Trimethylphosphine Complexes of Niobium(IV) and Tantalum(IV). Crystal, Molecular, and Electronic Structures of $[M_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ (M = Nb or Ta)†

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Reaction of $[NbCl_4(NCMe)_3]$ or $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran) with three equivalents of PMe_3 gives the seven-co-ordinate complex $[NbCl_4(PMe_3)_3]$. In refluxing benzene this complex converts to $[Nb_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ which is obtained in good yield by reacting $[NbCl_4(NCMe)_3]$ with two equivalents of PMe_3. $[NbCl_4(thf)_2]$ reacts with one equivalent of PMe_3 in acetonitrile to give $[\{NbCl_4(PMe_3)\}_n]$. $[Ta_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ was obtained by reacting dilithium t-butylphosphide and PMe_3 with $TaCl_5$. Reduction of $TaCl_5$ with Na–Hg amalgam in the presence of $[NEt_4]Cl$ gave $[NEt_4]_2[TaCl_6]$. *X*-Ray structure determinations show the $[M_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ complexes (M = Ta or Nb) are isostructural (space group *Im*3), containing four symmetrical chlorine bridges [Ta–Cl 2.544(2), Nb–Cl 2.545(1) Å] across two metal centres [Ta–Ta 2.830(1), Nb–Nb 2.836(1) Å] each of which have co-ordinated two terminal chlorines [Ta–Cl 2.497(2), Nb–Cl 2.506(1) Å] and two terminal phosphine ligands [Ta–P 2.677(3), Nb–P 2.675(1) Å]. Scattered wave Xα calculations on the electronic structure of the dinuclear complexes $[M_2Cl_4(\mu\text{-}Cl)_4(PH_3)_4]$ (M = Nb or Ta) indicate the formation of a metal–metal single σ bond between the metal atom d_{z^2} orbitals. The σ–σ* energy separation suggests greater metal–metal interaction for the tantalum complex.

The heavier Group 5 d^1 transition metals show an interesting range of co-ordination number and structural type.[1] Variation of co-ordination number is a feature of high-oxidation-state stable complexes of early transition metals.[2] Thus, for example, eight-co-ordination has been found in $[NbX_4(pdma)_2]$[3] [M = Nb or Ta; pdma = *o*-phenylenebis(dimethylarsine); X = Cl, Br, or I] and $[Nb(S_2CNMe_2)_4]$[4] and nine-co-ordination suggested in [Nb(acac)$_4$(diox)] (acac = acetylacetonate, diox = 1,4-dioxane).[5] Complexes of niobium(IV) and tantalum(IV) tetrachlorides with phosphine have been reported as six-, seven-, and eight-co-ordinate monomeric molecules[6–9] and as metal–metal bonded species.[10–12]

We report in this work our studies of the niobium(IV) and tantalum(IV) trimethylphosphine complexes. In particular the *X*-ray and electronic structure of the complexes $[M_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ (M = Nb or Ta) indicate the existence of a single metal–metal σ bond between the metal atoms. A preliminary account of the tantalum complex has been reported.[10]

Results and Discussion

Preparation of Complexes.—Addition of three or more equivalents of trimethylphosphine to $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran) or $[NbCl_4(NCMe)_3]$ in dichloromethane or benzene leads to extremely air-sensitive green solutions from which green crystals of $[NbCl_4(PMe_3)_3]$ are obtained on reducing the solution volume and cooling. A magnetic susceptibility determination of the complex by the Evans method gave $\mu_{eff.}$ = 1.68 while the i.r. spectrum was identical to that shown by the related $[MCl_4(PMe_3)_3]$ complexes (M = Mo or W)[13–15] which exhibit capped octahedral structures.‡

$[NbCl_4(PMe_3)_3]$ does not lose PMe_3 when held under vacuum {*cf.* $[NbCl_4(NCMe)_3]$ which forms $[NbCl_4(NCMe)_2]$} and freshly prepared samples redissolve in dichloromethane or benzene, but dissolution is incomplete after the complex is left to stand under nitrogen for longer periods (*ca.* 3 d) and a red-brown solid is left which does not dissolve when excess trimethylphosphine is present. Pure samples of this material were obtained by refluxing a benzene solution of $[NbCl_4(PMe_3)_3]$ whereby red crystals analysing as $[\{NbCl_4(PMe_3)_2\}_n]$ were formed. As reported,[6] this complex can be prepared by addition of two equivalents of trimethylphosphine to $[NbCl_4(thf)_2]$ but the samples are often contaminated. We have found that the cleanest bulk preparation results from adding two equivalents of the phosphine to $[NbCl_4(NCMe)_3]$ dissolved in benzene, while highly crystalline material can be obtained by reacting trimethylphosphine with $[NbCl_4(thf)_2]$ in dichloromethane and allowing the solution to stand. Although other material also precipitates from dichloromethane solution, the complex can be obtained analytically pure by washing away the contaminating substance with ethanol.

The red bis-trimethylphosphine complex is stable in air, is insoluble in organic solvents, and does not redissolve when heated with excess trimethylphosphine to form the tris-phosphine complex. These properties contrast with those exhibited by the octahedral monomers $[MCl_4(PMe_3)_2]$ (M = Mo or W) which dissolve and react with excess phosphine to produce capped octahedral $[MCl_4(PMe_3)_3]$ complexes.[14,15] The properties of the niobium complex are explained by the structure, determined by *X*-ray crystallography, which shows the molecule to be a dimer containing a $(\mu\text{-}Cl)_4$ bridge across two niobium centres (see later). While triethylphosphine and ethyldiphenylphosphine form monomeric *trans*-$[NbCl_4P_2]$ complexes,[11] the sterically less demanding trimethylphosphine ligand apparently allows the formation of the bridge structure. The dimeric complex also forms in the presence of EtC≡CEt or PhC≡CPh. Our attempts to solubilise the complex by reaction with magnesium or lithium alkyls have so far been unsuccessful, generally leading to intractable brown materials.

