

collected at  $-162 \pm 4$  °C, and the structure was solved by direct methods and Fourier techniques. Statistical tests and the successful solution and refinement<sup>23</sup> indicate the centrosymmetric space group to be correct.  $\psi$  scans of several reflections were not flat, so an analytical absorption correction was applied. All atoms, with the exception of the butyl group hydrogens, were located and their positional and thermal parameters (anisotropic for W, P, F, O, and C) refined by full-matrix least squares.<sup>24</sup> Hydrogen atoms were placed in idealized fixed positions for the final cycles. An isotropic extinction parameter introduced earlier did not differ significantly from zero and was omitted from the final cycles. A final difference Fourier revealed several peaks ( $1.2$ – $2.3$  e  $\text{\AA}^{-3}$ ) in the vicinity of the tungsten atoms but was otherwise featureless.

$\text{W}_2(\text{TFA})_4 \cdot 3\text{PMe}_3$ . Inside the drybox, a concentrated toluene solution of  $\text{W}_2(\text{TFA})_4$  was placed in an 8-mm Pyrex tube topped with a Kontes greaseless high-vacuum stopcock. This solution was carefully layered—first with a few millimeters of pure toluene and then with a toluene solution containing 3 equiv of  $\text{PMe}_3$ . The tube was sealed, removed from the drybox, and left undisturbed for 1 week. Large, dark-green crystals had formed by this time; they were filtered off, washed with a small amount of hexane, and dried in vacuo. A suitable fragment was obtained by cleaving a larger sample inside a nitrogen-filled drybag and transferring to the goniostat. A systematic search of a limited hemisphere of reciprocal space revealed an orthorhombic lattice with systematic absences of  $l = 2n + 1$  for  $0kl$  and  $h + k = 2n + 1$  for  $hk0$ . Statistical tests, the Patterson synthesis, and successful solution and refinement of the structure led to the assignment of the noncentric space group  $Pc2_1n$ .<sup>25</sup> Diffraction data were collected at

$-163 \pm 4$  °C, and the structure was solved by Patterson and Fourier techniques.  $\psi$  scans of several reflections were essentially flat, and due to the irregular shape of the crystal and its small size, no absorption correction was performed. The structure was refined by full-matrix least squares. All atoms, with the exception of the  $\text{PMe}_3$  hydrogens, were located and their positional and thermal parameters (anisotropic for W, P, F, O, and C) refined. The atomic coordinates reported are for the proper enantiomorph for the crystal chosen, based on residuals for both settings. Hydrogen atoms were placed in idealized staggered positions for the final cycles of the refinement. A secondary extinction parameter introduced in the final cycles did not differ significantly from zero. A final difference Fourier was essentially featureless; the two largest peaks of  $1.2$  and  $1.4$  e  $\text{\AA}^{-3}$  were found within  $0.5$  Å of the two tungstens. Numerous peaks of  $0.8$ – $1.2$  e  $\text{\AA}^{-3}$  were located in the vicinity of F atoms.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, calculated hydrogen atom positions, and structure factors for 2c and 3 (18 pages). Ordering information is given on any current masthead page. The complete structural reports (MSC82920, 2c; MSC82914, 3) are available, in microfiche form only, from the Chemistry Library, Indiana University.

- (22) Equivalent positions for  $I2/a$  are  $1/2, 1/2, 1/2$  and  $0, 0, 0 \pm x, y, z; 1/2 - x, y, -z$ .
- (23) All computations were performed with use of the Indiana University Molecular Structure Center XTEL program library. The XTEL library consists of local programs and code from J. A. Ibers (Northwestern University) and A. C. Larson (Los Alamos Scientific Laboratory).
- (24) Neutral-atom scattering factors were from: "International Tables for X-ray Crystallography"; Kynoch Press; Birmingham, England, 1974; Vol. IV. For hydrogen atoms, the values used were given by: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175.

- (25)  $Pc2_1n$  is a nonstandard setting of  $Pna2_1$ , with the following equivalent positions:  $x, y, z; 1/2 - x, y, 1/2 + z; 1/2 + x, 1/2 + y, 1/2 - z; -x, 1/2 + y, -z$ .

