

Niobium tetrahalide complexes with neutral diphosphine ligands

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Abstract

The reactions of NbCl₄ with diphosphine ligands *o*-C₆H₄(PMe₂)₂, Me₂PCH₂CH₂PMe₂ or Et₂PCH₂CH₂PEt₂ in a 1:2 molar ratio in MeCN solution produced eight-coordinate [NbCl₄(diphosphine)₂]. [NbBr₄(diphosphine)₂] (diphosphine = *o*-C₆H₄(PMe₂)₂ or Me₂PCH₂CH₂PMe₂) were made similarly from NbBr₄. X-ray crystal structures show that [NbCl₄{*o*-C₆H₄(PMe₂)₂}₂] has a dodecahedral geometry but the complexes with dimethylene backboned diphosphines are distorted square antiprisms. The Nb-P and <P-Nb-P angles are very similar in the two types, but Nb-Cl distances are ~ 0.1 Å longer in the square antiprismatic complexes. These paramagnetic (d¹) complexes were also characterised by microanalysis, magnetic measurements, IR and UV-visible spectroscopy. Using a 1:1 molar ratio of NbCl₄ : diphosphine (diphosphine = Me₂PCH₂CH₂PMe₂, Et₂PCH₂CH₂PEt₂, Cy₂PCH₂CH₂PCy₂ and Ph₂PCH₂CH₂CH₂PPh₂) afforded [NbCl₄(diphosphine)] and [NbBr₄(Me₂PCH₂CH₂PMe₂)] was obtained similarly. These 1 : 1 complexes are unstable in solution, preventing X-ray crystallographic study, but based upon their diamagnetism, IR, UV-visible and ³¹P{¹H} NMR spectra they are formulated as halide-bridged dimers [(diphosphine)_X2Nb(μ-X)₄NbX₂(diphosphine)] with single Nb-Nb bonds and chelating diphosphines. The Nb(IV) complexes are prone to hydrolysis and oxidation in solution and the structures of the Nb(V) complexes [NbBr₄(Me₂PCH₂CH₂PMe₂)₂][NbOBr₄(MeCN)] with a dodecahedral cation, and [{NbOC1₃{Et₂P(CH₂)₂PEt₂}₂}₂{μ-Et₂P(CH₂)₂PEt₂}] which contains seven-coordinate Nb(V) centres with a symmetrical diphosphine bridge are reported. The structure of niobium tetrabromide, conveniently made from NbCl₄ and BBr₃, is a chain polymer with edge-linked NbBr₆ octahedra and alternating long and short Nb-Nb distances, the latter ascribed to Nb—Nb bonds.

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Introduction

Phosphine complexes of niobium chlorides and bromides are known in oxidation states II-V, and with a wide range of stoichiometries and structures,¹⁻³ and we recently reported six- and eight-coordinate phosphine complexes with NbF₅.⁴ Whilst the complexes of niobium(V) chloride and bromide are mononuclear and based upon six- or eight-coordinate metal centres, those in lower oxidation states are more varied. For Nb(IV) with tertiary phosphines, there are well-characterised mononuclear examples with six- e.g. *trans*-[NbCl₄(PEtPh₂)₂],⁵ and seven- e.g. [NbCl₄(PMe₃)₃]⁶ and [NbBr₄(PMe₂Ph)₃]⁷ coordination. Dinuclear eight-coordinate complexes include the M–M bonded [Nb₂Cl₄(μ-Cl)₄(PMe₃)₄], which appears to dissociate into a six-coordinate monomer in solution.^{8,9} There is also spectroscopic evidence for the existence of an eight-coordinate [NbCl₄(PMe₃)₄] monomer in solution.⁶ As pointed out by Cotton,^{5,6,8} the speciation often differs between the solids and solutions in thf or CH₂Cl₂, and the solution speciation is only partially understood. EPR measurements on the solution species have also proved controversial.¹⁰ Surprisingly, for compounds of the corresponding 4d and 5d metals in the same oxidation state, there are significant differences between the Nb(IV) and Ta(IV) complexes.^{6,8,9,11} Even further complexity is caused by the production of mono- or di-nuclear M(III) complexes, under only slightly different experimental conditions,^{7,12,13} whilst air-oxidation to M(V) complexes readily occurs. We have recently been exploring the chemistry of Nb and Ta complexes in oxidation states III-V with thio- or seleno-ether ligands, and their possible use as single source precursors for NbS₂ or NbSe₂ films via low pressure or aerosol assisted chemical vapour deposition.^{14,15} The chemistry of Nb(IV) chloride with bidentate group 16 ligands has also proved to be complicated, and in order to obtain a better understanding of the latter, we explored some chemistry with diphosphine ligands, and describe our results below. Only a few complexes of types [NbCl₄(diphosphine)₂] or [NbCl₄(diphosphine)] have been described previously,^{16,17} and none have been structurally characterised. The structure of [TaCl₄(Me₂PCH₂CH₂PMe₂)₂]¹⁸ has been determined, but curiously the tantalum is coordinated in a square antiprismatic geometry, whilst the Nb(V) or Ta(V) complexes are dodecahedral.^{4,18} Several diarsine complexes of NbCl₄ have been briefly described,¹⁹⁻²¹ and the structure of [NbCl₄{*o*-C₆H₄(AsMe₂)₂}₂] (dodecahedral) determined.²²

Here we describe the preparations, structural and spectroscopic properties of a series of NbX₄ (X = Cl or Br) complexes incorporating neutral C₂-linked diphosphine ligands, illustrating the variability in both the stoichiometries present in this chemistry and the subtle dependence of the structures produced as a function of the diphosphine.

Experimental

Infrared spectra were recorded as Nujol mulls or thin films between CsI plates using a Perkin Elmer Spectrum 100 over the range 4000–200 cm⁻¹ and UV/visible spectra as powdered solids diluted with BaSO₄, using the diffuse reflectance attachments of a Jasco V-670 or Perkin Elmer 750S spectrometer. Magnetic measurements

were made on a Quantum Design MPMS XL7. ^1H NMR spectra were recorded from CD_2Cl_2 or CDCl_3 solutions using a Bruker AV II 400 spectrometer and are referenced to the residual protio-solvent resonance. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using a Bruker AV II 400 spectrometer and are referenced to external H_3PO_4 . Microanalyses were performed 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 Na/benzophenone ketyl (diethyl ether, toluene, n-hexane). NbCl_5 , NbBr_5 , Nb powder, BBr_3 (Aldrich) and the diphosphines, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$, *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)_2$, $(\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_{11})_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (Aldrich or Strem) were used as received, and *o*- $\text{C}_6\text{H}_4(\text{PMe}_2)_2$ was made by the literature route.²³

[NbCl_4]

NbCl_5 (540 mg, 2.0 mmol) and niobium powder (92 mg, 1.0 mmol) were loaded in a thick walled glass tube and the tube sealed *in vacuo*. The tube was placed in a furnace and heated to 350°C for 2 days. After cooling down, the tube was opened in a glove box and the crystals removed (small amounts of yellow NbCl_5 were found at the cooler end of the tube). The brown-black crystals were characterised by powder X-ray diffraction and IR spectra as NbCl_4 . Yield: 505 mg, 86%. IR (Nujol/ cm^{-1}): 429, 388, 356, 265 (Nb-Cl). Rietveld refinement of the PXRD pattern gave lattice parameters $a = 8.128(4)$ Å, $b = 6.838(4)$ Å, $c = 8.871(4)$ Å, $\beta = 91.73(2)^\circ$ ($R_{\text{wp}} = 6.97\%$, $R_{\text{p}} = 4.89\%$), which compare with literature values of $a = 8.140(5)$ Å, $b = 6.823(4)$ Å, $c = 8.852(6)$ Å, $\beta = 91.92(5)^\circ$.²⁴

[NbBr_4]

To BBr_3 (5 mL) was added finely powdered NbCl_4 (200 mg, 0.851 mmol), and the solution was refluxed under a slow stream of nitrogen for four days. After cooling down, a black solid precipitated from the solution. The supernatant liquid was removed by syringe, and the solid was dried *in vacuo* at 50°C , producing a dark red powder. Yield: 295 mg, 84%. IR (Nujol/ cm^{-1}): 309, 287, 214 (Nb-Br).

[$\text{NbCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$]

NbCl_4 (140 mg, 0.6 mmol) was added to refluxing CH_3CN (20 mL), and when the solid had mostly dissolved, the pale green solution was cooled and filtered. A solution of $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (270 mg, 1.8 mmol) in CH_3CN (*ca.* 1 mL) was added to the filtrate, when a light green powder formed immediately and then redissolved. The solution was stirred for 1 h, the solvent were reduced to *ca.* 5 mL *in vacuo* and the solid filtered off, and dried *in vacuo*, to give a yellow-green powder. Yield: 265 mg, 82%. Required for $\text{C}_{12}\text{H}_{32}\text{Cl}_4\text{NbP}_4$ (535.00): C, 26.94; H, 6.03. Found: C, 26.95; H, 5.89%. IR (Nujol/ cm^{-1}): 322(m), 290(s) (Nb-Cl). UV/vis / cm^{-1} : 33 670, 29 000(sh), 22 700, 15 150, 12 580, 11 430(sh), $\mu_{\text{B}} = 1.74$ B.M. Blue crystals formed in the filtrate from the reaction mixture over ~ 1 week at -18°C .