$[NbCl_4(thf)_2]$, prepared by the reduction of $NbCl_5$ with aluminium powder,[6,16] readily dissolves in acetonitrile but after

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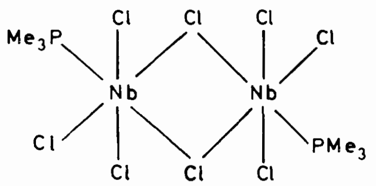
† Tetra-μ-chloro-bis[dichlorobis(trimethylphosphine)-niobium(IV)] and -tantalum(IV)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ The capped octahedral structure for $[NbCl_4(PMe_3)_3]$ has now been confirmed.[12]



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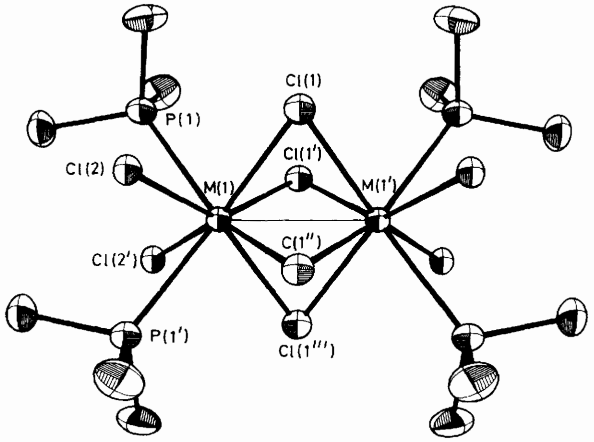

Figure 1. Molecular structure of the $[M_2Cl_4(\mu-Cl)_4(PMe_3)_4]$ molecule (M = Nb or Ta)

removal of the solvent and washing the residues with thf the yellow product obtained does not react with PMe_3 to produce either $[NbCl_4(PMe_3)_3]$ or $[Nb_2Cl_4(\mu-Cl)_4(PMe_3)_4]$ but gives a yellow intractable gum. However, reaction of trimethylphosphine with an acetonitrile solution of $[NbCl_4(thf)_2]$, prepared by the reduction of $NbCl_5$ with sodium–mercury amalgam in acetonitrile and washing the product with thf, gave a small quantity of a light yellow complex which analysed as $[\{NbCl_4(PMe_3)\}_n]$. Insolubility has precluded complete characterisation of this material but the chloro-bridge structure (**1**) is proposed, based on that given for $[\{NbCl_4(SMe_2)\}_n]$ for which a molecular weight determination showed the complex to be dimeric.[17]

Our attempts to prepare the tantalum complexes $[TaCl_4(PMe_3)_x]$ (x = 1, 2, or 3) using the reactions outlined for niobium have been less successful. Addition of PMe_3 to thf or MeCN solutions of $TaCl_5$ reduced with one-third of an equivalent of aluminium powder resulted in the formation of intractable products. Reaction of $TaCl_5$ in acetonitrile with PMe_3 and reduction with one equivalent of sodium–mercury amalgam gave an insoluble yellow complex analysing as $[\{TaCl_4(PMe_3)_2\}_n]$ for which we are at present attempting to obtain crystals. $[Ta_2Cl_4(\mu-Cl)_4(PMe_3)_4]$ was produced in small quantities as a side product in the reaction of dilithium t-butylphosphide, $TaCl_5$, and trimethylphosphine. The complex does not form when one equivalent of n-butyl-lithium or lithium metal reacts with $TaCl_5$ in the presence of PMe_3.* When $TaCl_5$ was reduced with one equivalent of sodium–mercury amalgam in acetonitrile with two equivalents of tetraethylammonium chloride present, the tantalum(IV) complex $[NEt_4]_2[TaCl_6]$ was readily formed but failed to react with PMe_3 even when reaction was carried out at elevated temperature in a pressure bottle.

Table 1. Selected average bond lengths (Å) and angles (°) for the $[M_2Cl_4(\mu-Cl)_4(PMe_3)_4]$ complexes

	M = Ta	M = Nb	$[Nb_2Cl_4(\mu-Cl)_4(PMe_2Ph)_4]$*
$M-Cl_b$	2.544(2)	2.545(1)	2.541(6)
$M-Cl_t$	2.497(2)	2.506(1)	2.484(10)
M–P	2.677(3)	2.675(1)	2.700(3)
M–M	2.830(1)	2.836(1)	2.838(1)
M–Cl–M	67.6(1)	67.7(1)	69.90(3)
Cl_t-M-Cl_t	113.6(1)	112.6(1)	110.74(4)
P–M–P	114.1(5)	111.6(4)	114.68(4)

* Data obtained from ref. 8.

Crystallographic Studies.—*X*-Ray crystal structure determinations of $[Ta_2Cl_4(\mu-Cl)_4(PMe_3)_4]$[10] and $[Nb_2Cl_4(\mu-Cl)_4(PMe_3)_4]$ showed both to be isostructural with eight-fold co-ordination geometries about each metal atom. The molecular structure is shown in Figure 1. The two metal centres are bridged symmetrically by four chlorine atoms with each metal atom also having two terminal chlorine atoms and two PMe_3 groups. The co-ordination geometry about each metal atom is a slightly distorted square antiprism with *mm* symmetry imposed by the space group, whereby the metal atoms lie at the intersection of two crystallographic mirror planes. One of these planes includes the phosphorus atoms and a carbon and hydrogen of each phosphine ligand while the other includes the terminal chlorine atoms.

About the MCl_4M bridging structure, the co-ordination geometry consists of two square antiprisms which share a square face. Both sets of terminal ligands are eclipsed while the bridging and terminal chlorines are staggered.

Interatomic distances are contained in Table 1 where they are compared with those of $[Nb_2Cl_4(\mu-Cl)_4(PMe_2Ph)_4]$ reported by Cotton *et al.*[8,11] All three complexes are virtually identical with the bond lengths of the symmetrical bridge structures being slightly longer than the terminal M–Cl bond lengths. These terminal M–Cl bond lengths are significantly longer than for known monomeric metal(IV) complexes, including $[TaCl_4(PMe_3)_3]$,[9] while the terminal M–P bond lengths are larger than for known tantalum(IV) monomeric complexes[9] but nearer to those observed for niobium(IV) monomers.[11] Clearly these lengthened bonds result from less efficient overlap of metal and ligand orbitals for the imposed eight-fold co-ordination geometry.

