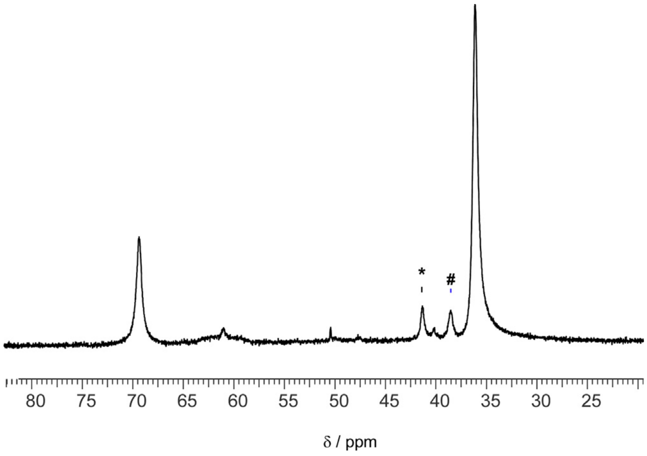

Fig. 4. The $^{19}F\{^1H\}$ NMR spectrum of $[TaF_5(AsEt_3)]$ in d^8-toluene at 195 K. The resonances marked # is $[TaF_6]^-$ and * an unidentified impurity.

2.5. Attempted preparation of $[MF_5(SbMe_3)]$

Attempts to prepare stibine complexes by similar routes to their lighter analogues were unsuccessful. An excess (~3 molar equivalents) of $SbMe_3$ in Et_2O was added to a frozen solution of TaF_5 in Et_2O at 77 K and the mixture allowed to warm. On melting, a colourless solution was obtained, and after 1 h. at ambient temperature, volatiles were removed *in vacuo* to yield a white solid. This was identified by a combination of ^1H and $^{19}F\{^1H\}$ NMR spectroscopy as the known [2,10] diethyl ether complex, and the $SbMe_3$ was found in the trap of the vacuum line. Combining NbF_5 and $SbMe_3$ also gave the ether adduct, although in this case some black material was also produced. The results show that the weak soft $SbMe_3$ cannot compete with the ether for the hard metal centre.

3. Conclusions

Trimethylphosphine has been shown to form $[MF_5(PMe_3)]$ and *trans*-$[MF_4(PMe_3)_2][MF_6]$ complexes, which are the first isolated examples of six-coordinate metal centres with heavy Group 15 donor ligands. The corresponding arsine complexes, $[MF_5(AsR_3)]$, have also been obtained. The complexes are extremely moisture sensitive, readily decomposed by common solvents, and are much less robust than the eight-coordinate cations $[MF_4(\text{diphosphine})_2]^+$ or $[MF_4(\text{diarsine})_2]^+$ reported previously [5]. The instability has prevented X-ray quality crystals being obtained, but their identities have been confirmed by microanalysis and multinuclear NMR spectroscopic studies. The successful isolation and characterisation of the six-coordinate complexes with mono-phosphines and -arsines, completes our studies of soft donor complexes of niobium and tantalum pentafluorides [3–5].

4. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin Elmer Spectrum 100 over the range 4000–200 cm^{-1}. ^1H NMR spectra were recorded from CD_2Cl_2 or d^8-toluene solutions using a Bruker AVII 400 spectrometer and are referenced to the residual solvent resonance. $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and ^{93}Nb NMR spectra were recorded in CD_2Cl_2 or d^8-toluene solutions using a Bruker AVII 400 spectrometer and are referenced to external $CFCl_3$, external 85% H_3PO_4, and $[Et_4N][NbCl_6]$ in MeCN, respectively. Microanalyses on new complexes were undertaken by London Metropolitan University. Preparations used standard Schlenk and glove box techniques under a N_2 atmosphere with rigorous exclusion of moisture. Solvents were dried by distillation from CaH_2 (CH_2Cl_2 or CH_3CN) or Na/benzophenone ketyl (diethyl ether or toluene). NbF_5, TaF_5, PMe_3, PPh_3, PMe_2Ph, $AsMe_3$ and $AsEt_3$ were obtained from Aldrich, Strem or Apollo and used as received. $SbMe_3$ was made from $SbCl_3$ and 3MeLi in diethyl ether, and the ether azeotrope distilled from the reaction mixture. Many of the complexes deteriorate even in sealed glass ampoules or in Schlenks stored in a glove box, and the ^{19}F NMR spectra of aged samples show resonances due to fluorosilicate anions indicating attack on the glass. All measurements, except for outsourced microanalyses, were made on freshly prepared samples within 1 day of isolation.

