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New Synthetic Routes for the Preparation of Niobium(III) and Tantalum(III) Triangular Cluster Compounds

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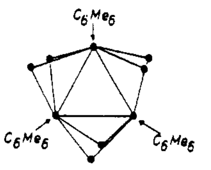
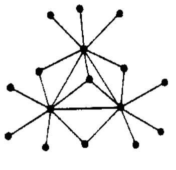
Six triangular cluster compounds, four of niobium and two of tantalum, are reported. These complexes contain six d electrons available for forming three metal–metal bonds, and their structures were determined by X-ray crystallography. Compounds $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PMe_2Ph)_3]\cdot 2THF$ (**1**) $[HPEt_3][Nb_3Cl_{10}(PEt_3)_3]$ (**2**) and $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PEt_3)_3]\cdot 2THF$ (**3**) were prepared by the magnesium reduction of $NbCl_4(THF)_2$ in the presence of the appropriate phosphine. Compound **1** crystallizes in $P\bar{1}$ with $a = 14.033$ (5) Å, $b = 14.185$ (5) Å, $c = 20.464$ (6) Å, $\alpha = 77.59$ (3)°, $\beta = 87.55$ (3)°, $\gamma = 82.36$ (3)°, $V = 3943$ (2) Å^3, and $Z = 2$. Compound **2** crystallizes in $P2_1/n$ with $a = 11.887$ (3) Å, $b = 20.584$ (6) Å, $c = 18.718$ (5) Å, $\beta = 97.42$ (2)°, $V = 4542$ (2) Å^3, and $Z = 4$. Compound **3** crystallizes in $P\bar{1}$ with $a = 13.969$ (8) Å, $b = 22.949$ (8) Å, $c = 13.732$ (6) Å, $\alpha = 91.88$ (4)°, $\beta = 117.75$ (4)°, $\gamma = 84.52$ (4)°, $V = 3878$ (6) Å^3, and Z = 2. $Ta_3Cl_9(THF)_4\cdot C_6H_6\cdot THF$ (**4**) and $Na[Ta_3Cl_{10}(THF)_3]$ (**5**) were synthesized by the reduction of $TaCl_5$ with 2 equiv of Na/Hg in aromatic solvents and subsequent addition of THF. Compound **4** crystallizes in $C2/c$ with $a = 28.847$ (8) Å, $b = 22.226$ (7) Å, $c = 12.122$ (3) Å, $\beta = 112.90$ (2)°, $V = 7159$ (7) Å^3, and $Z = 8$. Compound **5** crystallizes in $P2_13$ with $a = 15.280(3)$ Å, $V = 3567$ (3) Å^3, and $Z = 4$. $Na[Nb_3Cl_{10}(THF)_3]\cdot 3THF$ (**6**) was synthesized by the reduction of $NbCl_4(THF)_2$ with 1 equiv of Na/Hg in THF. This compound crystallizes in $P2_1/c$ with $a = 12.211$ (4) Å, $b = 14.593$ (3) Å, $c = 22.349$ (5) Å, $\beta = 95.01$ (2)°, $V = 3967$ (3) Å^3, $Z = 4$. In **1–3**, the anions have all phosphorus atoms trans to the μ_3-Cl atom, and thus the central $Nb_3Cl_{10}P_3$ cores have C_{3v} ($3m$) symmetry. The Nb–Nb distances are all in the range 2.96–2.97 Å. In **6**, the THF ligands are unsymmetrically arranged with only one trans and the other two cis to the μ_3-Cl atom, although they are distributed one to each Nb atom. The average Nb–Nb distance is 2.933 [10] Å. In **5**, there is one THF on each metal atom and all are cis to the μ_3-Cl atom in accord with crystallographic C_3 (3) symmetry. The Ta–Ta distance is 2.875 (2) Å. In **4** the distribution of THF ligands is without symmetry (two cis and two trans to μ_3-Cl; two on one Ta atom and one each on the others), and the Ta–Ta distances to the doubly substituted Ta atom, 2.868 (1) and 2.850 (1) Å, are appreciably shorter than the other one, 2.932 (1) Å. The Nb analogue of **4** has been prepared, but its extreme sensitivity to air and moisture discouraged further study of it.

