Tertiary Phosphine Adducts of [Nb(O)Cl$_3$]

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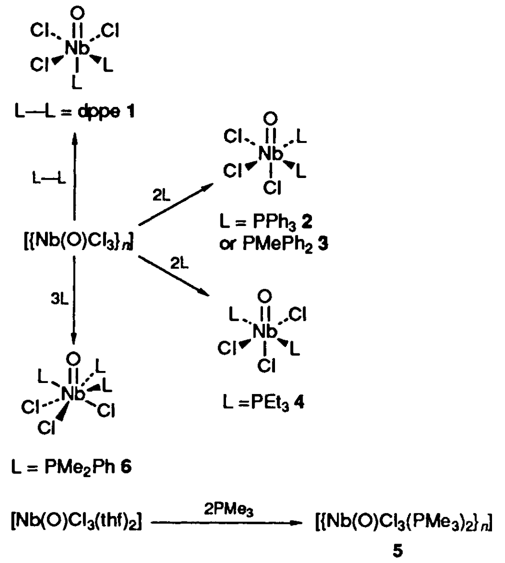
A series of tertiary phosphine adducts of [Nb(O)Cl$_3$] is described. The compounds [Nb(O)Cl$_3$L$_2$] (L = PMe$_3$, PMePh$_2$, PPh$_3$ or PEt$_3$), [Nb(O)Cl$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] and [Nb(O)Cl$_3$(PMe$_2$Ph)$_3$] have been prepared *via* reaction of either [{Nb(O)Cl$_3$}$_n$] or [Nb(O)Cl$_3$(thf)$_2$] (thf = tetrahydrofuran) with a stoichiometric amount of the phosphine in dichloromethane solvent. The influence of the differing ligand fields on the infrared stretching frequency of the niobium–oxygen bond is discussed in terms of the geometry of the complex and the stereoelectronic properties of the attendant ligands.

Simple adducts of [Nb(O)Cl$_3$] containing a variety of neutral donor ligands such as NR$_3$,[1] RCN,[2] OPR$_3$,[3] OAsR$_3$,[3] OSMe$_2$,[4] OP(NMe$_2$)$_3$,[5] and bipyridine[6] have been reported (R = alkyl or aryl) but it is only recently that tertiary phosphine derivatives have been described. The yellow seven-co-ordinate trimethylphosphine complex [Nb(O)Cl$_3$(PMe$_3$)$_3$][7] was the first tertiary phosphine complex to be described and was shown by X-ray crystallography to possess a monocapped octahedral co-ordination geometry. Subsequently, a second form of this compound was isolated, differing from the first in its colour (green) and Nb=O stretching frequency. A crystal structure determination indicated it to be isostructural and isomorphous with the first, implying that these compounds could be elusive examples of bond stretch isomers.[8] The current interest surrounding the phenomenon of bond stretch isomerism[9–12] has prompted us to examine other tertiary phosphine adducts of [Nb(O)Cl$_3$] to see if there is any evidence for such an effect in related six- and seven-co-ordinate complexes of niobium bearing phosphine ligands other than PMe$_3$. We envisaged that IR spectroscopy would provide the most convenient method for screening these compounds since, to date, all proposed examples of bond stretch isomers have displayed small but distinct differences in their IR spectra, particularly in the M=O stretching region. The results of these investigations are described herein.