The metal–metal separations for the three complexes are not significantly different. For the tantalum complex the distance [2.830(1) Å] is intermediate between that found in the $[Ta_6Cl_{12}]^{2+}$[18] cation (Ta–Ta 2.96 Å), where the bond order is two-thirds, and the tantalum(III) complexes $[\{TaCl_3(PMe_3)_2\}_2]$[19] [Ta–Ta 2.721(1) Å],† $[Ta_2Cl_6(tht)_3]$,[20] [tht = tetrahydrothiophene; Ta–Ta 2.681(1) Å], and $[Ta_2Cl_6(PhC\equiv CPh)(thf)_2]$[21] [Ta–Ta 2.677(1) Å] which contain metal–metal double bonds. The metal–metal interaction in the present complex is, however, significantly longer than that observed in $[Ta_2Cl_4(\mu-Cl)_2(\mu-H)_2(PMe_3)_4]$[22] [Ta–Ta 2.621(1) Å], a tantalum(IV) complex. Electronic-structure calculations (see later) support the existence of a single σ metal–metal interaction in the $[M_2Cl_4(\mu-Cl)_4(PMe_3)_4]$ complexes but the distance of 2.830(1) Å does not represent a lower limit for the single bond. A

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* While this work was in progress Cotton *et al.*[9] reported preparations and crystal structures for *cis*-$[TaCl_4(PMe_2Ph)_2]$, *trans*-$[TaCl_4(PEt_3)_2]$, and $[TaCl_4(PMe_2Ph)_3]$ (capped octahedron).

† For other $[M_2Cl_6L_4]$ (L = phosphine) complexes see L. Hubert-Pfalzgraf, M. Tsunoda, and J. G. Riess, *Inorg. Chim. Acta*, 1980, **41**, 283; S. M. Rocklage, J. D. Fellmann, G. A. Rupprecht, L. W. Messerle, and R. R. Schrock, *J. Am. Chem. Soc.*, 1981, **103**, 1440; L. Hubert-Pfalzgraf and J. G. Riess, *Inorg. Chim. Acta*, 1978, **29**, L251.

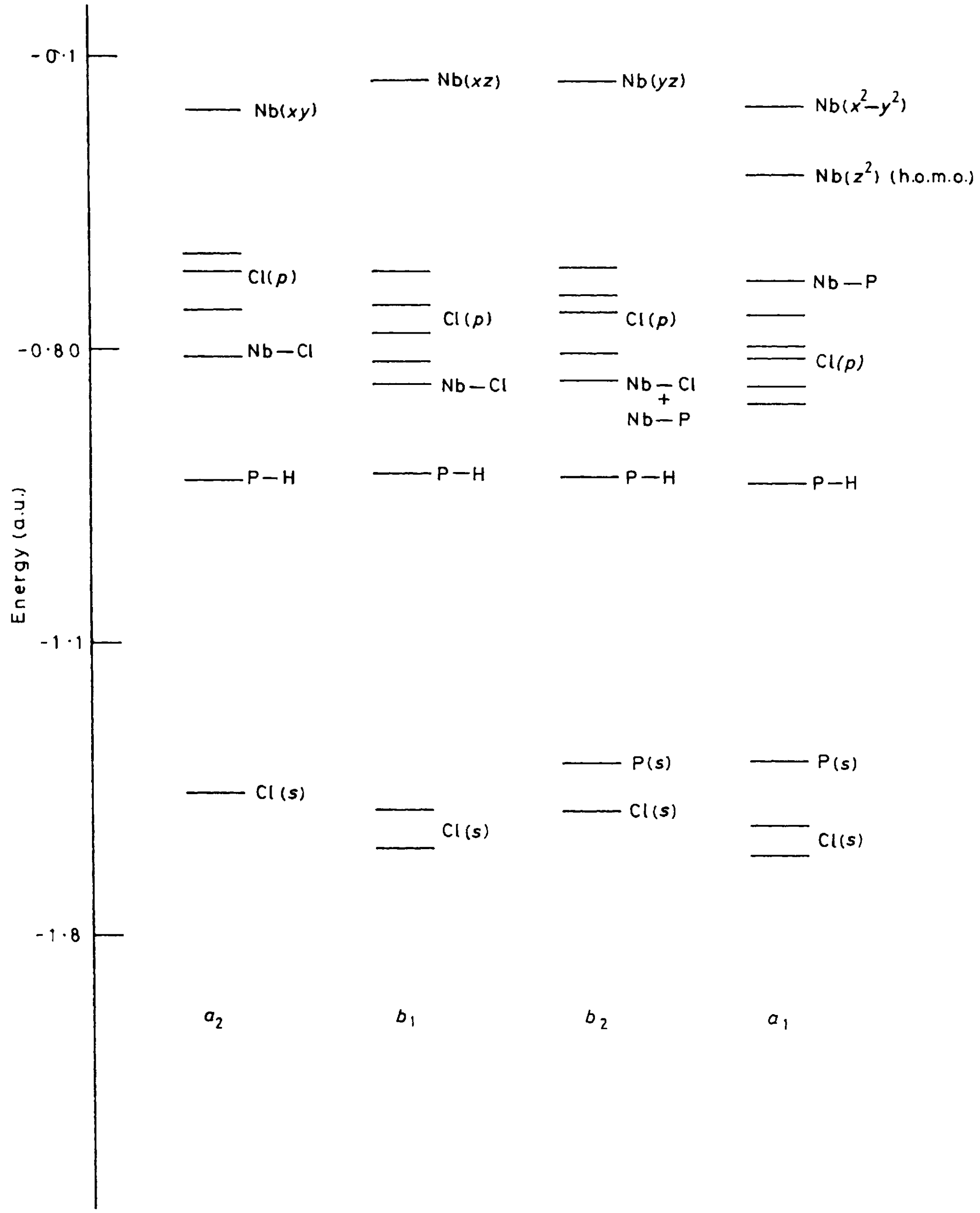

Figure 2. Scattered wave Xα orbital energies for the $[NbCl_6(PH_3)_2]^{2-}$ fragment (1 a.u. = 2.1799 × 10^{-18}J)

hydrido bridge can apparently reduce this value to 2.621(1) Å which is shorter than the metal–metal separations observed in the dinuclear tantalum(III) complexes. In $[\{NbCl_4\}_n]$ the metal–metal separation is longer, at 3.029(2) Å.[23]