Introduction

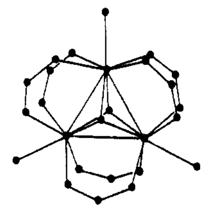
In 1980, when the chemistry of metal–metal-bonded trinuclear Mo and W complexes was beginning its rapid expansion, Cotton and Müller published a paper classifying the early-transition-metal trinuclear clusters into three categories:[1] without capping ligands (I), with one capping ligand (II), and with two capping ligands (III). The diagrams below represent the arrangement of the ligands around the triangle of the metal atoms for each of these categories. The most common structure of trinuclear clusters for Mo, W, Nb, and Ta has been II, where one capping ligand and three edge-bridging ligands are present. In these complexes it is known that the number of valence electrons available to form metal–metal bonds can vary. Mo and W clusters containing six or eight electrons are known[1,2] whereas Nb trimers with six,[3] seven[4] and eight[3b,5] electrons have all been synthesized. The following work describes new Nb and Ta trimers of type II where the neutral ligands are either monodentate phosphines or tetrahydrofuran (THF) and the number of cluster electrons (i.e., electrons available for metal-metal bonding) is in each case 6. Therefore, *formally* there are three single bonds around the equilateral triangle of metal atoms in each case.



I



II



III

It is pertinent to note that the entire subject of discrete trinuclear cluster chemistry of niobium and tantalum is still very new. The first type II cluster, $Nb_3Cl_7(PMe_2Ph)_6$, was reported only in 1987.[5a] This is an eight-electron species, and the first six-electron species were first described even more recently (1988) when the $[M_3Cl_{10}(PEt_3)_3]^-$ anions[3a] were reported. Thus the six new compounds described in this paper constitute a major addition (they triple the previous number of compounds) to this emerging field. In particular, the two new tantalum species show that tantalum is probably comparable to niobium in its ability to form compounds with the $Ta_3(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_3$ core. This was a moot point previously when only one such tantalum compound was known.

Experimental Section

All manipulations were carried out using standard Schlenk techniques or glovebox procedures. $NbCl_5$ and $TaCl_5$ were purchased from Aesar Chemicals and used without further purification. PEt_3, PMe_2Ph, and $Bu^n{}_3SnH$ were purchased from Strem Chemicals, Mg turnings and sodium metal were purchased from Fischer Scientific, and mercury was triply distilled grade by D. F. Goldsmith Chemical and Metal Corp. and was degassed prior to use. Sodium amalgam for the reactions was measured and transferred into the reaction flask via a syringe, which was pretreated with the solvent used during the reaction.

All the solvents were kept over molecular sieves for at least 4 weeks prior to use. Benzene, toluene, tetrahydrofuran, and hexane were further dried over potassium–sodium benzophenone ketyl and were allowed to reflux over the drying agent at least 8 h before use. $NbCl_4(THF)_2$ was prepared by following the published procedure.[6]

Syntheses: $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PMe_2Ph)_3]\cdot 2THF$ (1). $NbCl_4(THF)_2$ (1.52 g, 4 mmol), Mg turnings (46 mg, 2 mmol), and PMe_2Ph (1.2 mL, 8 mmol) were stirred in THF (40 mL) for 2 days. A purple crystalline precipitate (ca. 0.5 g) was filtered out, and the brown filtrate was layered in a long Schlenk tube with 30 mL of hexane. After 2-3 weeks of standing, purple-red crystals of the formula $[Mg_2Cl_3(THF)_6][Nb_3CL_{10}(PMe_2Ph)_3]\cdot 2THF$ started growing, and the solution

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[1] Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.

[2] For some representative papers giving earlier references, see: (a) Birnbaum, A.; Cotton, F. A.; Dori, A.; Kapon, M.; Marler, D.; Reisner, G. M.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 2405. (b) Cotton, F. A. *Polyhedron* **1986**, *5*, 3. (c) Cotton, F. A.; Llusar, R.; Eagle, C. T. *J. Am. Chem. Soc.* **1989**, *111*, 4332.

[3] (a) Cotton, F. A.; Kibala, P. A.; Roth, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 298. (b) Cotton, F. A.; Diebold, M. P.; Feng, X.; Roth, W. J. *Inorg. Chem.* **1988**, *27*, 3413.