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## A Metal–Metal–Bonded Dinuclear Phosphine Complex of Niobium(IV) Chloride, $[\text{NbCl}_2(\text{PMe}_2\text{Ph})_2]_2(\mu\text{-Cl})_4$

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The crystal structure of a compound that was expected to be (and in solution probably is)  $\text{NbCl}_4(\text{PMe}_2\text{Ph})_2$  has revealed a remarkable and unprecedented binuclear structure. The molecule is centrosymmetric and consists of two square-antiprismatic  $\text{Nb}(\text{PMe}_2\text{Ph})_2\text{Cl}_2$  units sharing a square  $\text{Cl}_4$  face. The outer square faces, which have a  $\text{trans P}_2\text{Cl}_2$  ligand set, are staggered with respect to the central  $\text{Cl}_4$  face. The Nb–Nb distance, 2.838 (1) Å, indicates that a metal–metal single bond is formed. On dissolving in  $\text{CH}_2\text{Cl}_2$  or THF, this red-brown compound immediately gives a green solution, suggesting that dissociation to  $\text{NbCl}_4(\text{PMe}_2\text{Ph})_2$  molecules accompanies dissolution. The crystals belong to space group  $P2_1/n$  with unit cell dimensions of  $a = 8.545$  (2) Å,  $b = 14.277$  (3) Å,  $c = 19.634$  (2) Å,  $\beta = 101.33$  (1)°,  $V = 2349$  (2) Å<sup>3</sup>, and  $Z = 2$ . The structure was refined to  $R = 0.0385$  and  $R_w = 0.0588$ . Some mean distances are Nb–Cl<sub>b</sub> = 2.541 [6] Å, Nb–Cl<sub>t</sub> = 2.484 [10] Å, and Nb–P = 2.700 [2] Å.

### Introduction

In the course of a lengthy study of the mixed halo–phosphine complexes of tantalum and niobium in oxidation states of IV or less, we have encountered a result sufficiently novel and unexpected that we wish to report it separately. The main body of our work on the stabilities and stereochemistries of  $\text{MX}_n(\text{PR}_3)_x$  species in both the solid state and solution, which is not yet complete, will be reported later.

Because of some unusual features in the behavior of  $\text{NbCl}_4(\text{PMe}_2\text{Ph})_2$  in solution, we decided to determine the crystal structure to see if that information would be helpful.

We have found that in the crystal the molecules are dinuclear with an unprecedented type of structure. That structure is described and discussed here.

### Experimental Section

**Preparation.** All manipulations (including later handling of the crystalline product) were carried out in an atmosphere of argon. Niobium(V) chloride and phenyldimethylphosphine were purchased from Aldrich and Strem Chemicals, Inc., respectively, and used as received.

To a 100-mL three-neck flask were added  $\text{NbCl}_5$  (2.0 g, 7.4 mmol), 40 mL of toluene, and  $\text{PMe}_2\text{Ph}$  (3.5 mL, 24.5 mmol). Sodium

**Table I.** Summary of X-ray Diffraction Analysis for  $\text{Nb}_2\text{Cl}_8(\text{PMe}_2\text{Ph})_4\cdot\text{C}_6\text{H}_6$ 

formula	$\text{Nb}_2\text{Cl}_8\text{P}_4\text{C}_{38}\text{H}_{50}$
$M_r$	1100.15
space group	$P2_1/n$
$a$ , Å	8.545 (2)
$b$ , Å	14.277 (3)
$c$ , Å	19.634 (2)
$\beta$ , deg	101.33 (1)
$V$ , Å <sup>3</sup>	2349 (2)
$Z$	2
$d_{\text{calcd}}$ , g/cm <sup>3</sup>	1.556
cryst size, mm	$0.3 \times 0.4 \times 0.4$
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	10.877
data colln instrument	Enraf-Nonius CAD-4
radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
temp, °C	22
scan method	$\omega-2\theta$
data colln range	$2 \leq 2\theta \leq 50$ ; $+h, +k, \pm l$
no. of unique data	3414
no. of data with $F_o^2 \geq 3\sigma(F_o^2)$	2968
no. of parameters refined	232
$R^a$	0.0385
$R_w^b$	0.0588
quality-of-fit indicator <sup>c</sup>	1.746
largest shift/esd, final cycle	0.84

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2] / \sum w|F_o|^2$ . <sup>c</sup> Quality of fit =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$ .