Results and Discussion

Synthesis and Characterisation of Tertiary Phosphine Adducts of Niobium Trichloride Oxide.—Although only sparingly soluble in dichloromethane, [{Nb(O)Cl$_3$}$_n$] readily dissolves in the presence of tertiary phosphines to afford yellow-orange solutions from which microcrystalline samples of the adducts [Nb(O)Cl$_3$L$_n$] [n = 1, L = Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe) **1**; n = 2, L = PPh$_3$ **2**, PMePh$_2$ **3**, PEt$_3$ **4**, PMe$_3$ **5** and n = 3, L = PMe$_2$Ph **6**] may be isolated in high yields (Scheme 1). The stoichiometry of the products is determined by the ratio of reactants and also by the nature of the phosphine ligands. Thus, with relatively large phosphines such as PPh$_3$, PMePh$_2$ and PEt$_3$, which have cone angles (θ) of 145, 136 and 132° respectively,[13] only two phosphines co-ordinate even when an excess of the ligand is present; whereas with the smaller phosphine PMe$_2$Ph (θ = 122°) three donor ligands can be accommodated. This is also the case for PMe$_3$ (θ = 118°), [Nb(O)Cl$_3$(PMe$_3$)$_3$][7] being the only isolable product from the reaction of [Nb(O)Cl$_3$] with PMe$_3$ in CH$_2$Cl$_2$ even when less than 3 equivalents of the phosphine are employed. However, if [Nb(O)Cl$_3$(thf)$_2$][14] (thf = tetrahydrofuran) is used as the starting material in place of [{Nb(O)Cl$_3$}$_n$], the white sparingly soluble bis-phosphine complex **5** precipitates from CH$_2$Cl$_2$ solution in modest yield. All the compounds are moisture sensitive, decomposing to white powders upon exposure to moist air: a qualitative order of hydrolytic sensitivity is **4**,**6** > **2**,**3** > **1**,**5**, an ordering reflected in the C,H,N analyses which were consistently low in both carbon and hydrogen for **4** and **6** presumably due to the particular lability of the ligands in these complexes.



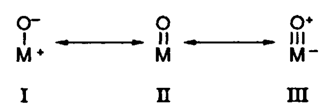
Scheme 1

All of the phosphine adducts display strong IR absorptions between 920 and 940 cm^{-1} indicative of the terminal metal–oxo unit (Table 1).[15] The IR patterns in the Nb–Cl stretching region (400–250 cm^{-1})[16] for **2** and **3** are similar and show three strong bands. This, along with the observation of a single resonance in the ^{31}P-{^{1}H} NMR spectrum for **2**, is supportive of a *cis*, *fac* geometry (Scheme 1) similar to that established for [Re(O)Cl$_3$(dppe)].[17] However, the broad ^{31}P resonance for **2** may reflect a degree of solution fluxionality, analogous to that reported for [Nb(O)Cl$_3$(hmpa)$_2$] [hmpa = P(NMe$_2$)$_3$O].[5] The similarities in the metal–chloride stretching region of **1** and [Nb(O)Cl$_3$(MeCN)$_2$] and [Nb(O)Cl$_3$(thf)$_2$][14] indicate that the former has a *cis*, *mer* geometry as found for [Nb(O)Cl$_3$(MeCN)$_2$][2] and the isoelectronic imido complex, [Ta(NPh)Cl$_3$(PMe$_3$)$_2$].[18] Whilst solubility and mass spectral data indicate that **5** is at least dimeric, the strong absorption at 923 cm^{-1} in the IR spectrum assignable to ν(Nb=O) further

Table 1

Compound	ν(Nb=O)[a]/cm^{-1}	c.n.[b]	Ref.
$[Nb(O)Cl_3(thf)_2]$	960	6	14
$[Nb(O)Cl_3(MeCN)_2]$	960	6[c]	14
$[Nb(O)Cl_3(hmpa)_2]$[d]	940	6[c]	5
$[Nb(O)Cl_3(PPh_3)_2]$ **2**	939	6	This work
$[Nb(O)Cl_3(OPPh_3)_2]$	935	6	3
$[Nb(O)Cl_3(bipy)]$[e]	934	6	6
$[Nb(O)Cl_3(dppe)]$ **1**	931	6	This work
$[Nb(O)Cl_3(PEt_3)_2]$ **4**	930	6	This work
$[Nb(O)Cl_3(PMePh_2)_2]$ **3**	929	6	This work
$[\{Nb(O)Cl_3(PMe_3)_2\}_n]$ **5**	923	7, 8	This work
$[Nb(O)Cl_2(OPr^n)(bipy)]$	912	6	15
$[Nb(O)Cl_3(PMe_3)_3]$	882	7[c]	7

[a] All spectra recorded as Nujol mulls. [b] c.n. = Co-ordination number. [c] Structurally characterised. [d] hmpa = $P(NMe_2)_3O$. [e] bipy = 2,2′-Bipyridine.