[$\text{NbCl}_4(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2$]

NbCl₄ (70 mg, 0.3 mmol) was dissolved in refluxing CH₃CN (15 mL), which was cooled and filtered, and treated with Et₂PCH₂CH₂PEt₂ (80 mg, 0.4 mmol) in CH₃CN (*ca.* 1 mL) when it became blue-green. After removal of half the solution for crystal growing, the rest of the solution was taken to dryness *in vacuo* and the solid obtained washed with diethyl ether (4 mL) leaving a grass-green powder. Yield: 64 mg, 49.5%. Required for C₂₀H₄₈Cl₄NbP₄ (647.20): C, 37.12; H, 7.48. Found: C, 37.43; H, 7.53%. IR (Nujol/cm⁻¹): 303(s), 280 (s) (Nb-Cl). UV/vis /cm⁻¹ 30 865, 22 950, 14 080, 11 615. Blue crystals grew from the second portion of the reaction mixture in a freezer over a few days.

[NbCl₄{*o*-C₆H₄(PMe₂)₂}]₂

was made similarly, as a green powder. Yield 44.5%. Required for C₂₀H₃₂Cl₄NbP₄ (631.08): C, 38.06; H, 5.11. Found: C, 38.21; H, 5.25%. IR (Nujol/cm⁻¹): 318 (sh) 307 (vs) (Nb-Cl). UV/vis /cm⁻¹): 29 410, 22 700(sh), 15 060, 11 560. Recrystallisation of a portion of the sample from CH₃CN/ diethyl ether gave a green powder and some blue crystals.

[NbBr₄(Me₂PCH₂CH₂PMe₂)₂]

NbBr₄ (82.5 mg, 0.2 mmol) was dissolved in refluxing CH₃CN (20 mL), the solution cooled, filtered, and to the yellow-orange filtrate a solution of Me₂PCH₂CH₂PMe₂ (90 mg, 0.6 mmol) in CH₃CN 1 mL) was added. After stirring for a half hour, the solution was evaporated to dryness, the powder rinsed with CH₃CN (5 mL), and the solid dried *in vacuo*. Yield: 40 mg, 28%. Required for C₁₂H₃₂Br₄NbP₄ (712.8): C, 20.22; H, 4.52. Found: C, 20.39; H, 4.41%. IR (Nujol/cm⁻¹): 245(sh), 231(s) (Nb-Br). UV/vis / cm⁻¹): 33 500, 26 650 (sh), 21 300, 16 950, 14 500, ~12 500. Some dark blue crystals were obtained by storing a CH₃CN solution of the complex in a fridge (5 °C).

[NbBr₄{*o*-C₆H₄(PMe₂)₂}]₂

NbBr₄ (57 mg, 0.14 mmol) was dissolved in CH₃CN (15 mL) and the mixture refluxed until most of the solid had dissolved. The solution was cooled, filtered and a solution of *o*-C₆H₄(PMe₂)₂ (82 mg, 0.41 mmol) and CH₃CN (*ca.* 1 mL) was added to the filtrate. After stirring for a 1/2 hour, the solution was taken to dryness *in vacuo*. The solid was dissolved in CH₃CN (10mL) and the solution filtered to remove some white solid. The green filtrate was stored in a freezer (-18 °C) for a week when light green powder precipitated, which was filtered off and dried *in vacuo*. Yield: 10 mg, 9%, Required for C₂₀H₃₂Br₄NbP₄ (808.9): C, 29.7; H, 3.99. Found: C, 29.69; H, 4.07%. UV/vis / cm⁻¹): 33 560, 27 780, 21 300(sh), 11 560.

[NbCl₄(Me₂PCH₂CH₂PMe₂)]

NbCl₄ (93 mg, 0.4 mmol) was dissolved in hot CH₃CN (20 mL). The pale green solution was filtered and a solution of Me₂PCH₂CH₂PMe₂ (64mg, 0.4 mmol) in CH₃CN (1 mL) was added resulting in formation of a light green powder. The solution was stirred for 5 mins, the solid filtered off and dried *in vacuo*, giving a blue green

powder. Yield: 69 mg, 45%. Required for $C_6H_{16}Cl_4NbP_2$ (384.86): C, 18.72; H, 4.19. Found: C, 18.82; H, 4.28%. 1H NMR (CD_3CN , 295 K): $\delta = 1.73$ (br s, [12H], CH_3), 2.23 (br, [4H], CH_2). $^{31}P\{^1H\}$ NMR (CD_3CN , 295 K): $\delta = 8.53$ ($\Delta = 55$). IR (Nujol/ cm^{-1}): 326(sh), 301 (br, s) 275(sh), 203 (Nb-Cl). UV/vis / cm^{-1}): 34 800, 22 200, 19 800(sh), 15 250, 11 620. $\mu =$ diamagnetic.

[NbCl₄(Et₂PCH₂CH₂PEt₂)]

was made similarly as a green powder. Yield: 26.5%. Required for $C_{10}H_{24}Cl_4NbP_2$ (440.96): C, 27.24; H, 5.49. Found: C, 27.35; H, 5.61%. 1H NMR (CD_3CN , 295 K): $\delta = 1.2$ (br s, [12H], CH_3), 2.2 (br, [12H], PCH_2CH_2P and CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN , 295 K): $\delta = 45.0$ ($\Delta = 64$). IR (Nujol/ cm^{-1}): 301(s), 275(s) (Nb-Cl). UV/vis (diffuse reflectance diluted with $BaSO_4/cm^{-1}$): 31 850, 22 940, 17 180, 13 990, 11 750.

[NbCl₄(Cy₂PCH₂CH₂PCy₂)]

was obtained similarly as a yellow-green powder by reaction of $NbCl_4$ and $Cy_2PCH_2CH_2PCy_2$ in a 1:2 mol ratio. Yield: 55%. Required for $C_{26}H_{44}Cl_4NbP_2$ (653.30): C, 47.80; H, 6.79. Found: C, 47.46; H, 6.58%. 1H NMR (CD_3CN , 295 K): $\delta = 1.35$ -1.83 (m, cyclohexyl), 2.32 (br, CH_2). $^{31}P\{^1H\}$ NMR (CD_3CN , 295 K): $\delta = 42.7$ ($\Delta = 43$). IR (Nujol/ cm^{-1}): 301(s), 294(sh), 206(s) (Nb-Cl). UV/vis / cm^{-1}): 32 050, 23 260 (sh), 14085, 11 750. $\mu =$ diamagnetic.

[NbCl₄{*o*-C₆H₄(PPh₂)₂}]

made similarly to $[NbCl_4(Me_2PCH_2CH_2PMe_2)]$ as a green powder. Yield: 65%. Required for $C_{30}H_{24}Cl_4NbP_2$ (681.18): C, 52.90; H, 3.55. Found: C, 53.03; H, 3.47%. 1H NMR (CD_3CN , 295K): $\delta = 7.1$ -7.7 (br m). $^{31}P\{^1H\}$ NMR (CD_3CN , 295 K): $\delta = +1.8$ ($\Delta = 15$). IR (Nujol/ cm^{-1}): 324 (br) (Nb-Cl). UV/vis / cm^{-1}): 30 300, 25 000, 16 660, 11 700. $\mu =$ diamagnetic.

[NbBr₄(Me₂PCH₂CH₂PMe₂)]

$NbBr_4$ (62 mg, 0.15 mmol) was dissolved in hot CH_3CN (15 mL) and the solution filtered. The yellow-orange filtrate was treated with $Me_2PCH_2CH_2PMe_2$ (13 mg, 0.09 mmol) in CH_3CN (*ca.* 2 mL), when a dark green powder formed immediately. After stirring for 30 min., the solvent was removed *in vacuo*, and the green solid was washed by 3 mL CH_3CN , filtered and dried *in vacuo*. Yield: 28 mg, 57%. Required for $C_6H_{16}Br_4NbP_2$ (562.66): C, 12.81; H, 2.87. Found: C, 12.68; H, 2.85%. 1H NMR (CD_3CN , 295 K): $\delta = 1.97$ (br, [12H], CH_3), 2.73 (br, [4H], CH_2). $^{31}P\{^1H\}$ NMR (CD_3CN , 295 K): $\delta = 8.7$ ($\Delta = 56$). IR (Nujol/ cm^{-1}): 230 (s). UV/vis / cm^{-1}): 29 400, 14 240, 11 550.

[NbCl₄(Ph₂PCH₂CH₂CH₂PPh₂)]

$NbCl_4$ (70 mg, 0.3 mmol) was dissolved in CH_3CN (15 mL). The solution was refluxed until all solid had dissolved. The green solution was filtered and added into a solution of $Ph_2PCH_2CH_2CH_2PPh_2$ (124 mg, 0.3 mmol) in CH_2Cl_2 (10 mL) with stirring 20 min.. The solution changed colour from green to yellow green without

any precipitation. The solution was evaporated in *vacuo* leaving yellow green and white solids. The solid was washed with CH₂Cl₂ (2 mL), filtered off and dried in *vacuo*. Yield: 16 mg, 8.2%. Required for C₂₇H₂₆Cl₄NbP₂ (647.16): C, 50.11; H, 4.05%. Found: C, 50.26; H, 3.92%. IR (Nujol/cm⁻¹): 318, 205 (Nb-Cl). UV/vis / cm⁻¹): 33 900, 31 750(sh), 23 360, 14 300, 11 760.

X-Ray Experimental

Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum ($\lambda = 0.71073$) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2013 or SHELX-2014/7 and were straightforward^{25,26} except for some disorder. In [NbCl₄(Et₂PCH₂CH₂PEt₂)₂], the Et groups showed disorder which was modelled satisfactorily using split atom occupancies. H atoms were placed in calculated positions. Details of the crystallographic parameters are given in Table 1.