4.1. *[TaF5(PMe$_3$)]*

TaF_5 (0.28 g, 1.0 mmol) was dissolved in anhydrous diethyl ether (15 mL) and PMe_3 (0.08 g, 1.1 mmol) added. Initially a clear solution formed, which deposited a white powder after $\sim$20 min stirring. The solvent was reduced to $\sim$5 mL *in vacuo*, and the white solid was filtered off and dried *in vacuo*. Yield: 0.24 g, 69%. Anal: Required for $C_3H_9F_5PTa$ (352.0): C, 10.2; H, 2.6. Found: C, 10.4; H, 2.6%. ^{1}H NMR (d^8-toluene, 293 K): δ = 2.12 (s); (195 K): 2.14 (s). ^{19}F{^{1}H} NMR (d^8-toluene, 293 K): δ = 70.3 (br, s); (195 K): 82.4 (s, [F]), 43.1 (s, [4F]). ^{31}P{^{1}H} NMR (d^8-toluene, 293 K): $\delta = -16.4$ (s); (195 K): +11.0 (s). IR (Nujol)/cm^{-1}: 586 (sh), 573 (vbr,s), 555 (sh) (TaF).

4.2. *[NbF5(PMe$_3$)]*

NbF_5 (0.18 g, 1.0 mmol) was added to anhydrous diethyl ether (15 mL) and stirred until a clear solution was formed ($\sim$5 min), followed by addition of PMe_3 (0.08 g, 1.1 mmol). A fine pale yellow precipitate formed slowly, and after 20 min the solution was concentrated *in vacuo* to $\sim$5 mL the solid was filtered off, rinsed with diethyl ether (2 mL) and dried *in vacuo*. Cream microcrystalline solid. Yield: 0.20 g, 76%. Anal: Required for $C_3H_9F_5NbP$ (264.0): C, 13.7; H, 3.5. Found: C, 13.8; H, 3.4%. ^{1}H NMR (d^8-toluene, 293 K): δ = 2.19 (s); (195 K): 2.25 (s). ^{19}F{^{1}H} NMR (d^8-toluene, 293 K): δ = 156.7 (vbr); (193 K): 155.2 (s, [F]), 108.7 (s, [4F]). ^{31}P{^{1}H} NMR (d^8-toluene, 293 K): $\delta = -20.9$ (br s); (195 K): +6.5 (br s). ^{93}Nb NMR (d^8-toluene, 293 K or 195 K): not observed. IR (Nujol)/cm^{-1}: 605 (vs), 574 (s,br) (NbF).

4.3. *[NbF$_5$(PPh$_3$)]*

NbF_5 (0.18 g, 1.0 mmol) was added to anhydrous diethyl ether (20 mL) and stirred until a clear solution was formed, followed by addition of powdered PPh_3 (0.26 g, 1.0 mmol). A clear solution formed rapidly, and on stirring a precipitate slowly deposited. After 2 h. the solution was concentrated *in vacuo* to $\sim$5 mL and the white solid was filtered off, rinsed with diethyl ether (2 mL) and dried *in vacuo*. White solid. Yield: 0.29 g, 63%. Anal: Required for $C_{18}H_{15}F_5NbP$ (457.1): C, 48.0; H, 3.4. Found: C, 48.3; H, 3.6%. IR (Nujol)/cm^{-1}: 622 (sh), 609 (vs) (NbF).

^{1}H NMR *(data correspond to [PPh$_3$H][NbF$_6$] see text)* (CD$_2$Cl$_2$, 293 K): δ = 9.30 (d, [H], $^1J_{PH}$ = 512 Hz), 8.02-7.75 (m [15H])^{19}F{^{1}H} NMR (CH$_2$Cl$_2$, 293 K): δ = 104.2 (10 lines, $^1J_{Nb\text{-}F}$ = 330 Hz). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 293 K): δ = 6.8 (s). ^{93}Nb NMR (CH$_2$Cl$_2$, 293 K): $\delta = -1554$ (7 lines, $^1J_{Nb\text{-}F}$ = 335 Hz).

4.4. *[TaF$_5$(PPh$_3$)]*

was made similarly to the niobium analogue. Yield: 55%. Anal: Required for $C_{18}H_{15}F_5PTa$ (538.2): C, 40.2; H, 2.8. Found: C, 40.1; H, 2.8%. IR (Nujol/cm^{-1}): 602 (sh), 587 (vs), 576 (vs) (TaF).

^{1}H NMR *(data correspond to [PPh$_3$H][TaF$_6$] see text)* (CD$_2$Cl$_2$, 293 K): δ = 9.30 (d, [H], $^1J_{PH}$ = 512 Hz), 8.04-7.75 (m, [15H]).^{19}F{^{1}H} NMR (CH$_2$Cl$_2$, 293 K): δ = 38.0 (s). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$, 293 K): δ = 6.9 (s).