[4] (a) Schnering, H. G. v.; Wohrle, H.; Schafer, H. *Naturwissenschaften* **1961**, *48*, 159. (b) Simon, A.; Schnering, H. G. v. *J. Less-Common Met.* **1966**, *11*, 31.

[5] Cotton, F. A.; Diebold, M. P.; Roth, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 2833.

[6] Manzer, L. *Inorg. Chem.* **1977**, *16*, 525.

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Table I. Crystal Data for $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PMe_2Ph)_3]\cdot 2THF$ (**1**), $[HPEt_3][Nb_3Cl_{10}(PEt_3)_3]$ (**2**), $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PEt_3)_3]\cdot 2THF$ (**3**), $Ta_3Cl_9(THF)_4\cdot C_6H_6\cdot THF$ (**4**), $Na[Ta_3Cl_{10}(THF)_3]$ (**5**), and $Na[Nb_3Cl_{10}(THF)_3]\cdot 3THF$ (**6**)

	1	**2**	**3**	**4**	**5**	**6**
formula	$Nb_3Cl_{13}Mg_2O_8$-$P_3C_{56}H_{97}$	$Nb_3Cl_{10}P_4C_{24}H_{61}$	$Nb_3Cl_{13}Mg_2O_8$-$P_3C_{50}H_{109}$	$Ta_3Cl_9O_5C_{26}H_{46}$	$Ta_3Cl_{10}NaO_3$-$C_{12}H_{24}$	$Nb_3Cl_{10}NaO_6$-$C_{24}H_{48}$
fw	1779.55	1106.90	1719.97	1300.57	1136.69	1088.88
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_13$	$P2_1/c$
a, Å	14.033 (5)	11.887 (3)	13.969 (8)	28.847 (8)	15.280 (3)	12.211 (4)
b, Å	14.185 (5)	20.584 (6)	22.949 (8)	22.226 (7)	15.280 (3)	14.593 (3)
c, Å	20.464 (6)	18.718 (5)	13.732 (6)	12.122 (3)	15.280 (3)	22.349 (5)
α, deg	77.59 (3)	90.0	91.88 (4)	90.0	90.0	90.0
β, deg	87.55 (3)	97.42 (2)	117.75 (4)	112.90 (2)	90.0	95.01 (2)
γ, deg	82.36 (3)	90.0	84.52 (4)	90.0	90.0	90.0
V, Å^3	3943 (2)	4542 (2)	3878 (6)	7159 (7)	3567 (3)	3967 (3)
Z	2	4	2	8	4	4
d_{calc}, g/cm^3	1.499	1.619	1.473	2.408	2.116	1.823
μ(Mo Kα), cm^{-1}	9.739	14.636	9.872	97.360	98.562	15.411
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)					
temp, °C	20	20	20	−80	−80	−80
trans factors: max; min	0.9996; 0.8402	0.9995; 0.7901	0.9996; 0.9507	0.9999; 0.9555	0.9989; 0.7825	0.9995; 0.6954
R^a	0.054	0.041	0.083	0.0340	0.0385	0.050
$R_w{}^b$	0.070	0.068	0.115	0.0412	0.0604	0.065

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

was shaken and kept in a refrigerator at −10 °C for another 2 or 3 weeks (yield: ca. 0.3 g, 13%).

$[HPEt_3][Nb_3Cl_{10}(PEt_3)_3]$ (2). $NbCl_4(THF)_2$ (1.52 g, 4 mmol), Mg turnings (50 mg, 2.06 mmol), and PEt_3 (1.2 mL, 8 mmol) were stirred in a 30 mL of 1:1 mixture of THF/toluene at room temperature. The brown solution gradually changed to green. After several hours, Mg turnings dissolved completely and small green acicular crystals were formed. The quantity of the crystals gradually reached a maximum in ca. 12 h and then they redissolved in about 1 day to form a green-brown solution. Hexane was added and the solution was kept in a refrigerator at −10 °C for several days. Brown fiberlike crystals and purple-red platelike small crystals were isolated by filtration, and redissolved in THF (15 mL). The solution was filtered again and layered in a long Schlenk tube with 20 mL of hexane. Purple-red needle-like crystals of the formula $[HPEt_3][Nb_3Cl_{10}(PEt_3)_3]$ started growing in about a week (yield: ca. 0.5 g, 34%).