Powder X-ray diffraction (PXD) data were collected using a Bruker D2 diffractometer (Cu-K α) and a sealed aluminium sample holder with a hemicylindrical Kapton window. Phase matching and Rietveld refinement used the GSAS package.^[27] The sealed sample holder has no beam knife and an artefact is always observed at 50° 2 θ when it is used, hence a small excluded region was introduced to remove this artefact.

Results and Discussion

Niobium(IV) chloride has been prepared by reduction of NbCl₅ with H₂ or a variety of metals including Nb, Al and Zn.^{24,28} We found that reduction of NbCl₅ with Nb powder in a sealed tube at 350 °C gave, after removal of any residual NbCl₅, a good yield of brown-black needle crystals of NbCl₄.^{24,29} These were identified as NbCl₄ via PXRD (see Supplementary Information). In contrast, repeated attempts to produce NbBr₄ by a similar method from NbBr₅ and Nb powder over a temperature range of 300–600°C, failed to give useful quantities of NbBr₄, the products containing substantial amounts of Nb₃Br₈, NbOBr₂ and NbBr₅. This probably reflects inadequate temperature control, since both reduction of the NbBr₅ and disproportionation of NbBr₄ occur over a small temperature range^[28] However, NbCl₄ was easily and cleanly converted into NbBr₄ by refluxing with excess BBr₃, a route described by Druce and Lappert³⁰ for many other bromides (although not previously used to obtain NbBr₄). The PXD pattern of NbBr₄ was noted to be very similar to the literature pattern for NbCl₄,^{24,31} except that the peaks were shifted to lower 2 θ positions, consistent with the larger anions. Rietveld refinement produced a good fit to this structure (Fig. 1) with $a = 8.6119(6)$, $b = 7.1821(5)$ and $c = 9.3626(8)$ Å and $\beta = 92.212(5)^\circ$.

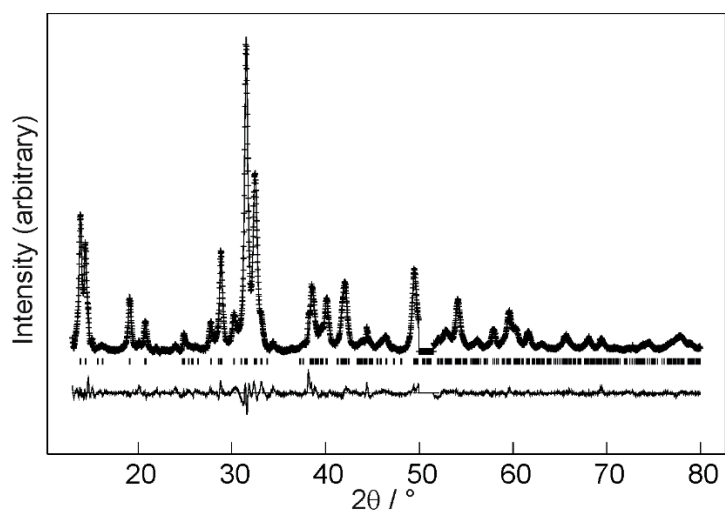


Figure 1 Fit to the PXD data for NbBr_4 ($R_{\text{wp}} = 3.7\%$, $R_p = 2.7\%$). Crosses mark the data points, the upper continuous line the fit, the lower continuous line the difference and tick marks the positions of allowed reflections in $I2/m$. Atom positions: Nb 0, 0.2168(7), 0; Br1 0.0399(7), 0, 0.2175(7); Br2 -0.2795(3), 0.2649(7), 0.0269(3); Br3 0.0261(7), $\frac{1}{2}$, 0.1951(6).

The structure of niobium bromide consists of chains of edge-linked NbBr_6 octahedra (Figure 2). As previously observed in NbCl_4 these chains contain alternating long (4.0686(3) Å) and short (3.113(10) Å) Nb-Nb distances, with the latter ascribed to metal-metal bonding between the $d^1 \text{Nb}^{4+}$ centres.²⁴ In NbCl_4 the metal-metal bond distance is 3.029 (2) Å.

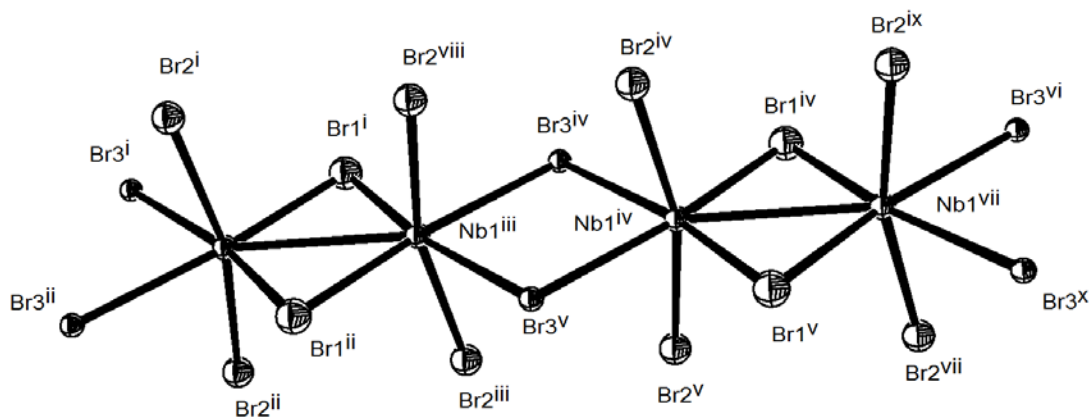
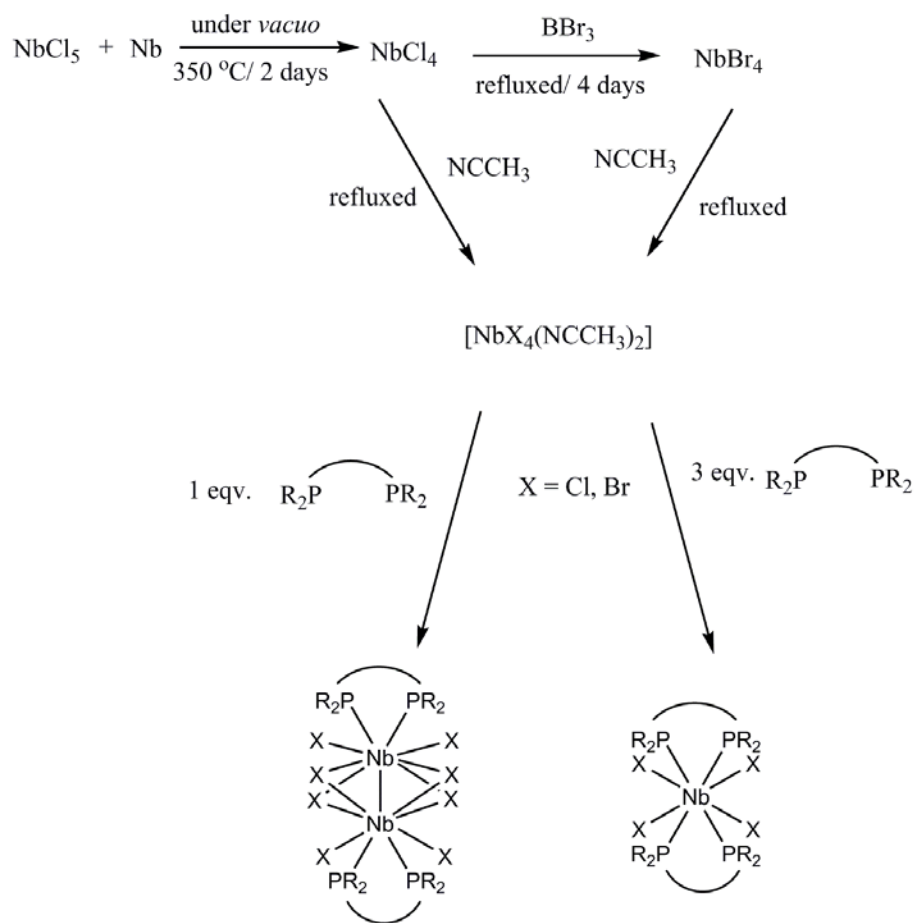


Figure 2 View of the structure of NbBr_4 refined from the powder X-ray diffraction data. Selected bond lengths (Å) and angles ($^\circ$): Nb-Br1 = 2.575(5), Nb-Br2 = 2.454(2), Nb-Br3 = 2.738(6), Nb-Nb^v = 3.113(10), Br1-Nb-Br1ⁱⁱⁱ = 105.6(3), Br1-Nb-Br2 = 96.04(14), Br1-Nb-Br2ⁱⁱⁱ = 93.73(15), Br1-Nb-Br3 = 85.21(8), Br1-Nb-Br3ⁱⁱⁱ = 169.0(2), Br2-Nb-Br2ⁱⁱⁱ = 163.81(19), Br2-Nb-Br3 = 83.24(14), Br2-Nb-Br3 = 84.74(15), Br3-Nb-Br3ⁱⁱⁱ = 84.0(2), Nb-Br1-Nb^v = 74.4(3), Nb-Br3-Nbⁱ = 96.0(2) : I = -x, 1-y, -z; iii = -x, y, -z; v = -x, -y, -z.

[NbX₄(diphosphine)₂]: The reaction of an NbCl₄ solution in anhydrous CH₃CN with 3 mol. equivalents of the diphosphines, Me₂PCH₂CH₂PMe₂, Et₂PCH₂CH₂PEt₂ or *o*-C₆H₄(PMe₂)₂ gave [NbCl₄(diphosphine)₂] as green powders in good yield (Scheme 1).