The bond angles for the three structures shown in Table 1 are also not significantly different. The M–Cl–M bond angles of 67.6—69.9° are similar to those found for the μ-chloro bridge in the tantalum(III) dimer $[Ta_2Cl_4(\mu\text{-}Cl)_2(PMe_3)_4]$[19] but significantly larger than that in the tantalum(IV) hydrido-bridged complex $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}H)_2(PMe_3)_4]$.[22] The P–Ta–P bond angles of 114° in the present eight-co-ordinate complex compare with *cis*- and *trans*-orientated PMe_3 groups at 89.9(1) and 164.5(1)° respectively in the distorted octahedral geometry in the tantalum(III) dimer $[Ta_2Cl_4(\mu\text{-}Cl)_2(PMe_3)_4]$.[19]

Electronic Structure of $[M_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ *Complexes.* —The ligand atoms in the dinuclear molecules $[M_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ have near square-antiprismatic geometry about each metal atom. Ligand-field theory predicts for a d^1 complex, with regular square-antiprismatic geometry, that the single unpaired electron lies in a d_{z^2} orbital. This would have a principal lobe pointing along the metal–metal vector in these molecules. A scattered wave Xα calculation on the fragment $[NbCl_6(PH_3)_2]^{2-}$ (Figure 2) supports this picture. The highest occupied molecular orbital (h.o.m.o.) is the $11a_1$ [population Nb(z^2), 0.91]. The lower unoccupied molecular orbitals occur in two near-degenerate pairs ($7a_2$, $12a_1$) and ($9b_1$, $9b_2$) corresponding to the Nb(*xy*, x^2-y^2) and Nb(*xz*, *yz*) orbitals. The energy ordering is as predicted from ligand-field theory.

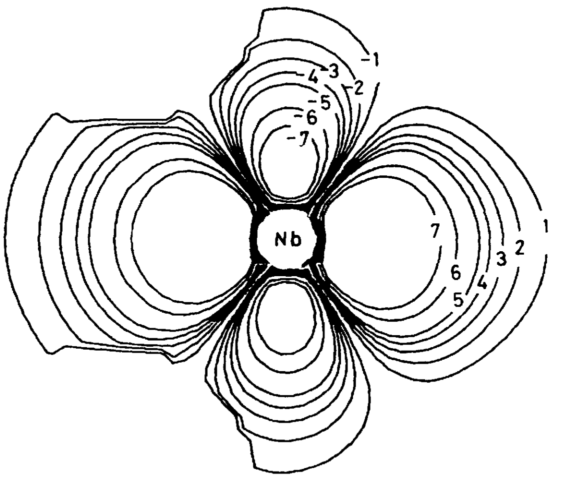

Figure 3. Contour plot of the Nb(d_{z^2}) s.o.m.o. ($11a_1$) for $[NbCl_6(PH_3)_2]^{2-}$ (Contours ±1, ±2, ±3, ±4, ±5, ±6, and ±7 represent values of ±0.01, ±0.02, ±0.03, ±0.04, ±0.05, ±0.08, and ±0.11 a.u. respectively; 1 a.u. = 1.081×10^{12}C m^{-3})

Figure 3 shows the semi-occupied molecular orbital (s.o.m.o.) for this fragment. Overlap between two of these would lead to a metal–metal σ bond between niobium atoms.

Scattered wave Xα calculations of the electronic structure of both the niobium and tantalum dinuclear complexes (Figure 4) indicate that these d_{z^2} orbitals overlap forming σ and σ* metal–metal bonding orbitals $10a_g$ and $8b_{2u}$ respectively. It is of interest that the σ^*_{MM} antibonding orbital lies below the unoccupied π and δ metal–metal orbitals in both cases. A measure of the strength of the interaction between the individual metal σ orbitals may be given by the σ–σ* separation which is 0.155 a.u. (atomic units) for the niobium and 0.275 a.u. for the tantalum dimers respectively. The d_{z^2} orbital populations for the $10a_g$ metal–metal bonding orbitals are 0.68 and 0.64 for the niobium and tantalum atoms respectively.† Figure 5 shows a contour plot of the $10a_g$ orbital in the metal–terminal chlorine plane of $[Nb_2Cl_8(PH_3)_4]$. The terminal chlorine atom *p* orbitals are the other major contributor [population $Cl_t(p)$, 0.055]. Table 2 gives the gross orbital populations and atomic charges for the two complexes. Except for the *s* and *p* orbitals of the metals the orbital populations of the atoms in both molecules are remarkably similar.

Conclusions

The reactions carried out indicate that a series of niobium(IV) complexes, $[NbCl_4(PMe_3)_x]$ (x = 1, 2, or 3) may be formed with trimethylphosphine. The monomeric seven-co-ordinate species, $[NbCl_4(PMe_3)_3]$, is readily converted to the dinuclear bis complex $[Nb_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ containing a metal–metal interaction corresponding to a bond order of one. The transformation is unique in that we believe it represents the first case whereby loss of phosphine from a seven-co-ordinate species results in formation of a metal–metal bond.

The structural features exhibited by the $[M_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ complexes include both eight-fold co-ordination about each metal centre and a symmetrical M–Cl_4–M bridge across a metal–metal bond involving two d^1 centres. Apparently the small phosphine allows formation of this bridge which brings together orbitals of the correct symmetry and occupancy to form a σ bond. Larger phosphines such as triethylphosphine or dimethylphenylphosphine do not induce this change, giving monomeric octahedral complexes.[11] This behaviour contrasts with that observed for the +3 oxidation state of niobium and tantalum where $[M_2Cl_4(\mu\text{-}Cl)_2L_4]$ complexes are formed[19] and, in the case of tantalum and trimethylphosphine, result from decomposition of the monomeric complex $[TaCl_3L_3]$ (L = PMe_3).[24]

The niobium and tantalum chemistry presented here thus shows characteristics of both high- and low-valent complexes, *i.e.* > six-fold co-ordination geometries for M^{IV} and M^{V} and the metal–metal bonding of M^{III} chemistry.