**Table II.** Positional and Isotropic-Equivalent Thermal Parameters for  $\text{Nb}_2\text{Cl}_8(\text{PMe}_2\text{Ph})_4\cdot\text{C}_6\text{H}_6^a$ 

atom	$x$	$y$	$z$	$B$ , Å <sup>2</sup>
Nb	0.03086 (5)	0.07573 (3)	0.04757 (2)	2.459 (9)
Cl(1)	-0.0560 (2)	0.09495 (9)	-0.08271 (7)	3.11 (3)
Cl(2)	-0.2428 (2)	-0.00117 (9)	0.00946 (7)	3.26 (3)
Cl(3)	-0.1437 (2)	0.2145 (1)	0.04476 (7)	3.69 (3)
Cl(4)	0.2662 (2)	0.0877 (1)	0.14497 (7)	3.63 (3)
P(1)	0.2022 (2)	0.2279 (1)	0.02636 (8)	3.58 (3)
P(2)	-0.0743 (2)	0.0764 (1)	0.16867 (7)	3.29 (3)
C(1)	0.1238 (7)	0.2975 (4)	-0.0508 (3)	3.6 (1)
C(2)	0.0248 (7)	0.3752 (4)	-0.0481 (3)	4.2 (1)
C(3)	-0.0307 (9)	0.4264 (5)	-0.1084 (4)	5.6 (2)
C(4)	0.0060 (9)	0.4008 (5)	-0.1712 (4)	5.6 (2)
C(5)	0.101 (1)	0.3243 (5)	-0.1736 (4)	6.0 (2)
C(6)	0.1601 (8)	0.2719 (5)	-0.1156 (3)	4.8 (2)
C(7)	0.4104 (8)	0.2078 (5)	0.0193 (5)	6.2 (2)
C(8)	0.223 (1)	0.3129 (5)	0.0994 (4)	5.6 (2)
C(9)	-0.0286 (7)	0.1820 (4)	0.2211 (3)	3.9 (1)
C(10)	-0.1271 (8)	0.2609 (5)	0.2096 (3)	4.9 (2)
C(11)	-0.088 (1)	0.3419 (5)	0.2503 (4)	6.4 (2)
C(12)	0.049 (1)	0.3424 (5)	0.3045 (4)	6.7 (2)
C(13)	0.144 (1)	0.2621 (6)	0.3198 (4)	6.9 (2)
C(14)	0.1059 (9)	0.1828 (5)	0.2757 (4)	5.4 (2)
C(15)	-0.2904 (8)	0.0645 (5)	0.1606 (3)	4.7 (1)
C(16)	0.0008 (9)	-0.0203 (4)	0.2286 (3)	4.7 (2)
C(17)	0.640 (1)	0.4606 (9)	0.0427 (6)	5.7 (3)*
C(18)	0.588 (2)	0.4275 (8)	-0.0269 (7)	5.9 (3)*
C(19)	0.459 (2)	0.464 (1)	-0.0634 (6)	6.3 (3)*
C(17A)	0.395 (2)	0.498 (1)	0.9334 (9)	4.6 (4)*
C(18A)	0.626 (2)	0.444 (1)	0.0095 (9)	4.6 (4)*
C(19A)	0.534 (3)	0.438 (1)	0.945 (1)	5.8 (4)*

<sup>a</sup> Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $4/3(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23})$ .

amalgam (0.17 g, 7.4 mmol of Na in 5 mL of Hg) was then added and the mixture stirred vigorously. In 20 min the initial red color changed to green and then slowly to brown. After 10 h of stirring, the opaque brown solution was decanted and the reddish precipitate, which contains NaCl, was extracted with three 20-mL portions of THF. All solutions were combined and evaporated under vacuum to give an oily brown residue.