Scheme 1

The dry powdered samples are reasonably stable in air, but oxidise in MeCN or CH₂Cl₂ solutions exposed to air. Poor yields of [NbBr₄(diphosphine)₂] (diphosphine = Me₂PCH₂CH₂PMe₂ or *o*-C₆H₄(PMe₂)₂) were obtained similarly from NbBr₄. Green or blue-green X-ray quality crystals of four complexes were obtained as described in the Experimental section. As shown in Figures 3 and 4, all contain discrete neutral molecules with eight-coordinate niobium.

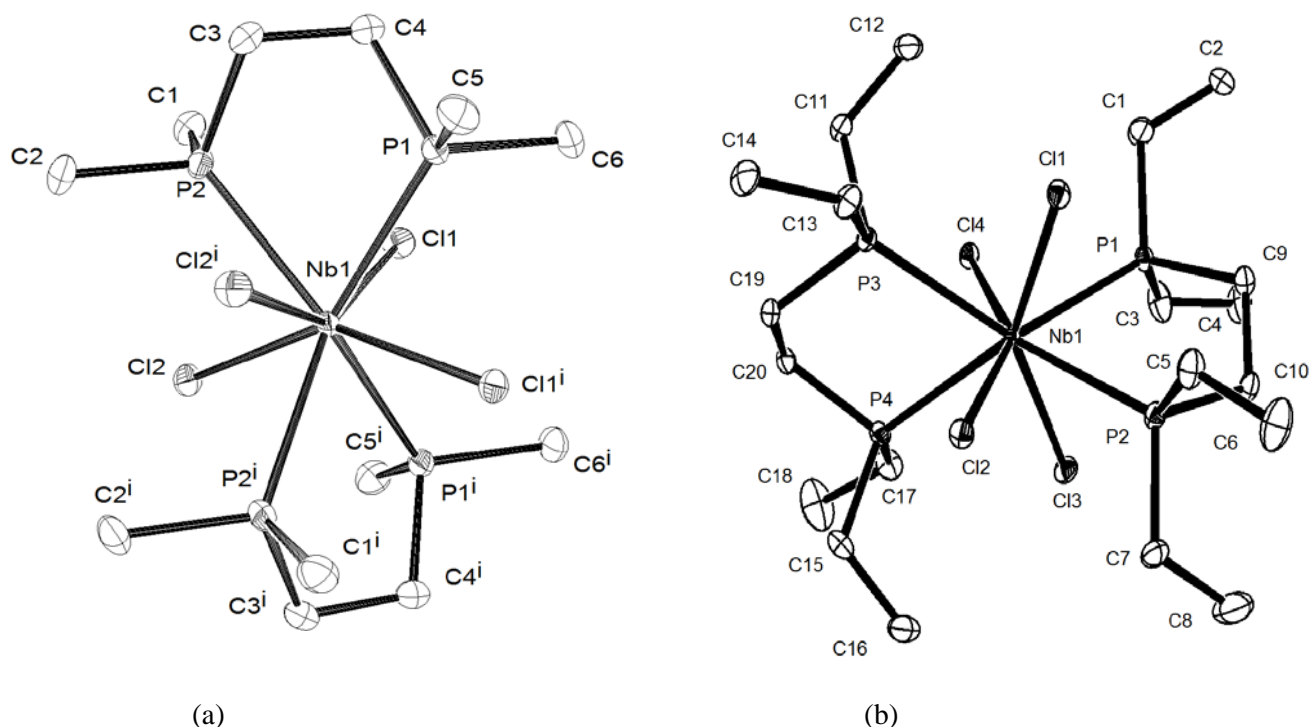


Figure 3 (a) The structure of $[\text{NbCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Nb1}-\text{Cl1} = 2.5224(8)$, $\text{Nb1}-\text{Cl2} = 2.5195(8)$, $\text{Nb1}-\text{P1} = 2.6553(8)$, $\text{Nb1}-\text{P2} = 2.6581(8)$, $\text{P1}-\text{Nb1}-\text{P2} = 73.81(3)$, $\text{Cl2}-\text{Nb1}-\text{Cl2}^i = 104.89(4)$, $\text{Cl2}-\text{Nb1}-\text{Cl1} = 85.59(3)$, $\text{Cl2}-\text{Nb1}-\text{Cl1}^i = 144.86(2)$, $\text{Cl1}-\text{Nb1}-\text{Cl1}^i = 105.15(4)$; symmetry operators: $i = -x, 2-y, z$. (b) The structure of $[\text{NbCl}_4(\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2)_2]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms and a disordered CH_3 are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Nb1}-\text{Cl2} = 2.5228(7)$, $\text{Nb1}-\text{Cl1} = 2.5235(7)$, $\text{Nb1}-\text{Cl4} = 2.5240(7)$, $\text{Nb1}-\text{Cl3} = 2.5273(7)$, $\text{Nb1}-\text{P2} = 2.6785(8)$, $\text{Nb1}-\text{P1} = 2.6818(7)$, $\text{Nb1}-\text{P4} = 2.7111(7)$, $\text{Nb1}-\text{P3} = 2.7157(7)$, $\text{P2}-\text{Nb1}-\text{P1} = 73.41(2)$, $\text{P4}-\text{Nb1}-\text{P3} = 72.95(2)$, $\text{Cl2}-\text{Nb1}-\text{Cl1} = 87.85(2)$, $\text{Cl2}-\text{Nb1}-\text{Cl4} = 146.19(2)$, $\text{Cl1}-\text{Nb1}-\text{Cl4} = 102.83(2)$, $\text{Cl2}-\text{Nb1}-\text{Cl3} = 100.59(2)$, $\text{Cl1}-\text{Nb1}-\text{Cl3} = 143.79(2)$, $\text{Cl4}-\text{Nb1}-\text{Cl3} = 89.57(2)$.

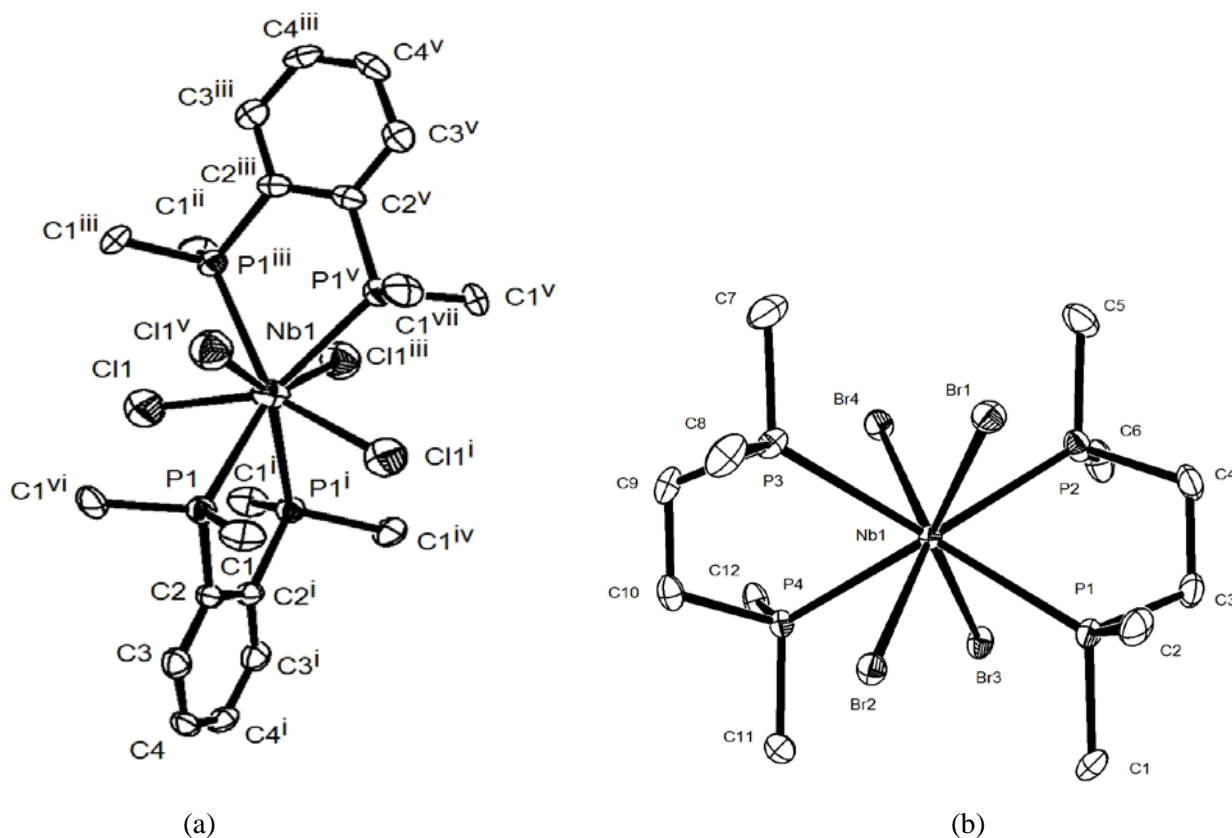


Figure 4 (a) The structure of $[\text{NbCl}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Nb1-Cl1} = 2.441(3)$, $\text{Nb1-P1} = 2.703(2)$, $\text{P1-Nb1-P1}^i = 71.89(10)$, $\text{Cl1-Nb1-Cl1}^i = 145.97(13)$, $\text{Cl1-Nb1-Cl1}^{iii} = 94.91(4)$, Symmetry operation: $i = -1+y, 1+x, z$; $ii = -1+y, 1-x, 2-z$; $iii = -x, 2-y, z$; $v = 1-y, 1+x, 2-z$; $vi = -x, y, 2-z$. (b) The structure of $[\text{NbBr}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Nb1-Br3} = 2.6883(7)$, $\text{Nb1-P2} = 2.6912(16)$, $\text{Nb1-Br4} = 2.6916(7)$, $\text{Nb1-P4} = 2.6929(15)$, $\text{Nb1-P3} = 2.6970(15)$, $\text{Nb1-Br1} = 2.6975(7)$, $\text{Nb1-P1} = 2.7062(15)$, $\text{Nb1-Br2} = 2.7116(7)$, $\text{P2-Nb1-P1} = 72.89(4)$, $\text{P4-Nb1-P3} = 72.30(4)$, $\text{Br3-Nb1-Br4} = 85.56(2)$, $\text{Br4-Nb1-Br1} = 104.80(2)$, $\text{Br3-Nb1-Br2} = 103.28(2)$, $\text{Br4-Nb1-Br2} = 146.55(2)$, $\text{Br1-Nb1-Br2} = 85.40(2)$.