Experimental

Analytical data (C, H, and N) were obtained by Dr. A. C. Campbell and associates, University of Otago, New Zealand. Chlorine was determined gravimetrically as AgCl. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 597 spectrometer. Melting points were determined in sealed tubes under nitrogen on an electrothermal melting point apparatus and are uncorrected.

Niobium and tantalum pentachlorides (Riedel de-Haën) were purified by sublimation before use. Trimethylphosphine was prepared by reaction of MgMeI on triphenyl phosphite.[25] Tetraethylammonium chloride was dried at 100 °C under vacuum for 24 h. Tetrahydrofuran was distilled from sodium dihydronaphthylide; acetonitrile, carbon tetrachloride, and dichloromethane from calcium hydride; and light petroleum (b.p. 40—60 °C), toluene, benzene, and diethyl ether from sodium wire. All distillations were carried out under dry nitrogen atmospheres. Manipulations were carried out under argon or nitrogen using standard air-sensitive techniques.[26]

Tris(acetonitrile)tetrachloroniobium(IV).—This complex was prepared by a slight modification of the published procedure.[6,16] To a solution of niobium pentachloride (3 g, 11.1 mmol) in acetonitrile (15 cm^3) was added a suspension of aluminium powder (0.1 g, 3.7 mmol) in acetonitrile (10 cm^3) *via* a stainless-steel transfer tube. The mixture was stirred for 2 h, giving a green precipitate and yellow-brown solution. After filtering, the solvent volume was reduced to *ca.* 5 cm^3 whereupon the complex formed as bright orange-red crystals which were filtered off, washed with carbon tetrachloride (20 cm^3) followed by light petroleum (30 cm^3).

The complex redissolves in acetonitrile from which it may be recrystallised but the yield is decreased by this procedure. Removal of solvent from the mother-liquors causes the solution to turn purple, finally leaving a purple flaky solid.

Orange-red tris(acetonitrile)tetrachloroniobium(IV) readily loses one acetonitrile ligand when held under vacuum for *ca.* 1 h giving brown crystalline bis(acetonitrile)tetrachloroniobium(IV) (Found: C, 15.1; H, 2.3; N, 8.1. $C_4H_6Cl_4N_2Nb$ requires C, 15.2; H, 1.9; N, 8.8%).

Tetrachlorobis(tetrahydrofuran)niobium(IV).—Bulk quantities of this complex were prepared by the literature method[16] but the following procedure gives a higher yield of product which is not contaminated with aluminium complexes. Niobium pentachloride (2.2 g, 8.2 mmol) dissolved in acetonitrile (50 cm^3) was added to sodium–mercury amalgam (0.19 g sodium, 8.2 mmol; 100 g mercury) and acetonitrile (30 cm^3) and the mixture was stirred for 4 h with periodic shaking. The yellow-brown solution was filtered from the residue and the solvent removed *in vacuo* to give a red-brown gummy material which solidified and turned a charcoal colour on further pumping down. The solid was cooled to 0 °C, thf (50 cm^3) was added, and the mixture was stirred and allowed to come to room

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† Calculated with the *z* axis parallel to the metal–metal vector.

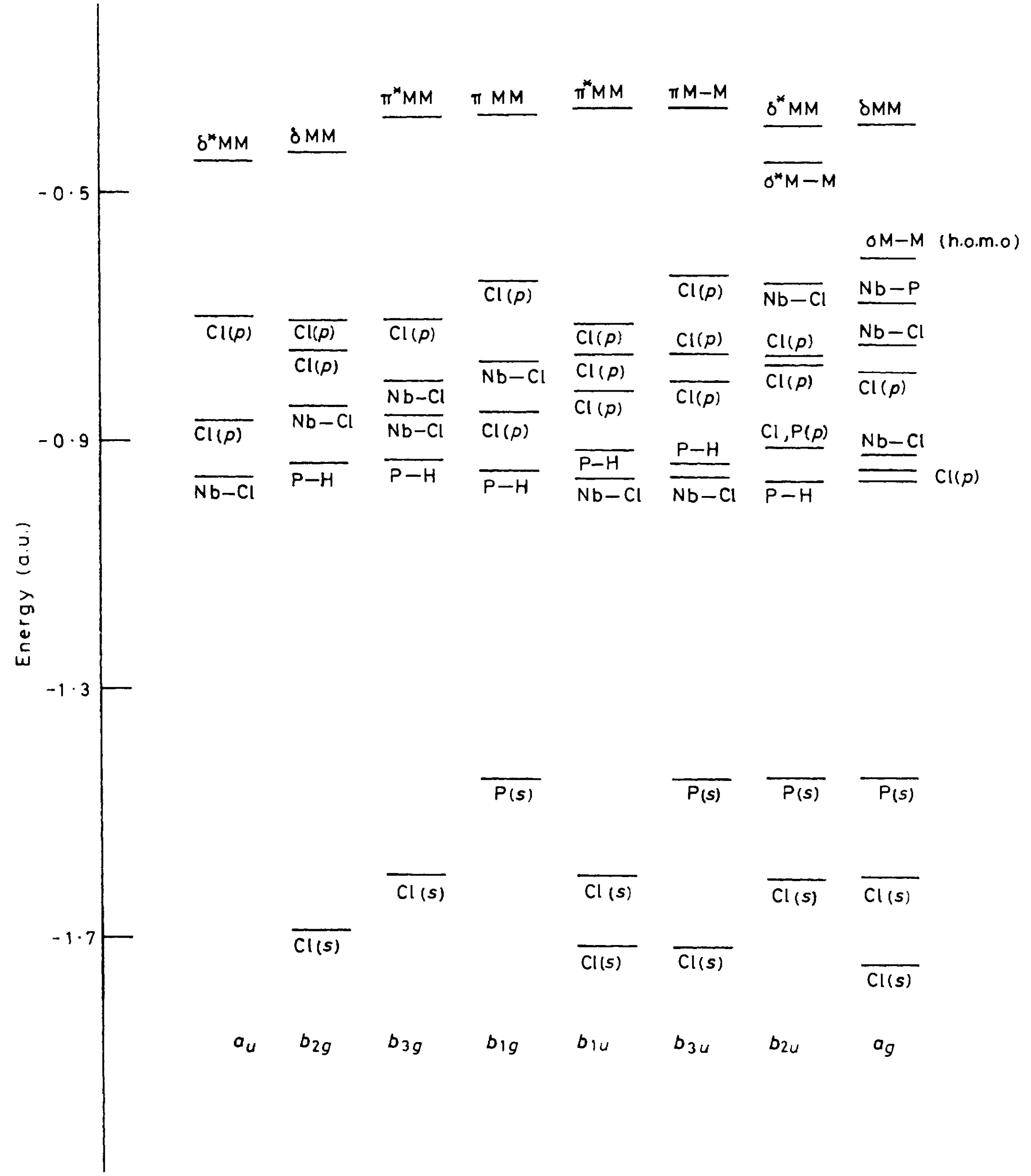

Figure 4. Scattered wave Xα orbital energies for [$NbCl_4(\mu\text{-}Cl)_4(PH_3)_4$] (1 a.u. = 2.1799 × 10^{-18}J)