This residue was then dissolved in benzene (15 mL), and the solution was filtered into a Schlenk tube and covered with a layer of hexane

**Table III.** Selected Interatomic Distances (Å) in the Molecule of  $\text{Nb}_2\text{Cl}_8(\text{PMe}_2\text{Ph})_4^a$ 

A. Bonding Contacts			
Nb-Nb'	2.838 (1)	Nb-Cl(3)	2.474 (1)
Cl(1)	2.534 (1)	Cl(4)	2.494 (1)
Cl(1)'	2.530 (1)	P(1)	2.697 (1)
Cl(2)	2.558 (1)	P(2)	2.702 (1)
Cl(2)'	2.542 (1)		
B. Short Nonbonding Contacts			
Cl(1)-Cl(2)	2.973 (1)	Cl(2)-Cl(4)	3.243 (2)
Cl(2)'	2.989 (1)	P(1)	3.345 (2)
Cl(3)	3.237 (2)	P(2)	3.362 (2)
Cl(4)	3.264 (1)	Cl(3)-P(1)	3.053 (2)
P(1)	3.346 (2)	P(2)	3.097 (2)
P(2)	3.288 (2)	Cl(4)-P(1)	3.038 (2)
Cl(2)-Cl(3)	3.233 (1)	P(2)	3.040 (2)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

**Table IV.** Selected Bond Angles (deg) in the Molecule of  $\text{Nb}_2\text{Cl}_8(\text{PMe}_2\text{Ph})_4^a$ 

Nb'-Nb-Cl(1)	55.85 (2)	Cl(1)'-Nb-P(1)	142.96 (4)
Cl(1)'	55.99 (3)	P(2)	77.78 (4)
Cl(2)	55.92 (3)	Cl(2)-Nb-Cl(2)'	112.38 (3)
Cl(2)'	56.46 (3)	Cl(3)	79.91 (4)
Cl(3)	124.21 (3)	Cl(4)	143.76 (4)
Cl(4)	125.05 (3)	P(1)	142.48 (4)
P(1)	123.25 (3)	P(2)	79.39 (4)
P(2)	122.06 (3)	Cl(2)'-Nb-Cl(3)	143.51 (4)
Cl(1)-Nb-Cl(1)'	111.83 (3)	Cl(4)	80.18 (4)
Cl(2)	71.44 (3)	P(1)	79.28 (4)
Cl(2)'	72.15 (3)	P(2)	141.06 (4)
Cl(3)	80.51 (4)	Cl(3)-Nb-Cl(4)	110.74 (4)
Cl(4)	143.00 (4)	P(1)	72.22 (4)
P(1)	79.46 (4)	P(2)	73.36 (4)
P(2)	143.68 (4)	Cl(4)-Nb-P(1)	71.52 (4)
Cl(1)'-Nb-Cl(2)	71.95 (4)	P(2)	71.49 (4)
Cl(2)'	71.78 (4)	P(1)-Nb-P(2)	114.68 (4)
Cl(3)	142.74 (4)	Nb'-Cl(1)-Nb	68.17 (3)
Cl(4)	81.04 (4)	Nb'-Cl(2)-Nb	67.62 (3)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

(20 mL). As the solvent layers interdiffused, a green band moved upward and large red-brown crystals were formed. After 1 week the liquid was decanted and the crystalline solid washed with benzene. Yield: 2.5 g (ca. 60%).

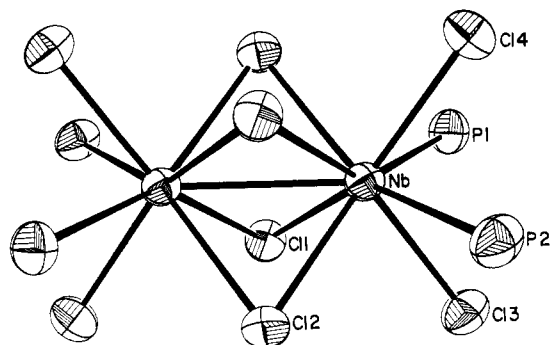
**X-ray Crystallography.** General procedures that have already been fully described elsewhere<sup>1</sup> were used to determine the crystal structure. The crystal parameters and basic information about data collection and structure refinement are summarized in Table I. Polarization and Lorentz corrections were applied to the intensity data; absorption and extinction corrections were not made.