Scheme 2

suggests that it is the chlorine rather than oxygen atoms that are bridging. However, due to the intractability of this compound we have not pursued a more detailed investigation of its structure. The seven-co-ordinate PMe_2Ph derivative **6** possesses equivalent phosphine ligands (by NMR) and, in the absence of crystallographic data, is presumed to adopt a monocapped octahedral geometry similar to that established for $[Nb(O)Cl_3(PMe_3)_3]$.[7]

The ν(Nb–Cl) region of the IR spectrum of **4** is significantly different to those of **1**, **2** and **3** indicating a different solid-state geometry. Since only a single, sharp resonance is observed in the $^{31}P-\{^1H\}$ NMR spectrum at δ 38.29, we favour a *trans*, *mer* geometry for **4** as found for $[Ta(NPh)Cl_3(PEt_3)_2]$.[18] Interestingly, the room-temperature ^1H NMR spectrum of **4** reveals unusual solution behaviour, where one ethyl group of a single phosphine ligand is unique and displays diastereotopic methylene hydrogens possibly indicating that this ethyl group is conformationally 'locked'. Attempts to grow crystals of **4** for an X-ray diffraction study have to date proved unsuccessful.

The Effect of the Ligand Field on ν(Nb=O) *for Complexes of the Type* $[Nb(O)Cl_3L_n]$.—Terminal ν(Nb=O) vibrational frequencies have been reported in the range 890–950 cm^{-1} as strong, sharp absorptions, whose frequency is sensitive to the metal co-ordination number and the nature of the ligand field.[15] The nature of the metal–oxygen bonding may be rationalised qualitatively on the basis of the canonical forms depicted in Scheme 2. Here, the oxo ligand acts as a zero-(**I**), two-(**II**) or four-(**III**) electron donor respectively. Increasing the metal basicity would then be anticipated to lower the contribution of canonical form **III** and result in a lowering of the ν(Nb=O) vibrational frequency. A similar rationale has been used to correlate ν(V=O) frequencies and (V–O) force constants with the basicity of the ligand field in a range of oxovanadium complexes.[19] The ν(Nb=O) frequencies for compounds **1**–**5** are reproduced in Table 1 along with selected data for a number of other complexes of the form $[Nb(O)X_3L_n]$. It can be seen that, in general, the complexes with the higher co-ordination numbers have lower ν(Nb=O) values, a result of the increased metal basicity and inter-ligand steric forces. All the six-co-ordinate compounds have ν(Nb=O) > 920 cm^{-1} apart from $[Nb(O)Cl_2(OPr^n)(bipy)]$ wherein it was assumed that increased p_π–d_π interactions between the metal and alkoxo group reduced the contribution from canonical form **III**.[15] Among the six-co-ordinate complexes, the highest frequencies and presumably the strongest (Nb=O) bonds are found with MeCN and thf ligands, both of which are very labile in these complexes and do not engage in extensive p_π–d_π interactions with the metal. The two other oxygen donor ligands, $OPPh_3$ and hmpa, appear to be stronger bases towards $[Nb(O)Cl_3]$ than MeCN or thf. The higher ν(Nb=O) value for the hmpa complex presumably reflects the lower basicity of hmpa over $OPPh_3$ resulting from the more electronegative NMe_2 substituents on phosphorus in the former.

With regard to the tertiary phosphine complexes, it was anticipated that sequential replacement of phenyl substituents for more electron-releasing alkyl groups would result in a lower ν(Nb=O) frequency and consequently a reduced niobium–oxygen bond order. This general trend is corroborated by the data in Table 1 where the relative ability of the tertiary phosphine ligand to lower the ν(Nb=O) frequency follows the sequence $PMe_3 > PMePh_2 \approx$ dppe $> PPh_3$. Unfortunately, we could neither assign unambiguously the ν(Nb=O) vibration for **6** due to extensive overlap with vibrations of the phosphine ligand nor more fully delineate the co-ordination number of **5** (although it must have a co-ordination number greater than six, both seven- and eight-co-ordinate complexes are known for niobium[20]) so the data set is not as complete as we would like: however, they do show that the ν(M=O) frequency can act as a useful guide to the basicity of a given ligand field and moreover, that in all the cases where ν(Nb=O) may be unambiguously assigned, there is no clear spectroscopic evidence for the existence of more than one isomer.