$[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PEt_3)_3]\cdot 2THF$ (3). $NbCl_4(THF)_2$ (1.52 g, 4 mmol), Mg turnings (50 mg, 2.06 mmol), PEt_3 (1.2 mL, 8 mmol) were stirred in 25 mL THF for 24 hours. The Mg turnings disappeared in several hours leaving a green solution and a large quantity of greenish blue fiberlike crystalline precipitate (ca. 0.76 g). The precipitate was removed by filtration, and the filtrate was layered with 40 mL of hexane in a Schlenk tube. Red-brown platelike crystals started growing in about a fortnight along with large clusters of brown crystalline material. Characterization of the brown crystals is still in progress. The red-brown crystals were shown to be $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PEt_3)_3]\cdot 2THF$ by X-ray crystallography.

$Ta_3Cl_9(THF)_4\cdot C_6H_6\cdot THF$ (4). Method A. A 100-mL three-neck, round-bottom flask containing a stirring bar was charged with 2.00 g (5.58 mmol) of $TaCl_5$ and 50 mL of benzene. While this mixture was stirred, 5.6 mL of 2 M Na/Hg was syringed into the flask. The yellow color of $TaCl_5$ immediately started to fade and a brown-black precipitate was formed. The mixture was stirred for 2 h. The black precipitate was then allowed to settle, much of the benzene (ca. 35 mL) was decanted via cannula, and 20 mL of THF was added. After an additional 1.5 h of stirring the green solution that had formed was filtered through Celite. The mercury waste was washed with 20 mL of THF and filtered, and the filtrate was added to the previous solution. About 20 mL of the above solution was placed in a 60-mL Schlenk tube and layered with 20 mL of hexane. After complete diffusion of the hexane layer, the solution was placed in a refrigerator at 10 °C for 35 days. Small green acicular crystals of **4** precipitated from the solution.

$Ta_3Cl_9(THF)_4\cdot C_6H_6\cdot THF$ (4). Method B. A 100-mL round-bottom flask equipped with a gas inlet and a stirring bar was charged with 2.00 g (5.58 mmol) of $TaCl_5$. Addition of 50 mL of benzene formed a yellow slurry. The solution was cooled to ca. 20 °C and 1.5 mL (5.6 mmol) of $Bu^n{}_3SnH$ was added. Addition of the $Bu^n{}_3SnH$ caused an immediate color change to dark green. The solution was warmed and stirred at room temperature for 20 h. After the stirring was stopped, a green solution and a black-green precipitate were observed. The green solution was decanted and the precipitate was dissolved in 25 mL of THF. Immediately upon addition of THF, most of the precipitate disappeared and a green solution was formed. This solution was stirred for an additional 2 h and filtered through 2 cm of Celite. The volume of the filtrate was reduced to ca. 35 mL and layered with 20 mL of hexane. After 10 days, green crystals of the product were formed. Approximate yield: 25%.

$Na[Ta_3Cl_{10}(THF)_3]$ (5). A 2.0-g (5.58-mmol) sample of $TaCl_5$ and a stirring bar were placed in a 125-mL round-bottom flask containing a gas inlet. Then 100 mL of toluene was added to the flask, 5.6 mL of 2 M Na/Hg was syringed into the flask, and the mixture was stirred vigorously for 6 h. After the stirring was stopped, a black-brown precipitate and a clear solution were observed. A 20-mL aliquot of the toluene was decanted, and 20 mL of THF was added to the solution. Upon addition of THF, a green solution began to form. This solution was stirred for an additional 4 h and filtered via cannula through 2 cm of Celite. The volume of this solution was reduced, in vacuo, to 15 mL and layered with 20 mL of hexane. The crystalline $Na[Ta_3Cl_{10}(THF)_3]$ (1.0 g, 20% yield) was recovered from the reaction. An attempt to collect a second batch of product by dropwise addition of hexane to the filtrate resulted in an oily substance.