The position of the Nb atom was obtained from a three-dimensional Patterson function. The remainder of the structure was determined by subsequent series of difference Fourier syntheses and least-squares refinements. The molecule of benzene present in the crystal lattice and residing on a crystallographic inversion center was found to be disordered over two positions. They were related to each other by a rotation of about 30° around the axis perpendicular to the ring and passing through its center. The fractional occupancy for each orientation was determined by least-squares refinement and found to be equal approximately to  $5/8$  and  $3/8$ , respectively. Refinement of the structure was completed with all atoms except those of the disordered solvent molecule having anisotropic thermal parameters. The final values of  $R$  and  $R_w$  were equal to 0.0385 and 0.0588, respectively. The largest residual peak in the last difference Fourier map had an intensity of ca.  $0.5 \text{ e}/\text{Å}^3$ . A table of observed and final calculated structure factors is available as supplementary material.

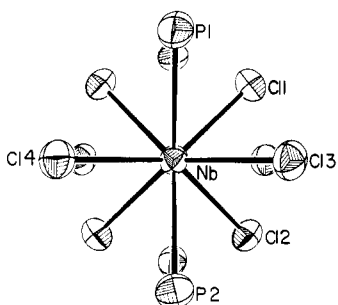
## Results and Discussion

The final atomic parameters are listed in Table II except for the anisotropic thermal parameters which are available as

(1) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* 1979, 18, 3558.



**Figure 1.** ORTEP drawing of the central portion of the  $\text{Nb}_2\text{Cl}_8(\text{PMe}_2\text{Ph})_4$  molecule. There is a crystallographic inversion center relating the halves of the molecule. Each atom is represented by its ellipsoid of thermal vibration at the 40% probability level. Substituents on the phosphorus atoms were omitted for clarity.



**Figure 2.** View of the central portion of the molecule of  $\text{Nb}_2\text{Cl}_8(\text{PMe}_2\text{Ph})_4$  along the Nb-Nb axis.

supplementary material. Selected bond distances and angles are listed in Tables III and IV. The molecule of  $\text{Nb}_2\text{Cl}_8(\text{PPhMe}_2)_4$ , which, excluding the methyl and phenyl groups, is represented by its ORTEP drawing in Figure 1, resides on a crystallographic inversion center. A figure defining the numbering scheme within the  $\text{PMe}_2\text{Ph}$  ligands is available in the supplementary material. The coordination sphere around the  $\text{Nb}_2$  core consists of two square antiprisms sharing a square face. The other square faces are almost planar (the ligands are located 0.022–0.023 Å away from the least-squares plane) and parallel to the common one (dihedral angle equals  $0.4^\circ$ ), which is rigorously planar because it contains the inversion center. The square bases have edge lengths of 3.057 [7] and 2.981 [8] Å for the terminal and central ones, respectively. The adjacent squares are fully staggered with deviations from the ideal torsional angle ( $45^\circ$ ) not exceeding  $1.7^\circ$ . The two sets of terminal ligands are rigorously eclipsed. A view of the molecule down the Nb-Nb axis is shown in Figure 2. The Nb-Cl(bridge) distances are appreciably longer than the Nb-Cl(terminal) distances, with mean values of 2.541 [6] and 2.484 [10] Å, respectively.

The Nb-Nb distance, 2.838 (1) Å, indicates that a bond is formed between the metal atoms. For nonbonded niobium(IV) ions a considerable repulsive force would be expected, leading to a considerably longer Nb...Nb distance as well as evidence of repulsion in the Cl-Nb-Cl angles. In fact the two  $\text{Cl}_b\text{-Nb-Cl}_b$  angles, 111.83 (3) and 112.38 (3) $^\circ$ , are slightly larger than the  $\text{Cl}(3)\text{-Nb-Cl}(4)$  angle, 110.74 (4) $^\circ$ , which is the opposite of what would be expected if the metal atoms were repelling each other.