temperature. After 4 h the solution was filtered leaving the complex as a yellow solid (2.3 g, yield 77%).

The complex may also be prepared from the purple solid isolated by removal of solvent from the mother-liquors obtained after crystallisation of tris(acetonitrile)tetrachloroniobium(IV). Tetrahydrofuran (30 cm^3) was added to the solid and the mixture stirred for 3 h. The yellow thf complex was filtered off, washed several times with thf (50 cm^3) followed by light petroleum (10 cm^3), and dried *in vacuo.*

Tetrachlorotris(trimethylphosphine)niobium(IV).—Trimethylphosphine (3.2 cm^3, 29 mmol) in dichloromethane (30 cm^3) was added to a suspension of tetrachlorobis(tetrahydrofuran)niobium(IV) (3.5 g, 9.2 mmol) and the mixture was stirred for 3 h. The green solution was filtered off from a small amount of white solid and the volume reduced to *ca.* 5 cm^3. On cooling to 0 °C, green crystals of the complex formed which were filtered off, washed with light petroleum (2 × 10 cm^3), and dried *in vacuo* (3.2 g, yield 74%), decomposes above 125 °C (Found: C, 23.5; H, 5.9; Cl, 29.7. $C_9H_{27}Cl_4NbP_3$ requires C, 23.3; H, 5.9; Cl, 30.6%). I.r. (Nujol): 1 450s, 1 408s, 1 295w, 1 272w, 950s, 856m, 735s, 675m, 340s, and 248m cm^{-1}.

Tetra-μ-chloro-bis[dichlorobis(trimethylphosphine)niobium(IV)].—Tris(acetonitrile)tetrachloroniobium(IV) (1.5 g, 4.2 mmol) was dissolved in benzene (40 cm^3) and the solution filtered off from a small amount of residue. Trimethylphosphine (1 cm^3, 9.1 mmol) in benzene (30 cm^3) was added to the solution and the mixture was rapidly stirred for 2 h. The red precipitate was filtered off, washed with benzene (30 cm^3)

Table 2. Gross orbital populations and atomic charges

	M			P		Cl^1		Cl^2	
Molecule	*s*	*p*	*d*	*s*	*p*	*s*	*p*	*s*	*p*
$[NbCl_6(PH_3)_2]^{2-}$	0.33	0.56	3.62	1.45	3.29	1.98	5.55	1.97	5.45
Charge		0.489		0.254		−0.53		−0.428	
$[Nb_2Cl_8(PH_3)_4]$	0.31	0.48	3.82	1.42	3.27	1.96	5.23	1.97	5.39
Charge		0.395		0.311		−0.188		−0.356	
$[Ta_2Cl_8(PH_3)_4]$	0.35	0.54	3.81	1.42	3.27	1.95	5.20	1.96	5.37
Charge		0.298		0.308		−0.148		−0.330	