4.5. *[NbF$_4$(PMe$_3$)$_2$][NbF$_6$]*

PMe_3 (0.24 g, 3.0 mol) was dissolved in anhydrous Et$_2$O (30 mL) and powdered NbF_5 (0.18 g, 1.0 mmol) was added slowly. An initial cream precipitate formed and then on stirring redissolved to give a colourless solution. After 3 h. the solution had deposited a cream powder. The solution was concentrated to $\sim$10 mL and the solid was filtered off, rinsed with diethyl ether (2 mL) and dried *in vacuo*. Cream microcrystalline solid. Yield: Yield: 0.22 g, 83%. Anal: Required for $C_6H_{18}F_{10}Nb_2P_2$ (528.0): C, 13.7; H, 3.5. Found: C, 13.8; H, 3.6%. ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ = 1.32 (br, s); (195 K): 1.38 (s). ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): δ = 118.5 (s, [4F]), 103.4 (vbr s, [6F]); (193 K): 112.9 (s, [4F]), 103.5 (10 lines, [6F], $^1J_{NbF}$ = 334 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): δ = +6.1 (s); (195 K): +10.2 (s). ^{93}Nb NMR (CD$_2$Cl$_2$, 293 K): -1549 (septet [NbF$_6$]$^-$). IR (Nujol)/cm^{-1}: 603 (vs, br), 583 (sh) (NbF).

4.6. *[TaF$_4$(PMe$_3$)$_2$][TaF$_6$]*

PMe_3 (0.24 g, 3.0 mmol) was dissolved in anhydrous Et$_2$O (30 mL) and powdered TaF_5 (0.28 g, 1.0 mmol) was added slowly which resulted in an initial white precipitate. On stirring the precipitate redissolved and after $\sim$3 h. a further white solid had deposited. The solvent was reduced to $\sim$5 mL *in vacuo*, and the white solid filtered off and dried *in vacuo*. Yield: 0.25 g, 71%. Anal: Required for $C_6H_{18}F_{10}P_2Ta_2$ (704.0): C, 10.4; H, 2.6. Found: C, 10.9; H, 2.8%. ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ = 1.40 (s); (195 K): 1.53 (s). ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): δ = 56.2 (s, [4F]), 39.5 (s [6F]); (195 K): 55.0 (s, [4F]), 39.5 (s, [6F]). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): δ = +2.1 (s); (195 K): +4.7 (s). IR (Nujol)/cm^{-1}: 577 (vbr,s), 550 (sh) (TaF).

4.7. *[TaF$_5$(AsMe$_3$)]*

TaF_5 (0.28 g, 1.0 mmol) was added to anhydrous diethyl ether (15 mL) and $AsMe_3$ (0.12 g, 1.0 mmol) added. The mixture was stirred for 1 h. during which some precipitate formed. The solution was concentrated to $\sim$5 mL and the white solid filtered off and dried *in vacuo*. 0.25 g, 62%. Anal: Required for $C_3H_9AsF_5Ta$ (396.0): C, 9.1; H, 2.3. Found: C, 9.1; H, 2.3%. ^{1}H NMR (d^8-toluene, 293 K): δ = 1.12(s). ^{19}F{^{1}H} NMR (d^8-toluene, 293 K): δ = not observed; (195 K): 70.2 (s, [F]), 27.2 (s, [4F]). IR (Nujol)/cm^{-1}: 620 (br), 586 (vbr,s) (TaF).

4.8. *[NbF$_5$(AsMe$_3$)]*

was made similarly from NbF_5 (0.18 g, 1.0 mmol) and $AsMe_3$ (0.12 g, 1.0 mmol). Cream solid 0.22 g, 73%. Anal: Required for $C_3H_9AsF_5Nb$ (307.9): C, 11.7; H, 3.0. Found: C, 12.1; H, 3.1%. ^{1}H NMR (d^8-toluene, 293 K): δ = 1.13 (s). ^{19}F{^{1}H} NMR (d^8-toluene, 293 K): δ = not observed; (195 K): 135.1(s, [F]), 98.9(s, [4F]). IR (Nujol)/cm^{-1}: 607 (br), 560 (sh) (NbF).

4.9. *[TaF$_5$(AsEt$_3$)]*

TaF_5 (0.28 g, 1.0 mmol) was added to anhydrous diethyl ether (15 mL) and $AsEt_3$ (0.16 g, 1.0 mmol) added. A clear solution formed, which was stirred for 2 h, then the Et$_2$O removed *in vacuo* at ambient temperature and the residue pumped on (0.5 mm Hg) for 2 h. The product was a clear oil which could not be purified further and decomposed slowly at ambient temperatures. The complex was identified by low temperature NMR spectroscopy. ^{1}H NMR (d^8-toluene, 293 K): δ = 2.00 (s [3H]), 2.19 (s, [2H]); (195 K): 2.06 (s, [3H]), 2.13 (s, [2H]). ^{19}F{^{1}H} NMR (d^8-toluene, 293 K): not observed; (195 K): 69.2 (s, [F]), 34.6 (s, [4F]).

4.10. *[NbF$_5$(AsEt$_3$)]*

[NbF$_5$(AsEt$_3$)] was obtained similarly as a fawn oil. ^{1}H NMR (d^8-toluene, 293 K): δ = 2.06 (s [3H]), 2.17 (s, [2H]); (195 K): 2.26 (s, [3H]), 2.30 (s, [2H]). ^{19}F{^{1}H} NMR (d^8-toluene, 293 K): not observed; (195 K): 143.9 (s, [F]), 103.3 (s, [4F]).

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