We do not believe that the dinuclear molecule we have found in the solid state exists in solution in any significant concentration or is otherwise relevant to the behavior of  $\text{MX}_4(\text{PR}_3)_2$  compounds in solution.  $\text{Nb}_2\text{Cl}_8(\text{PMe}_2\text{Ph})_4$  dissolves in  $\text{CH}_2\text{Cl}_2$

and THF but with a drastic change of color to green, suggesting strongly a dissociation to mononuclear  $\text{NbCl}_4(\text{PMe}_2\text{Ph})_2$ . The green solution in  $\text{CH}_2\text{Cl}_2$  has a 10-line ESR spectrum consistent with this. It dissolves appreciably in benzene only when additional  $\text{PMe}_2\text{Ph}$  is present, and we believe that this is because some soluble species of coordination number 7 or higher, e.g.,  $\text{NbCl}_4(\text{PMe}_2\text{Ph})_3$ , is formed.

There are but few prior examples of dinuclear structures with four monatomic ligands bridging the metal ions.<sup>2,3</sup> In many of them, some or all of the bridging atoms are hydrogen atoms. Examples are  $\text{M}_2(\mu\text{-H})_4\text{H}_4\text{L}_4$ , where  $\text{M} = \text{Re}^4$  or  $\text{Ru}^5$  and  $\text{L} =$  a phosphine, and  $\text{Ta}_2(\mu\text{-H})_2(\mu\text{-Cl})_2\text{Cl}_4(\text{PMe}_3)_4$ .<sup>6</sup> Bridging RS groups occur in the  $[\text{ArM}(\text{SR})_2]_2$  molecules with  $\text{M} = \text{V}$ ,<sup>7</sup>  $\text{Ar} = \eta^5\text{-C}_5\text{H}_5$ , and  $\text{R} = \text{CH}_3$  or  $(\text{CF}_3\text{C}=\text{CCF}_3)_{1/2}$  and with  $\text{M} = \text{Mo}$ ,<sup>8</sup>  $\text{Ar} = \eta^5\text{-C}_5\text{H}_5$ , and  $\text{R} = \text{CH}_3$ ,  $(\text{CH}_2\text{CH}_2)_{1/2}$ , or  $(\text{CHMeCH}_2)_{1/2}$ , as well as in the cation<sup>8b</sup> with  $\text{M} = \text{Mo}$ ,  $\text{Ar} = \text{CH}_3\text{Ph}$ ,  $\text{R} = \text{CH}_3$ . Structural studies have been carried out on one  $\text{Re}^4$  and one  $\text{Ta}^6$  compound and on several molybdenum compounds.<sup>8</sup>

We believe that  $\text{Nb}_2(\mu\text{-Cl})_4\text{Cl}_4(\text{PMe}_2\text{Ph})_4$  is the first proven example of a compound with four bridging halide ions.<sup>14</sup> Such a structure was proposed<sup>9</sup> for  $[\eta^5\text{-C}_5\text{H}_5\text{TiCl}_2]_2$  but has never been verified.<sup>10</sup> In  $\text{Nb}_2(\mu\text{-Cl})_4\text{Cl}_4(\text{PMe}_2\text{Ph})_4$  there is considerably more crowding than in the previously reported compounds with quadruple bridging, where some of the ligands are hydrogen atoms or are  $\eta^5\text{-C}_5\text{H}_5$  groups, which are less sterically demanding than  $\text{Cl}_2(\text{PMe}_2\text{Ph})_2$ .

As a final interesting point, we have subsequently determined the structures of crystalline  $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$  and  $\text{NbCl}_4(\text{PEtPh}_2)_2$ . They are not isomorphous with  $\text{Nb}_2\text{Cl}_8(\text{PMe}_2\text{Ph})_4$ . The Ta compound is mononuclear with a cis disposition of the phosphine ligands, while the Nb compound is mononuclear with a trans structure. It may be noted that earlier studies<sup>11-13</sup> of  $\text{NbX}_4(\text{PR}_3)_2$  compounds are very few in number and are of very limited scope; none have provided crystallographic structural information.

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**Registry No.**  $\text{Nb}_2(\mu\text{-Cl})_4\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ , 88801-81-4;  $\text{NbCl}_5$ , 10026-12-7; Nb, 7440-03-1.

**Supplementary Material Available:** A figure defining the numbering scheme within the  $\text{PMe}_2\text{Ph}$  ligand and tables of anisotropic thermal parameters, complete bond lengths and angles, and structure factors (20 pages). Ordering information is given on any current masthead page.

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