Experimental

General.—All manipulations were performed on a conventional vacuum/inert atmosphere (nitrogen or argon) line using Schlenk and cannula techniques, or in a nitrogen-filled dry-box. Solvents were purified and dried by reflux and subsequent distillation from a suitable drying agent (in parentheses): dichloromethane (calcium hydride), light petroleum (b.p. 40–60 °C) (lithium aluminium hydride) and $[^2H_1]$chloroform [phosphorus(V) oxide] and were deoxygenated prior to use. Elemental analyses were performed by the microanalytical laboratory of this department. The collection of analytical and spectroscopic data was as described previously.[21]

The following chemicals were prepared by published procedures: $[Nb(O)Cl_3]$,[14] $[Nb(O)Cl_3(thf)_2]$,[14] PMe_3.[22] All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparations.—$[Nb(O)Cl_3(dppe)]$ **1**. Dichloromethane (40 cm^3) was added *via* cannula to a solid mixture of $[Nb(O)Cl_3]$ (0.5 g, 2.32 mmol) and dppe (0.92 g, 2.32 mmol) at room temperature. An immediate reaction ensued and within 2 h the solid had dissolved completely to afford a yellow-orange solution. This was filtered and the volatile components removed under reduced pressure to give a yellow solid, which was washed with light petroleum (2 × 10 cm^3) and dried *in vacuo*. Yield: 1.38 g (97%) (Found: C, 50.90; H, 4.10. $C_{26}H_{24}Cl_3NbOP_2$ requires C, 50.90; H, 3.95%). IR (Nujol, CsI): 3047w (br), 1584w, 1571w, 1484m, 1435s, 1414m, 1333w, 1189w, 1097m, 1070w, 1027m, 1000m, 931m, 892m, 863m, 827m, 742s, 693s, 518s, 395m (br), 415w, 357s (br) and 327m (br) cm^{-1}. ^1H NMR (250 MHz, $[^2H_1]$chloroform, 298 K): δ 7.34 (br s, 12 H, *m*-, *p*-H of Ph) and 2.72 (br s, 4 H, PCH_2CH_2P). Mass spectrum [chemical ionisation (CI), isobutane carrier gas, ^{35}Cl]: *m*/*z* 906 $[Nb(OH)(dppe)_2]^+$, 583 $[M - C_2H_5]^+$ and 399 [dppe + H]$^+$.

$[Nb(O)Cl_3(PPh_3)_2]$ **2**. Dichloromethane (40 cm^3) was added *via* cannula to a mixture of $[Nb(O)Cl_3]$ (0.5 g, 2.32 mmol) and PPh_3 (1.21 g, 4.64 mmol) at room temperature. An immediate reaction resulted in the mixture adopting a yellow coloration. After all the $[Nb(O)Cl_3]$ had reacted (*ca.* 12 h) the resulting yellow-orange solution was filtered and the volatiles removed under reduced pressure to afford a yellow solid, which was washed with light petroleum (2 × 10 cm^3) and dried *in vacuo*. Yield: 1.27 g (74%) (Found: C, 57.95; H, 4.10. $C_{36}H_{30}Cl_3NbOP_2$ requires C, 58.45; H, 4.10%). IR (Nujol, CsI): 3054w (br), 1586w, 1484m, 1438s, 1331w, 1311w, 1186w, 1164w, 1100s, 1029m, 999m, 939s, 750s, 701s, 696s, 523s, 509s, 500s, 454m, 445m, 379s, 332m and 316s cm^{-1}. NMR (250 MHz, [$^2H_1$]chloroform, 298 K): ^{1}H, δ 7.47 (br s, 12 H, *o*-H of Ph) and 7.40 (br s, 18 H, *m*-, *p*-H of Ph); ^{31}P (broad-band decoupled), δ 3.85 [br s, $\Delta_{\frac{1}{2}}$ = 50 Hz, 2 PPh_3]. Mass spectrum (CI, isobutane carrier gas, ^{35}Cl): *m/z* 735 $[M - 3\,H]^+$, 557 $[Nb(OH)(PPh_3)_2 - Ph]^+$, 279 $[Ph_3PO + H]^+$ and 263 $[Ph_3P + H]^+$.