The $[\text{NbCl}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$ contains a distorted dodecahedral (D_{2d}) geometry at the niobium, similar to the Nb(V) analogues, $[\text{NbX}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]^+$,⁴ and $[\text{NbCl}_4\{\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^+$.²² In contrast, the complexes of the diphosphines with a dimethylene backbone are distorted square antiprisms (D_2), as is $[\text{TaCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$.¹⁸ Since $[\text{TaCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]^+$ was dodecahedral, Cotton *et al.*¹⁸ tentatively suggested that the different structures might be due to some π -bonding with the phosphine in the Ta(IV) (d^1) complex, slightly favouring the D_2 geometry. However, the observation that $[\text{NbCl}_4\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$ is dodecahedral, shows that this cannot be the only factor, and indeed π -bonding from a high oxidation state early d-block metal with one d-electron seems likely to be minimal. Comparison of the geometric

data in the four $[\text{NbX}_4(\text{diphosphine})_2]$, shows the Nb–P distances are slightly shorter for a common diphosphine for X = Cl over X = Br, but not significantly different for a fixed halide. In contrast the Nb–Cl distances are $\sim 0.1\text{\AA}$ longer in the square antiprismatic complexes compared to the dodecahedron. The chelate angle $\angle\text{P–Nb–P}$ is very slightly smaller (71.8°) for the rigid aromatic backboned ligand, compared to the dimethylene linked cases ($72.3 - 73.8^\circ$), but whether this is a sufficient difference to account for the change in geometry seems unlikely. Examination of the literature,³² shows that all eight-coordinate d-block halides with *o*-phenylene backboned diphosphines or diarsines (L–L) are dodecahedral, in addition to the Nb or Ta complexes already discussed. These are $[\text{ZrX}_4(\text{L–L})_2]$,³³ $[\text{HfX}_4(\text{L–L})_2]$,³³ $[\text{TiX}_4(\text{L–L})_2]$,³⁴ $[\text{VCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]$,³⁵ $[\text{TaCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]$,³⁶ $[\text{MoCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^+$,³⁷ $[\text{TaBr}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^+$ ³⁸ and $[\text{TcCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^+$.³⁹ Fewer X-ray structures have been reported for $[\text{MX}_4(\text{L}'\text{–L}')_2]$ where L'–L' is a dimethylene backboned diphosphine. The $[\text{TiCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$,⁴⁰ is distorted square antiprismatic, but $[\text{WCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]^+$ ⁴¹ and $[\text{UCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ ⁴² are described as dodecahedral, albeit highly distorted in the uranium case. Thus for these eight-coordinate complexes, in all cases those with *o*-phenylene backboned ligands are dodecahedral, whilst for dimethylene backbones the pattern is unclear. All complexes show varying degrees of distortion from the regular polyhedra which are unavoidable given the short chelate bites of the diphosphines. No clear explanation emerges from consideration of this data and it seems probable that the energy differences between the two polyhedral are very small, and the shape adopted in practice may be the result of several small factors which are not easy to identify.^{18,43}

The far IR spectra of the chloro-complexes show strong $\nu(\text{Nb–Cl})$ bands in the regions $320\text{--}290\text{ cm}^{-1}$ very similar to those of the zirconium analogues,³³ but do not seem to distinguish the two geometries (theory $D_{2d} b_2 + e, D_2 b_{1+} b_2 + b_3$). In the solid state (diffuse reflectance) UV-visible spectra (Experimental Section), for the chloro-complexes, there are intense bands at $\sim 23\ 000$ and $\sim 30\ 000\text{ cm}^{-1}$ which may be assigned at $\text{P}(\sigma) \rightarrow \text{Nb}$ and $\text{Cl}(\pi) \rightarrow \text{Nb}$, which are consistent with charge transfer energies in the Nb(V) analogues,⁴ and with the six-coordinate $[\text{NbCl}_6]^{2-}$.⁴⁴ The higher energy regions of the spectra of the bromides are less clearly resolved, but similar. There are two or three weaker overlapping bands in the range $10\ 000\text{--}16\ 000\text{ cm}^{-1}$ which may be assigned as d-d transitions, and which agree well with the data reported for several niobium(IV)–diarsine complexes by Kepert.^{19,20} Solution spectra in CH_2Cl_2 were also recorded, but changed quite rapidly over time and the solutions changed colour from green to orange, indicative of decomposition, and thus the solution data are not presented. The complexes are paramagnetic, e.g. $[\text{NbCl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ has $\mu_B = 1.74\text{ B. M.}$ at 295K , as expected for a d^1 system.^{19,20,22}

$[\text{Nb}_2\text{X}_8(\text{diphosphine})_2]$: The reaction of NbCl_4 with the diphosphines $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$, $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2$, *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)_2$ and $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ in a 1:1 molar ratio in anhydrous CH_3CN gave green or yellow-green powders, which had the composition $[\text{NbCl}_4(\text{diphosphine})]$ by microanalysis. The complex $[\text{NbBr}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]$ was obtained similarly, but attempts to isolate 1:1 complexes with *o*- $\text{C}_6\text{H}_4(\text{PMe}_2)_2$ failed, only mixtures containing substantial amounts of the 2:1 complexes described above were formed.

Conversely $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2$, $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ and $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ gave only the 1:1 complex even with excess diphosphine: the formation of eight-coordinate 2:1 complexes by these ligands is presumably precluded by their large steric demands. The behaviour is reminiscent of that of ZrCl_4 or HfCl_4 with these ligands.³³ The $[\text{NbCl}_4(\text{diphosphine})]$ complexes are unstable in solution in CH_3CN or CH_2Cl_2 and repeated attempts to obtain crystals to establish their structures have been unsuccessful. However a probable structure can be inferred from the spectroscopic and magnetic data, and by analogy with the structurally characterised $[\text{Nb}_2\text{Cl}_4(\mu\text{-Cl})_4(\text{PR}_3)_4]$ ($\text{R}_3 = \text{Me}_3$ or Me_2Ph).^{5,8,9} The latter complexes have eight coordinate niobium centres with square antiprismatic geometries, sharing a common square face of four chloride ligands and with a single Nb–Nb bond. The $[\text{NbCl}_4(\text{diphosphine})]$ complexes are diamagnetic in the solid state inconsistent with a mononuclear d^1 system, but consistent with a single σ^2 Nb–Nb bond, and hence are formulated $[\text{Nb}_2\text{Cl}_4(\mu\text{-Cl})_4(\text{diphosphine})_2]$. Support for this comes from the observation of terminal $\nu(\text{Nb}\text{-Cl})$ frequencies at similar energies to those found in $[\text{NbCl}_4(\text{diphosphine})_2]$ (above), whereas by analogy with the zirconium systems a six-coordinate complex would be expected to exhibit $\nu(\text{Nb}\text{-Cl}) \sim 30 \text{ cm}^{-1}$ to higher frequency.³³ Several of the complexes show bands $\sim 200\text{-}210 \text{ cm}^{-1}$ which are tentatively assigned to the chloride bridge unit. Finally, although the complexes are unstable in CD_3CN solution, ^1H NMR spectra can be obtained from such solutions if run immediately on preparation. They show spectra typical of the coordinated diphosphine on a diamagnetic metal centre, with a single phosphorus environment in each. More informatively the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show single phosphorus resonances with large high frequency coordination shifts Δ , (Experimental section), which indicate the presence of five-membered chelate rings.⁴⁵ The $[\text{NbCl}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]$ decomposed rapidly in solution and the only $^{31}\text{P}\{^1\text{H}\}$ NMR resonance observed was that of the free diphosphine. Taken together the physical and spectroscopic data point to a structure such as [Figure 5], closely analogous to the tertiary phosphine complexes.^{5,8,9}

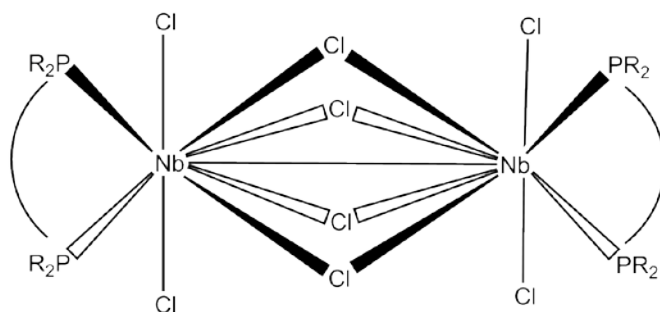


Figure 5 Proposed structure of the $[\text{Nb}_2\text{Cl}_4(\mu\text{-Cl})_4(\text{diphosphine})_2]$ complexes.

The large coordination shifts seem to rule out bridging diphosphines (across the Nb–Nb bond), and the form of the NMR spectra is confirmation of diamagnetism of the freshly prepared solutions. Over time the solutions change colour and the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR resonances are lost.