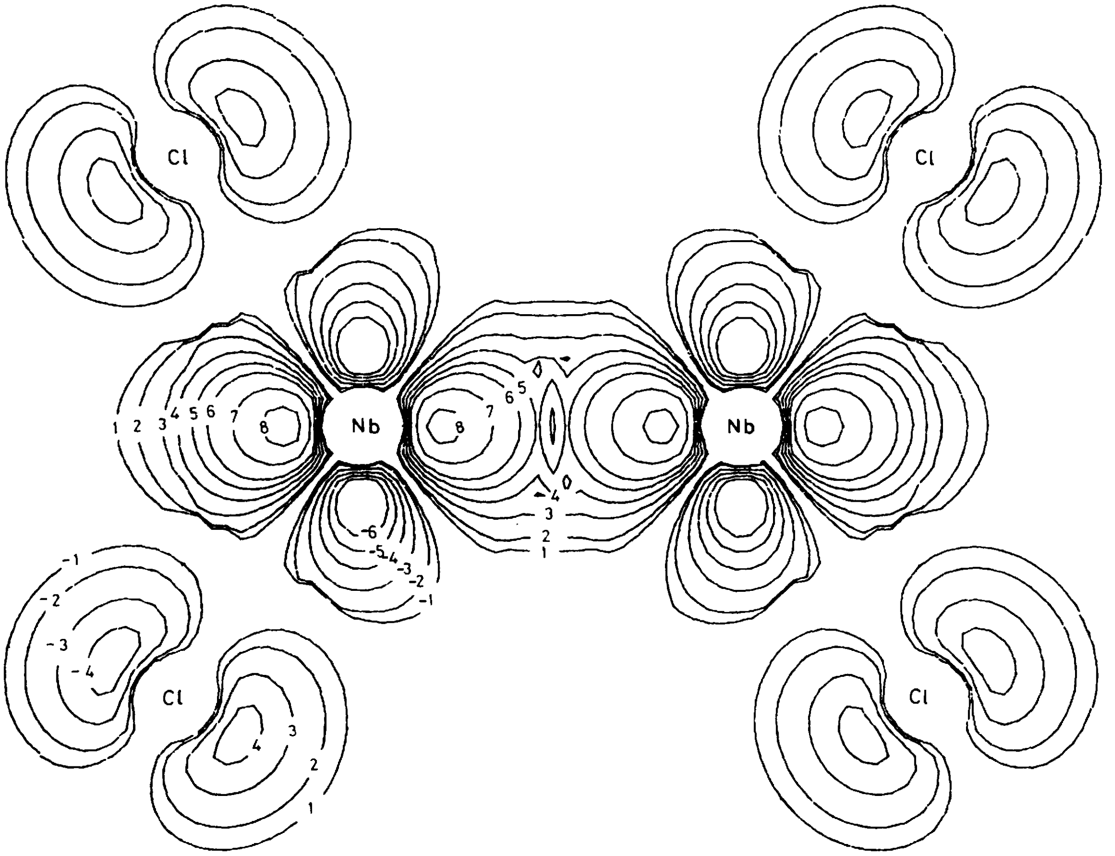

Figure 5. Contour plot of metal–metal bond orbital $10a_g$ for $[NbCl_4(\mu\text{-}Cl)_4(PH_3)_4]$ in the *yz* plane. (Contours ±1, ±2, ±3, ±4, ±5, ±6, ±7, and ±8 represent values of ±0.02, ±0.03, ±0.05, ±0.07, ±0.09, ±0.11, ±0.15, and ±0.2 a.u. respectively; 1 a.u. = 1.081×10^{12} C m^{-3})

followed by light petroleum (30 cm^3), and dried *in vacuo* (1.4 g, yield 72%). I.r. (Nujol): 1 450s, 1 408s, 1 295w, 1 272w, 950s, 858m, 735s, 672m, 338s, 310s, 284s, and 245m cm^{-1}.

Tetrachloro(trimethylphosphine)niobium(IV).—To a solution of tetrachlorobis(tetrahydrofuran)niobium(IV) (1.3 g, 3.4 mmol) (sample prepared by sodium–mercury amalgam procedure) in acetonitrile (30 cm^3) was added trimethylphosphine (1.1 cm^3, 10.0 mmol) in acetonitrile (20 cm^3) and the mixture stirred for 2 h, during which time the solution turned green followed by yellow and precipitation of a yellow solid. After filtering and washing the solid with acetonitrile (40 cm^3) the complex was obtained as a light yellow solid when dried *in vacuo* (0.6 g), decomposes above 180 °C (Found: C, 12.6; H, 3.3; Cl, 44.7. $C_3H_9Cl_4NbP$ requires C, 11.6; H, 2.9; Cl, 45.6%). I.r. (Nujol): 1 410w, 1 295m, 1 250s, 1 210w, 950s, 890w, 855w, 765m, 720w, 704w, 655w, 548w, 450m, 413w, 340m, and 280s cm^{-1}.

Tetraethylammonium Hexachlorotantalate(IV).—Tetraethylammonium chloride (1.85 g, 11.2 mmol) in acetonitrile (40 cm^3) was added to tantalum pentachloride (2 g, 5.6 mmol) dissolved in acetonitrile (40 cm^3) and the mixture was added to sodium–mercury amalgam (0.13 g, sodium, 5.6 mmol; 100 g mercury) and acetonitrile (30 cm^3) cooled to 0 °C. The mixture was stirred for 4 h (allowing slow warming to room temperature), filtered, and the amalgam residue extracted with warm acetonitrile (80 cm^3). The combined extracts were filtered and the volume reduced to *ca.* 5 cm^3 whereupon the complex formed as light yellow microcrystals which were filtered off, washed with cold acetonitrile (2 × 1 cm^3), and dried *in vacuo* (1.6 g, yield 44%). The complex was recrystallised by adding acetonitrile (*ca.* 20 cm^3), heating the solution to just below reflux temperature, and allowing to stand but this procedure diminishes the yield; complex decomposes above 245 °C (Found: C, 29.0; H, 6.1; N, 4.4. $C_{16}H_{40}Cl_6N_2Ta$ requires C, 29.4; H, 6.1; N, 4.3%).

Table 3. Fractional atomic co-ordinates for $[M_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ (M = Nb or Ta) with estimated standard deviations in parentheses

M = Nb				M = Ta			
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Nb	0.000 00	0.413 49(3)	0.000 00	Ta	0.000 00	0.413 73(0)	0.000 00
Cl(1)	0.091 6(1)	0.500 0	0.090 8(1)	Cl(1)	0.091 8(1)	0.500 0	0.090 6(1)
Cl(2)	0.000 0	0.328 7(1)	0.127 2(1)	Cl(2)	0.000 0	0.330 4(1)	0.127 4(1)
P	0.135 0(6)	0.321 8(1)	0.000 0	P	0.134 6(2)	0.322 4(2)	0.000 0
C(1)	0.113 7(3)	0.213 1(3)	0.000 0	C(1)	0.112 6(7)	0.213 4(6)	0.000 0
C(2)	0.204 2(2)	0.332 1(3)	0.085 3(3)	C(2)	0.205 6(5)	0.331 5(6)	0.085 5(5)

Table 4. Co-ordinates and radii used in SCF Xα calculations

Atom	*X*	*Y*	*Z*	Radius*
$[Nb_2Cl_4(\mu\text{-}Cl)_4(PH_3)_4]$				
Nb	0.0	0.0	−2.679	2.644
Cl(1)	−2.837	−2.812	0.0	2.554
Cl(2)	0.0	−3.940	−5.306	2.673
P	−4.181	0.0	−5.519	2.360
H(1)	3.667	0.0	−8.148	1.427
H(2)	−5.862	−2.072	−5.272	1.427
OUT	0.0	0.0	0.0	10.363
$[Ta_2Cl_4(\mu\text{-}Cl)_4(PH_3)_4]$				
Ta	0.0	0.0	−2.675	2.695
Cl(1)	2.814	2.808	0.0	2.508
Cl(2)	0.0	3.948	−5.253	2.637
P	4.171	0.0	−5.504	2.352
H(1)	3.648	0.0	−8.132	1.427
H(2)	5.879	2.055	−5.293	1.427
OUT	0.0	0.0	0.0	10.340

* Atom units; a.u. = 52.918 pm.

I.r. (Nujol): 1 455s, 1 400s, 1 358m, 1 305m, 1 180s, 1 120w, 1 075w, 1 030s, 1 004s, 892w, 850w, 800s, 790s, 520m, 470w, and 280s cm^{-1}. The complex does not react with trimethylphosphine at elevated temperatures (*ca.* 100 °C) in a pressure bottle using dichloromethane as solvent.