$[Nb(O)Cl_3(PMePh_2)_2]$ **3**. Methyldiphenylphosphine (0.93 g, 4.64 mmol) was added *via* syringe, to a stirred suspension of $[Nb(O)Cl_3]$ (0.5 g, 2.32 mmol) in dichloromethane solvent (40 cm^3) at room temperature. The $[Nb(O)Cl_3]$ reacted over 12 h to afford a yellow-orange solution. This was then filtered and the volatiles removed under reduced pressure to leave a microcrystalline yellow solid, which was washed with light petroleum (*ca.* 10 cm^3) and dried *in vacuo*. Yield: 1.2 g (84%) (Found: C, 50.40; H, 4.55. $C_{26}H_{26}Cl_3NbOP_2$ requires C, 50.70; H, 4.25%). IR (Nujol, CsI): 3047w (br), 1587w, 1574w, 1486m, 1437s, 1336m, 1311m, 1287m, 1190m, 1161w, 1101s, 1072w, 1029m, 1001m, 929s (br), 889s (br), 742s, 697s, 512s, 480m, 443m, 371s, 327s and 312s cm^{-1}. ^{1}H NMR (250 MHz, [$^2H_1$]chloroform, 298 K): δ 7.46 (br s, 8 H, *o*-H of Ph), 7.33 (br s, 12 H, *m*- and *p*-H of Ph) and 1.77 (br s, 6 H, $PMePh_2$). Mass spectrum (CI, isobutane carrier gas, ^{35}Cl): *m/z* 615 $[M + H]^+$, 595 $[M - H_2O]^+$, 383 $[NbCl_3(PPh_2)]^+$, 217 $[Ph_2MePO + H]^+$, 215 $[Nb(OH)Cl_3]^+$ and 201 $[Ph_2MeP + H]^+$.

$[Nb(O)Cl_3(PEt_3)_2]$ **4**. Triethylphosphine (0.96 g, 8.12 mmol) was added to a stirred suspension of $[Nb(O)Cl_3]$ (0.5 g, 2.32 mmol) in dichloromethane (40 cm^3) at room temperature. An immediate reaction led to complete dissolution of the $[Nb(O)Cl_3]$ within *ca.* 1 min to afford a yellow solution. After stirring for 2 h, the solution was filtered and the volatiles removed to give a yellow solid, which was washed with cold (*ca.* −30 °C) light petroleum (10 cm^3) and dried *in vacuo*. Yield: 0.95 g (91%) (Found: C, 30.45; H, 6.35. $C_{12}H_{30}Cl_3NbOP_2$ requires C, 31.90; H, 6.70%). IR (Nujol, CsI): 1412m, 1320w, 1143w, 1050m, 1042m, 930s (br), 842m, 810m, 786m, 776m, 738m, 726m and 330s (br) cm^{-1}. NMR (250 MHz, [$^2H_1$]chloroform, 298 K): ^{1}H, δ 4.01 [m, 1 H, *J*(PH) = 18.6, *J*(HH) = 6, PC*H*H], 3.02 [m, 1 H, *J*(PH) = 7.2, *J*(HH) = 6, PCH*H*], 2.46 [dq, 4 H, ^2J(PH) = 12.8, ^3J(HH) = 7.6, PCH_2], 1.90 [dq, 6 H, ^2J(PH) = 7.8, ^3J(HH) = 7.7, PCH_2], 1.33 [dt, 9 H, ^3J(PH) = 18.7, ^3J(HH) = 7.6, PCH_2CH_3] and 1.17 [dt, 9 H, ^3J(PH) = 14.0, ^3J(HH) = 7.8 Hz, PCH_2CH_3]; ^{31}P (broad-band decoupled), δ 38.29 (s). Mass spectrum (CI, isobutane carrier gas, ^{35}Cl): *m/z* 449 $[M - H]^+$, 313 $[M - PEt_3 - H_3O]^+$, 135 $[Et_3PO + H]^+$ and 119 $[Et_3P + H]^+$.