Niobium(V) Products: As we pointed out above, the Nb(IV) diphosphine complexes, are for a 4d metal, surprisingly prone to rearrangement or decomposition in solution; similar comments about the Nb(IV)-PR₃ complexes were made by Cotton and co-workers.^{5,6,8,9} During the course of our studies we obtained crystal structures of several by-products or products of adventitious hydrolysis/oxidation. These included [NbCl₄{*o*-C₆H₄(PMe₂)₂}]₂[NbOCl₄(MeCN)] which we previously made directly from NbCl₅, O(SiMe₃)₂ and *o*-C₆H₄(PMe₂)₂ in CH₃CN.⁴ The new bromide analogue [NbBr₄(Me₂PCH₂CH₂PMe₂)₂][NbOBr₄(MeCN)] was formed from a solution of [Nb₂Br₈(Me₂PCH₂CH₂PMe₂)₂] in CH₃CN which initially gave blue crystals of [NbBr₄(Me₂PCH₂CH₂PMe₂)₂]. After these had been removed the filtrate deposited dark red crystals of [NbBr₄(Me₂PCH₂CH₂PMe₂)₂][NbOBr₄(MeCN)] over several days. The complex which contains a dodecahedral cation and an octahedral anion with CH₃CN *trans* O is presented as Supplementary Information. Crystals of colourless [{NbOCl₃{Et₂P(CH₂)₂PEt₂}}₂{μ-Et₂P(CH₂)₂PEt₂}] formed on attempted recrystallisation of [Nb₂Cl₈(Et₂P(CH₂)₂PEt₂)₂] from diethyl ether. It is a close analogue of [{NbOCl₃{Me₂P(CH₂)₂PMe₂}}₂(μ-Me₂P(CH₂)₂PMe₂)]⁴ and spectroscopically very similar. The structure contains seven-coordinate niobium centres, each coordinated to one chelating diphosphine and symmetrically linked by a bridging diphosphine (see ESI).

Conclusions

A convenient new route to NbBr₄ via halide exchange from NbCl₄ and BBr₃ has been developed and the structure of the bromide established by Reitveld refinement of the PXRD data. Eight-coordinate [NbX₄(diphosphine)₂] complexes with both halides have been made and fully characterised, and shown to have either a dodecahedral (D_{2d}) or square antiprismatic (D₂) geometry, although the factors determining which is found in particular cases remain unclear. Unstable 1: 1 complexes have been made and although not supported by X-ray crystallographic data, the structures are also believed to be based upon eight coordination. As noted for the tertiary phosphine analogues,^{5,6,8,9} these complexes are surprisingly reactive for early 4d transition metal complexes, readily undergoing rearrangements and oxidation/hydrolysis in solution.

Acknowledgements

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Supplementary Data

Crystallographic data in cif format have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and given numbers 1453473-1453478, 1453489. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366033, e-mail: deposit@ccdc.cam.ac.uk or on the web at <http://www.ccdc.cam.ac.uk>.

ESI for this paper also contains the PXRD data on NbCl₄ and the refinement, and the X-ray crystallographic data for the Nb(V) byproducts [NbBr₄(Me₂PCH₂CH₂PMe₂)₂][NbOBr₄(NCMe)] and [{NbOC1₃{Et₂P(CH₂)₂PEt₂}₂}{μ-Et₂P(CH₂)₂PEt₂}₂].

Table 1: X-ray crystallographic parameters^a

Compound	[NbCl ₄ (Me ₂ PCH ₂ CH ₂ PMe ₂) ₂]	[NbCl ₄ (Et ₂ PCH ₂ CH ₂ PEt ₂) ₂]	[NbCl ₄ { <i>o</i> -C ₆ H ₄ (PMe ₂) ₂ } ₂]
Formula	C ₁₂ H ₃₂ Cl ₄ NbP ₄	C ₂₀ H ₄₈ Cl ₄ NbP ₄	C ₂₀ H ₃₂ Cl ₄ NbP ₄
Formula weight	534.96	647.17	631.04
Crystal system	Orthorhombic	Monoclinic	Tetragonal
Space group	P2 ₁ 2 ₁ 2	P2 ₁	I-42m
a/ Å	10.7216(9)	10.5571(5)	8.9852(6)
b/ Å	11.289(1)	11.6652(5)	8.9852(6)
c/ Å	9.4711(9)	11.9053(8)	16.140(1)
α/deg	90	90	90
β/ deg	90	95.008(7)	90
γ/ deg	90	90	90
U/ Å ³	1146.3(1)	1460.5(1)	1304.4(2)
Z	2	2	2
μ(Mo-Kα)/mm ⁻¹	1.263	1.005	1.124
F(000)	546	674	642
Total no. refl.	9661	12265	2204
Unique refl.	2248	4819	754
R _{int}	0.0364	0.0190	0.0346
No. of parameters, restraints	100, 0	280, 1	43, 2
R ₁ ^b [I _o >2σ(I _o)]	0.0209	0.0166	0.0477
R ₁ (all data)	0.0223	0.0170	0.0523
wR ₂ ^b [I _o >2σ(I _o)]	0.0453	0.0402	0.1111
wR ₂ (all data)	0.0457	0.0404	0.1149

Compound	[NbBr ₄ (Me ₂ PCH ₂ CH ₂ PMe ₂) ₂]
Formula	C ₁₂ H ₃₂ Br ₄ NbP ₄
Formula weight	712.80
Crystal system	Orthorhombic
Space group	Pca2 ₁
a/ Å	13.3974(9)
b/ Å	12.4285(9)
c/ Å	14.1808(10)
α/deg	90
β/ deg	90
γ/ deg	90
U/ Å ³	2361.2(3)
Z	4
μ(Mo-Kα)/mm ⁻¹	7.543
F(000)	1380
Total no. reflections	18564
Unique reflections	4641
R _{int}	0.0426
No. of parameters, restraints	199, 1
R ₁ ^b [I _o >2σ(I _o)]	0.0221
R ₁ (all data)	0.0250
wR ₂ ^b [I _o >2σ(I _o)]	0.0424
wR ₂ (all data)	0.0435

^a Common items: temperature = 100 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max)= 27.5°.

^b R₁ = Σ||F_o|-|F_c||/Σ|F_o|; wR₂=[Σw(F_o²-F_c²)²/ΣwF_o⁴]^{1/2}

References

- [1] L. G. Hubert-Pfalzgraf, M. Postel and J. G. Riess in G. Wilkinson, R. D. Gillard, J. A. McCleverty (Eds), *Comprehensive Coordination Chemistry*, Pergamon, Oxford, 1987, **3**, 586-697.
- [2] T. Waters, A. G. Wedd, M. Ziolek and I. Nowak, in J. A. McCleverty, T. J. Meyer (Eds) *Comprehensive Coordination Chemistry II*, Elsevier, Oxford 2004, **4**, 241-312.
- [3] W. Levason in F.R. Hartley (Ed), *The Chemistry of Organophosphorus Compounds*, Wiley NY, 1990, **1**, 568-641.
- [4] (a) W. Levason, M. E. Light, G. Reid and W. Zhang, *Dalton Trans.*, 2014, **43**, 9557-9566; (b) W. Levason, G. Reid and W. Zhang, *J. Fluor. Chem.*, 2015, **172**, 62-67.
- [5] F. A. Cotton, S. A. Duraj and W. J. Roth, *Inorg. Chem.*, 1984, **23**, 3592-3596.
- [6] F. A. Cotton, M. P. Diebold and W. J. Roth, *Polyhedron*, 1985, **4**, 1103-1108.
- [7] F. A. Cotton, M. P. Diebold and W. J. Roth, *Inorg. Chim. Acta*, 1985, **105**, 41-49.
- [8] F. A. Cotton and W. J. Roth, *Inorg. Chem.*, 1984, **23**, 945-947.
- [9] P. D. W. Boyd, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc., Dalton Trans.*, 1987, 307-314.
- [10] F. A. Cotton, M. B. Hall and M. A. Pietsch, *Inorg. Chem.*, 1994, **33**, 1473-1475, and refs therein.
- [11] F. A. Cotton, S. A. Duraj and, W. J. Roth, *Inorg. Chem.*, 1984, **23**, 4046-4050.
- [12] F. A. Cotton and W. J. Roth, *Inorg. Chem.*, 1983, **22**, 3654-3656.
- [13] S. M. Rocklage, H. W. Turner, J. D. Fellman and R.R. Schrock, *Organometallics*, 1982, **1**, 703-707.
- [14] S. L. Benjamin, Y-P. Chang, C. Gurnani, A. L. Hector, M. Huggon, W. Levason and G. Reid, *Dalton Trans.*, 2014, **43**, 16640-16648.
- [15] S. L. Benjamin, Y-P. Chang, M. Huggon, W. Levason and G. Reid, *Polyhedron*, 2015, **99**, 230-237.
- [16] L. E. Manzer, *Inorg. Chem.*, 1977, **16**, 523-528.
- [17] S. Sharma, S. Gupta, A. K. Narula, O.P. Vermani and P, N, Kapoor, *Ind. J. Chem.*, 1995, **30A**, 66-69
- [18] F. A. Cotton, L. R. Falvello and R. C. Najjar, *Inorg. Chem.*, 1983, **22**, 770-774.
- [19] D. L. Kepert and K. R. Trigwell, *J. Chem. Soc., Dalton Trans.*, 1975, 1903-1905.
- [20] R. L. Deutscher and D. L. Kepert, *Inorg. Chem.*, 1970, **9**, 2305-2310.