*Tetra-*μ*-chloro-bis[dichlorobis(trimethylphosphine)tantalum-*(IV)].—Dilithium t-butylphosphide (0.5 g, 4.9 mmol) (prepared from t-butyldichlorophosphine and four equivalents of lithium metal) in diethyl ether (50 cm^3) was added to a suspension of tantalum pentachloride (1.75 g, 4.9 mmol) and trimethylphosphine (1.1 cm^3, 10.0 mmol) in diethyl ether (100 cm^3) and the mixture was stirred for 24 h. The solution was filtered, the solvent removed, and the residue extracted with toluene (30 cm^3). On reducing the volume to *ca.* 10 cm^3 and standing the solution at −20 °C, red crystals of the complex were slowly formed along with other material, over a period of three weeks. The solids were filtered off, washed with ethanol to remove the contaminating products, and the complex dried *in vacuo*. Characterisation was carried out by *X*-ray crystallography. The i.r. spectrum is identical to that of the niobium analogue.

$[\{TaCl_4(PMe_3)_2\}_n]$.—Tantalum pentachloride (1.8 g, 5 mmol) dissolved in acetonitrile (60 cm^3) was cooled to 0 °C and added slowly to sodium–mercury amalgam (0.12 g sodium, 5.2 mmol; 60 g mercury) and acetonitrile (30 cm^3) cooled to 0 °C. The solution was allowed to warm to room temperature with stirring and occasional vigorous shaking. The solution became blue, then green, and after stirring for 4 h appeared yellow-brown in colour. After filtering the solution several times, trimethylphosphine (1.7 cm^3, 15.5 mmol) was added and the mixture stirred for a further 2 h. The solution was filtered from a small quantity of white material, reduced to about one-half volume and allowed to stand at −20 °C, whereupon the complex was deposited as a yellow amorphous solid, yield 1.5 g (Found: C, 17.8; H, 4.2, Cl, 29.3; P, 13.1. $C_6H_{18}Cl_4P_2Ta$ requires C, 15.2; H, 3.8; Cl, 29.2, P, 12.7%). I.r. (Nujol): 1 415m, 1 295m, 1 250s, 950s, 880w, 855w, 765w, 720w, 703w, 655w, 548w, 454m, 410w, 320w, and 280s cm^{-1}.

Crystallography.—Crystals of both complexes were sealed in Lindemann capillaries and mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å) in a ω–2θ scan mode. The intensity data were corrected for Lorentz polarisation and absorption effects.

Crystal data. $[Ta_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$, $C_{12}H_{36}Cl_8P_4Ta_2$, $M = 949.88$, cubic, space group *Im*3, $a = 16.400\,0(4)$ Å, $U = 4\,410.9$ Å^3, $Z = 6$, $D_c = 2.144$ g cm^{-3}, $F(000) = 2\,047.63$, μ(Mo-K_α) = 61.15 cm^{-1}.

$[Nb_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$, $C_{12}H_{36}Cl_8P_4Nb_2$, $M = 773.3$, cubic, space group *Im*3, $a = 16.390(3)$ Å, $U = 4\,404.3$ Å^3, $Z = 6$, $D_c = 1.749$ g cm^{-3}, $F(000) = 2\,315.5$, μ(Mo-K_α) = 16.21 cm^{-1}.

The structures were solved from Patterson and electron-density syntheses and refined by full-matrix least-squares methods. Non-hydrogen atoms were assigned anisotropic thermal parameters and hydrogen atoms included in idealised positions with common isotropic thermal parameters.

The final *R* and *R'* values were 0.031 and 0.032 for the tantalum complex {691 observed data with $I > 3\sigma(I)$, 867 measured, weights $w = [\sigma(F)^2 + 0.001F^2]^{-1}$}, and 0.032 and 0.033 for the niobium complex {790 observed data with $I > 3\sigma(I)$, 885 measured, weights $w = [\sigma(F)^2 + 0.001F^2]^{-1}$}.* Non-hydrogen atomic co-ordinates are given in Table 3.

Computational Details.—The electronic structures of $[NbCl_4(\mu\text{-}Cl)_4(PH_3)_4]$, $[TaCl_4(\mu\text{-}Cl)_4(PH_3)_4]$, and the fragment $[NbCl_6(PH_3)_2]^{2-}$ were calculated using the SCF-scattered wave Xα method[27,28] with the program XASW of Case and co-workers.[29,30] The geometric structures of the niobium and tantalum dimers were adapted from the crystal structures, presented in this paper, of the analogous trimethylphosphine complexes by the replacement of the phosphine methyl groups by protons, Table 4. In both cases the dimers possess exact D_{2h} symmetry. The fragment complex ion $[NbCl_6(PH_3)_2]^{2-}$ was taken with the co-ordination geometry around the individual niobium atom in the dimer; that is, approximately square antiprismatic C_{2v} symmetry, Table 4.

The starting molecular potentials were constructed from a superposition of atomic charge densities using overlapping

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* During the preparation of this manuscript the structure of $[Nb_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ was reported[11] and the structure of $[Ta_2Cl_4(\mu\text{-}Cl)_4(PMe_3)_4]$ confirmed.[12] Accordingly full details of the fractional atomic co-ordinates, bond lengths, and bond angles are contained in the supplementary data.

atomic spheres.[31] In the case of the tantalum atom the atomic charge density was generated from a modified restricted Hartree-Fock program of Herman and Skillman.[32] The values of α used (Nb, 0.7038; Ta, 0.6932; Cl, 0.7233; P, 0.7262; H, 0.7773) were those of Schwarz[33] except in the case of tantalum where the value was obtained by interpolation. The 'atomic sphere radii', Table 4, were chosen by the method of Norman[34] as the atomic number radii reduced by a factor of 0.88. Partial wave expansions were included up to $l = 4$ for the metal atoms, $l = 1$ for the phosphorus and sulphur, and $l = 0$ for the hydrogen atoms. In the case of the fragment $[NbCl_6(PH_3)_2]^{2-}$ a Watson sphere of charge +2 and radius equal to that of the outer sphere was used. The scattered wave calculation was continued until the relative change in potential at all points in the molecule was less than 10^{-4}. Charge distributions were calculated using the charge partitioning method of Case and co-workers.[30,35]

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