$[\{Nb(O)Cl_3(PMe_3)_2\}_n]$ **5**. Trimethylphosphine (0.34 g, 4.45 mmol) was condensed onto a frozen solution of $[Nb(O)Cl_3(thf)_2]$ (0.4 g, 1.11 mmol) in dichloromethane solvent at −196 °C. Upon warming to room temperature, argon (1 atm, 101 325 Pa) was admitted. The mixture was stirred for 12 h to afford a yellow-orange solution and a white solid. The solution was filtered from the solid residue which was washed with dichloromethane (2 × 5 cm^3) and dried *in vacuo*. Yield: 0.18 g (44%) (Found: C, 19.65; H, 4.45. $C_6H_{18}Cl_3NbOP_2$ requires C, 19.60; H, 4.95%). IR (Nujol, CsI): 1425m, 1309m, 1304s, 1227w, 1145w, 1037w, 981s, 964s, 923s, 882w, 844w, 776w, 738w, 650w and 318s (br) cm^{-1}. Mass spectrum (CI, isobutane carrier gas, ^{35}Cl): *m/z* 604 $[M_2 - PMe_3 - O - Cl - H]^+$, 590 $[M_2 - PMe_3 - O - Cl - CH_3]^+$, 575 $[M_2 - PMe_3 - O - Cl - 2CH_3]^+$, 561 $[M_2 - PMe_3 - O - Cl - 2CH_3 - CH_2]^+$, 549 $[M_2 - PMe_3 - O - Cl - 4CH_2]^+$, 535 $[M_2 - PMe_3 - O - Cl - 5CH_2]^+$, 521 $[M_2 - PMe_3 - O - Cl - 6CH_2]^+$, 507 $[M_2 - PMe_3 - O - Cl - 7CH_2]^+$, 369 $[M + 3H]^+$ and 77 $[Me_3P + H]^+$.

$[Nb(O)Cl_3(PMe_2Ph)_3]$ **6**. Dimethylphenylphosphine (1.12 g, 8.12 mmol) was added *via* syringe, to a stirred suspension of $[Nb(O)Cl_3]$ (0.5 g, 2.32 mmol) in dichloromethane (35 cm^3) at room temperature in a nitrogen-filled glove-box. An immediate reaction ensued leading to complete dissolution of the $[Nb(O)Cl_3]$ over a period of *ca.* 15 min to afford a yellow-orange solution. After stirring for 3 h, the solution was filtered and the volatiles removed under reduced pressure to give a slightly oily, yellow crystalline solid. This was washed with cold (−78 °C) light petroleum (*ca.* 8 cm^3) and dried *in vacuo*. Yield: 1.24 g (85%) (Found: C, 44.30; H, 5.00. $C_{24}H_{33}Cl_3NbOP_3$ requires C, 45.75; H, 5.30%). IR (Nujol, CsI): 3075w, 3045w, 1584w, 1571w, 1489m, 1439m, 1420m, 1407w, 1298m, 1283s, 1111m, 965m, 960s, 926s, 911s, 904m, 899m, 882m, 871s, 758m, 747s, 725m, 690s, 491s, 410m, 359w, 339s, 297s (br) and 250m cm^{-1}. ^{31}P NMR (250 MHz, [$^2H_1$]chloroform, 298 K, broad-band decoupled): δ −16.27 (br s, $\Delta_{\frac{1}{2}}$ = 500 Hz, PMe_2Ph]. Mass spectrum (CI, isobutane carrier gas, ^{35}Cl): *m/z* 215 $[Nb(OH)Cl_3]^+$ and 139 $[PhMe_2P + H]^+$.

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