- [21] R. J. H. Clark, D. L. Kepert, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2865-2871.
- [22] D. L. Kepert, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 652-657.
- [23] E. P. Kyba, S. T. Liu and R. L. Harris, *Organometallics*, 1983, **2**, 1877
- [24] D. R. Taylor, J. C. Calabrese and E. M. Larsen, *Inorg. Chem.* 1977, 16, 721-722.
- [25] G. M. Sheldrick, *Acta Cryst. Sect. C*, 2015, **71**, 3-8.
- [26] X CrystalClear-SM Expert 3.1 b27, Rigaku Corporation, Tokyo, Japan, 2012; CrystalClear-SM Expert 2.1 b29, Rigaku Corporation, Tokyo, Japan, 2013; CrysAlis PRO. Agilent Technologies Ltd. Yarnton, Oxfordshire, England.
- [27] A. C. Larson and R. B. Von Dreele, Generalized Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR (2004) 86-748; B. H. Toby, *J. Appl. Cryst.*, 2001, **34**, 210-213.
- [28] J. H. Canterford and R. Colton, *Halides of the second and third row transition metals*, Wiley, NY, 1968.
- [29] R. E. McCarley and B. A. Torp, *Inorg. Chem.*, 1963, **2**, 540-546.
- [30] P. M. Druce and, M. F. Lappert, *J. Chem. Soc. Dalton Trans.*, 1971, 3595-3599.
- [31] *Inorganic Crystal Structure Database* (Fiz Karlsruhe) accessed via the *National Chemical Database Service* hosted by the Royal Society of Chemistry.
- [32] Cambridge Crystallographic Data Base accessed February 1 2016.
- [33] W. Levason, M. L. Matthews, B. Patel, G. Reid and M. Webster, *Dalton Trans.*, 2004, 3305-3312.
- [34] R. Hart, W. Levason, B. Patel and G. Reid, *Eur. J. Chem.*, 2001, 2927-2933.
- [35] B. M. Gray, A. L. Hector, W. Levason, G. Reid, M. Webster, W. Zhang and M. Jura, *Polyhedron*, 2010, **29**, 1630-1638.
- [36] J. C. Dewan, D. L. Kepert, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 2031-2038.
- [37] M. G. B. Drew, G. M. Egginton and J. D. Wilkins, *Acta Crystallogr. Sect. B*, 1974, **30**, 1895-1900.
- [38] M. G. B. Drew, A. P. Wolters and J. D. Wilkins, *Acta Crystallogr. Sect. B*, 1975, **31**, 324-326.
- [39] K. A. Glavan, R. Whittle, J. F. Johnson, R. C. Elder and E. Deutsch, *J. Amer. Chem. Soc.*, 1980, **102**, 2103-2104.
- [40] V. Saboonchian, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1991, **10**, 595-603.

- [41] F. A. Cotton, J. H. Matonic, C. A. Murillo and M. A. Petrukhina, *Inorg. Chim. Acta*, 1998, **267**, 173-176.
- [42] B. S. Newell, T. C. Schwaab and M. P. Shores, *Inorg. Chem.*, 2011, **50**, 12108-12115.
- [43] G. W. A. Fowles, D. J. Tidmarsh and R. A. Walton, *Inorg. Chem.*, 1969, **8**, 631-638.
- [44] J. K. Burdett, R. Hoffmann and R. C. Fay, *Inorg. Chem.*, 1978, **17**, 2553-2568.
- [45] P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229-266.

SUPPLEMENTARY DATA FOR

Niobium tetrahalide complexes with neutral diphosphine ligands

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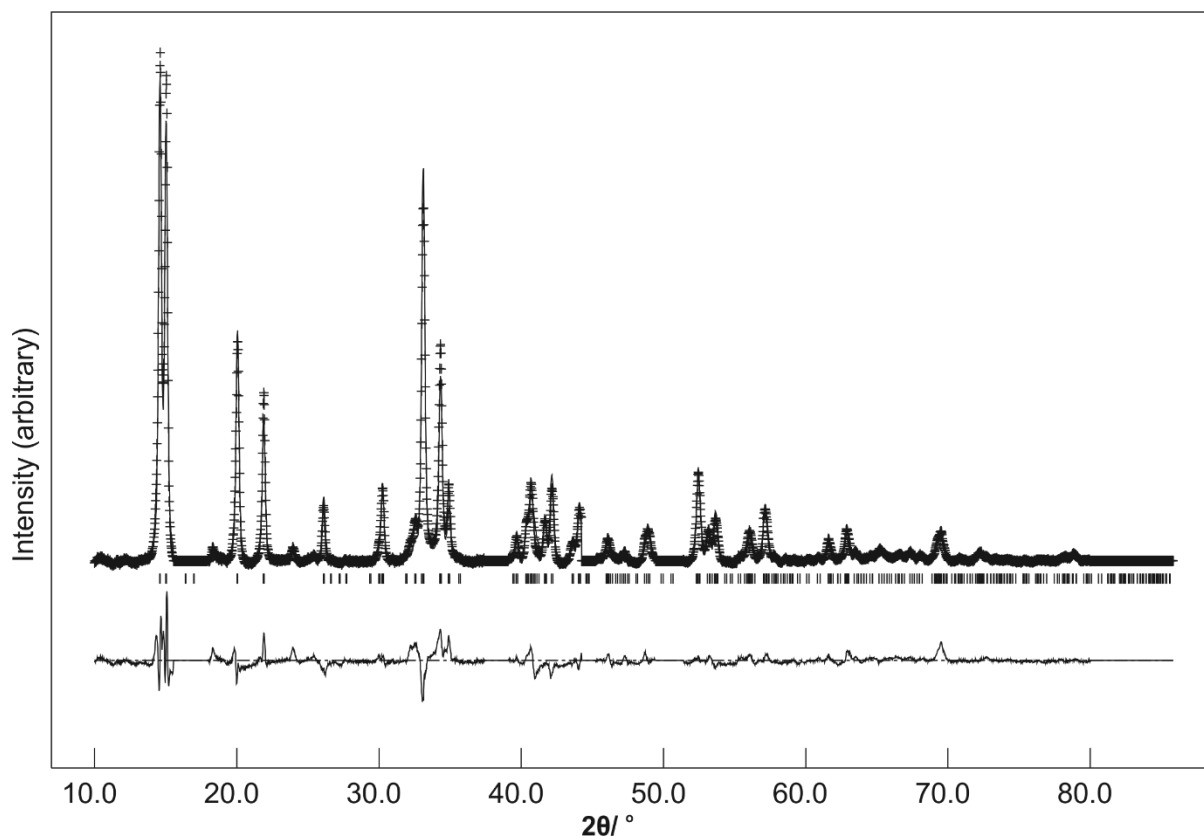


Figure S1. Fit to the PXD data for NbCl₄ ($R_{wp} = 6.92\%$, $R_p = 5.35\%$) fitted to the literature structure.²⁴ Crosses mark the data points, the upper continuous line the fit, the lower continuous line the difference and tick marks the positions of allowed reflections in *I*2/*m* with $a = 8.1431(6)$ Å, $b = 6.8405(4)$ Å, $c = 8.8854(8)$ Å and $\beta = 91.667(4)^\circ$. Literature values: $a = 8.140(5)$, $b = 6.823(4)$, $c = 8.852(6)$ and $\beta = 91.92(5)^\circ$.



Crystals of this complex formed on attempted recrystallisation of [Nb₂Cl₈(Et₂P(CH₂)₂PEt₂)₂] from diethyl ether. ¹H NMR (CD₂Cl₂, 295 K): $\delta = 1.1$ -1.37 (br, CH₃), 1.90-2.48 (br, CH₂). ³¹P{¹H} NMR (CD₂Cl₂, 295 K): $\delta = 21.2$ [2P], 47.0 [4P]. IR (Nujol/cm⁻¹): 980 (Nb=O) 304, 293sh, 282sh (Nb-Cl).

Table S1 X-Ray crystallographic data.^a

Compound	[NbBr ₄ (Me ₂ PCH ₂ CH ₂ PMe ₂) ₂]	[{NbOCl ₃ {Et ₂ P(CH ₂) ₂ PEt ₂ } ₂ }]
	[NbOBr ₄ (NCMe)]	{μ-Et ₂ P(CH ₂) ₂ PEt ₂ }
Formula	C ₁₄ H ₃₅ Br ₈ NNb ₂ OP ₄	C ₃₀ H ₇₂ Cl ₆ Nb ₂ O ₂ P ₆
Formula weight	1182.41	1049.21
Crystal system	Tetragonal	Monoclinic
Space group	P4/n	P2 ₁ /c
a/ Å	12.011(3)	9.8162(3)
b/ Å	12.011(3)	11.6449(3)
c/ Å	11.065(4)	20.2185(14)
α/deg	90	90
β/ deg	90	95.496(7)
γ/ deg	90	90
U/ Å ³	1596(1)	2300.5(1)
Z	2	2
μ(Mo-Kα)/mm. ⁻¹	10.942	1.082
F(000)	1112	1084
Total no. reflections	10587	20644
Unique reflections	1835	5247
R _{int}	0.0372	0.0349
No. of parameters, restraints	74, 0	214, 1
R ₁ ^b [I _o >2σ(I _o)]	0.0188	0.0288
R ₁ (all data)	0.0198	0.0358
wR ₂ ^b [I _o >2σ(I _o)]	0.0486	0.0637
wR ₂ (all data)	0.0490	0.0665

^a Common items: temperature = 100 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max)= 27.5°.

^b R₁ = Σ||F_o|-|F_c||/Σ|F_o|; wR₂=[Σw(F_o²-F_c²)²/ΣwF_o⁴]^{1/2}

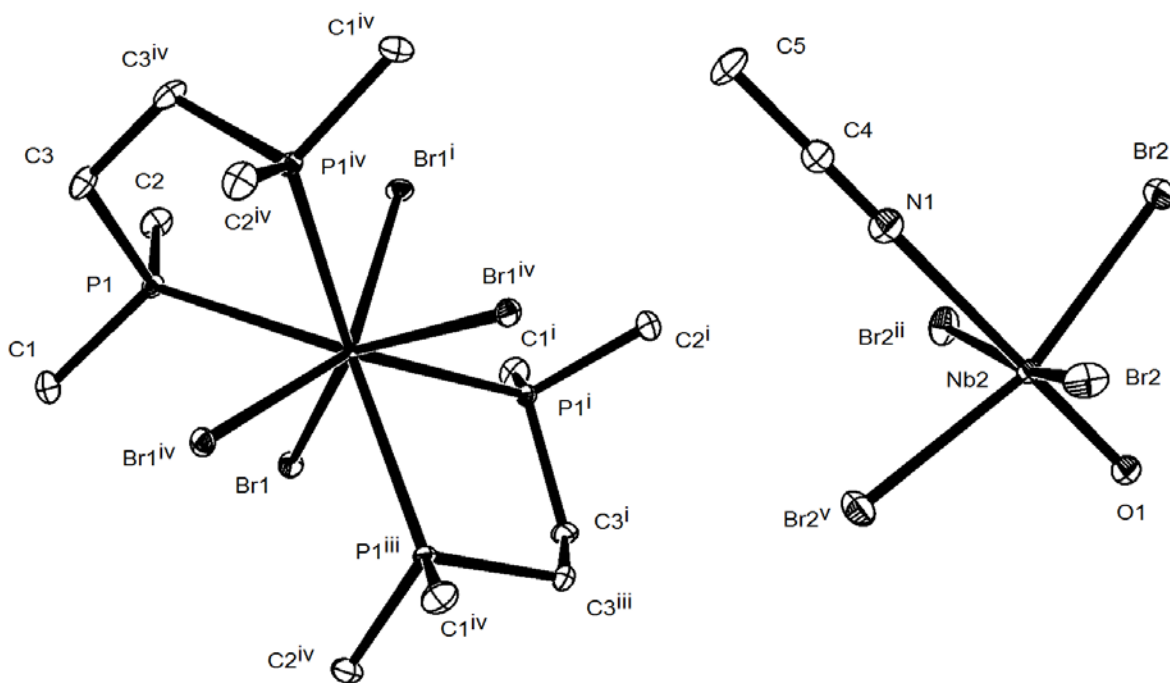


Figure S2 The structure of $[\text{NbBr}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2][\text{NbOBr}_4(\text{MeCN})]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Cation: $\text{Nb1}-\text{Br1} = 2.6017(6)$, $\text{Nb1}-\text{P1} = 2.7079(9)$, $\text{Br1}-\text{Nb1}-\text{Br1}^{\text{iv}} = 94.656(4)$, $\text{P1}-\text{Nb1}-\text{P1}^{\text{iv}} = 71.78(3)$. Anion: $\text{Nb2}-\text{O1} = 1.699(3)$, $\text{Nb2}-\text{N1} = 2.441(4)$, $\text{Nb2}-\text{Br2} = 2.5535(7)$, $\text{Br2}-\text{Nb2}-\text{Br2} = 88.968(3)$, $\text{O1}-\text{Nb2}-\text{Br2} = 97.712(11)$, $\text{O1}-\text{Nb2}-\text{N1} = 180.0$. Symmetry operation $i = \frac{1}{2}+y, 1-x, 1-z$; $ii = \frac{1}{2}-y, x, z$; $iii = 1.5-x, \frac{1}{2}-y, z$; $iv = 1-y, -\frac{1}{2}+x, 1-z$; $v = y, \frac{1}{2}-x, z$; $v = \frac{1}{2}-y, x, z$.

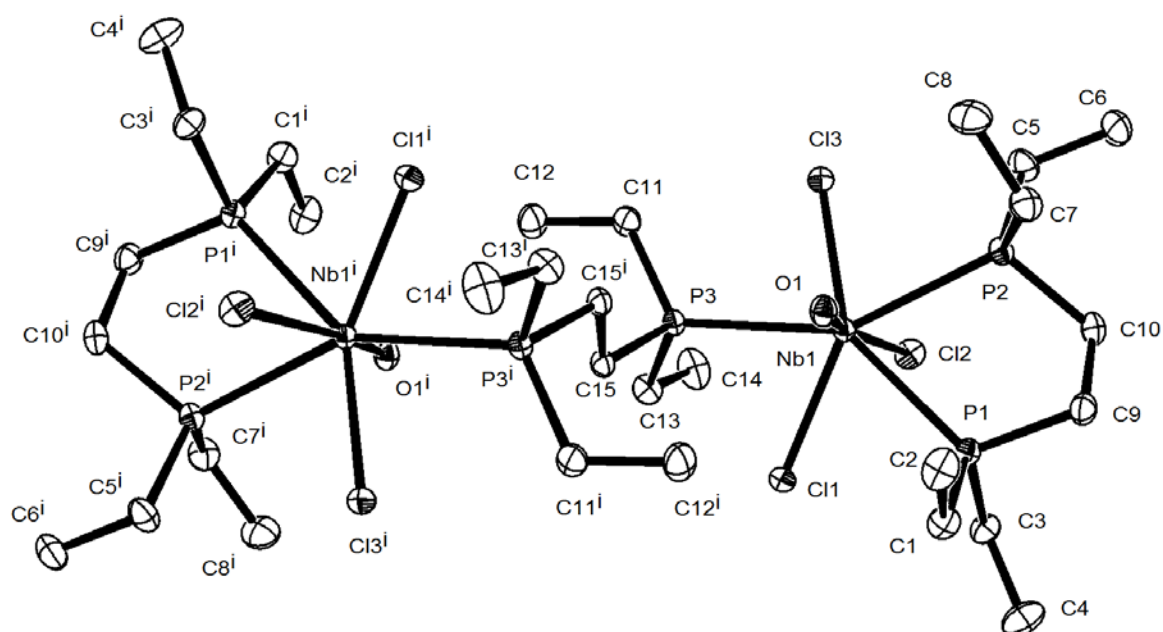
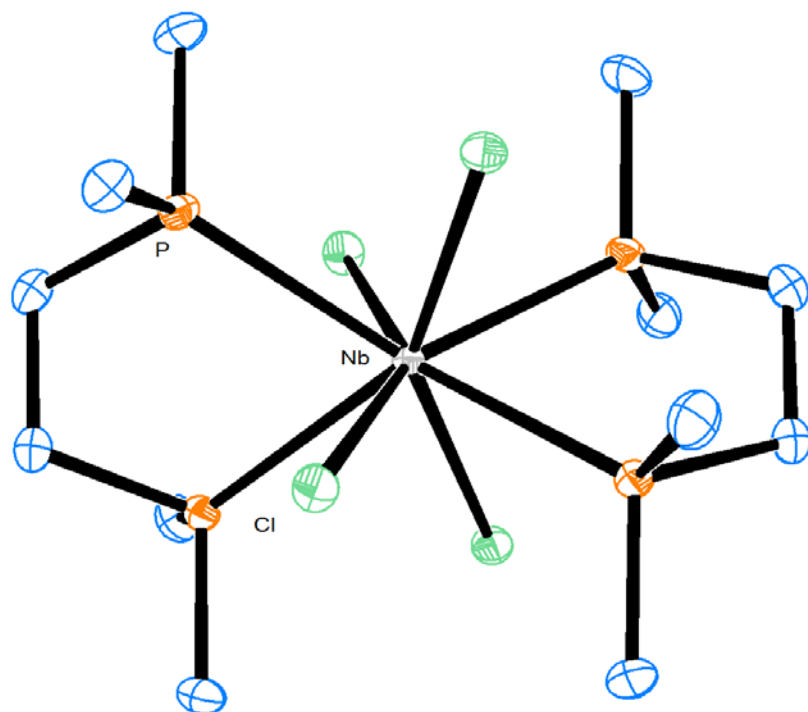


Figure S3 The structure of the centrosymmetric $[\{\text{NbOCl}_3\{\text{Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2\}\}_2(\mu\text{-Et}_2\text{P}(\text{CH}_2)_2\text{PEt}_2)]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nb1-O1 = 1.723(1), Nb1-Cl3 = 2.4717(6), Nb1-Cl1 = 2.4956(6), Nb1-Cl2 = 2.5774(6), Nb1-P2 = 2.6703(6), Nb1-P1 = 2.7007(6), Nb1-P3 = 2.7627(6), O1-Nb1-Cl3 = 94.84(6), O1-Nb1-Cl1 = 96.44(6), Cl3-Nb1-Cl2 = 87.64(2), Cl1-Nb1-Cl2 = 89.49(2), O1-Nb1-P2 = 88.83(5), Cl3-Nb1-P2 = 74.62(1), O1-Nb1-P1 = 88.57(5), Cl1-Nb1-P1 = 69.05(1), Cl2-Nb1-P1 = 81.51(1), P2-Nb1-P1 = 70.57(1), O1-Nb1-P3 = 94.05(5), Cl3-Nb1-P3 = 75.31(2), Cl1-Nb1-P3 = 70.34(2), Cl2-Nb1-P3 = 100.09 (2). Symmetry Operator $i = -x, -y, -z$.

Niobium tetrahalide complexes with neutral diphosphine ligands

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Two series of eight coordinate tetrahaloniobium(IV) diphosphine complexes, the monomeric $[\text{NbX}_4(\text{diphosphine})_2]$ with either dodecahedral or square antiprismatic geometries, and the dimeric $[\text{Nb}_2\text{X}_4(\mu\text{-X})_4(\text{diphosphine})_2]$ have been characterized.