Prismatic crystals suitable for X-ray structure determination were grown by slow diffusion of hexane into the toluene solution containing the product.

$Na[Nb_3Cl_{10}(THF)_3]\cdot 3THF$ (6). A 3.79-g (10-mmol) sample of $NbCl_4(THF)_2$ and Na/Hg (10 mmol) were stirred in 40 mL of THF for 10 h. The resulting green slurry was filtered through a 4–5.5-μm fritted funnel and the filtrate was reduced to 20 mL and layered first with 10 mL of THF and then with 20 mL of hexane. After about a fortnight, dark brown crystals of the formula $Na[Nb_3Cl_{10}(THF)_3]\cdot 3THF$ were isolated by filtration (yield: 0.55 g, 15%).

Reaction of $NbCl_5$ with $Bu^n{}_3SnH$. A 100-mL round-bottom flask equipped with a gas inlet was charged with 2.0 g (7.4 mmol) of $NbCl_5$. Addition of 45 mL of benzene formed an orange solution and some orange precipitate. When 2.0 mL (7.4 mmol) of $Bu^n{}_3SnH$ was added to this slurry, the color of the solution began to change slowly to dark brown. The reaction mixture was stirred for 2 h. After stirring was stopped, a brown precipitate and a pale yellow benzene solution were observed. The solution was decanted, and the brown precipitate was dissolved in 40 mL of THF. Upon addition of THF to the brown precipitate, a yellow precipitate and a dark orange solution were formed. The orange solution was decanted into a Schlenk tube and layered with 30 mL of hexane. Upon diffusion of the hexane into the orange solution, red crystals were formed. The unit cell dimensions of one of these crystals were determined as a = 29.24 Å, b = 22.48 Å, c = 12.13 Å, α = 90.1°, β = 112.6°, γ = 89.9°, and V = 7362 Å^3. The yellow precipitate from the original reaction was washed eight times with 10 mL of fresh THF and pumped overnight at room temperature. The microanalysis showed this yellow precipitate to be the known $NbCl_4(THF)_2$ compound (yield 48%). Anal. Found (calcd): Nb, 23.36 (24.54); Cl, 38.18 (37.47); C, 25.05 (25.33); H, 4.22 (4.22).

X-ray Crystallography. These air-sensitive Nb and Ta trimer crystals were examined under a layer of mineral oil that was previously treated with sodium and degassed for at least 8 h. If data were collected on Rigaku AFC5 and P3 Syntex diffractometers, the crystals were mounted inside capillaries. When the CAD4 diffractometer was used, the crystals were glued on the tip of quartz fibers, fastened on a goniometer head, and quickly transferred to a goniometer that had a continuous flow of cold nitrogen. The intensity data were all corrected for Lorentz and

Table II. Positional and Equivalent Isotropic Displacement Parameters for $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PMe_2Ph)_3]\cdot 2THF$ (**1**)

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
Nb(1)	0.50694 (7)	0.40693 (7)	0.26096 (5)	3.39 (2)	Cl(12)	0.9455 (2)	0.6152 (2)	0.0557 (2)	4.84 (7)
Nb(2)	0.66427 (7)	0.25642 (7)	0.31935 (5)	3.44 (2)	Cl(13)	0.9523 (2)	0.8514 (2)	0.0553 (2)	5.63 (9)
Nb(3)	0.56165 (7)	0.23462 (7)	0.20103 (5)	3.41 (2)	O(1)	0.8853 (6)	0.5952 (5)	0.2219 (4)	5.1 (2)
Cl(1)	0.6630 (2)	0.3646 (2)	0.2052 (1)	4.09 (7)	O(2)	0.7625 (5)	0.7340 (6)	0.1236 (4)	4.8 (2)
Cl(2)	0.5186 (2)	0.3150 (2)	0.3764 (1)	3.83 (6)	O(3)	0.8886 (6)	0.8068 (6)	0.2089 (4)	5.9 (2)
Cl(3)	0.5828 (2)	0.1200 (2)	0.3085 (2)	4.09 (7)	O(4)	1.1841 (5)	0.6019 (5)	0.0272 (4)	4.7 (2)
Cl(4)	0.4030 (2)	0.2890 (2)	0.2436 (1)	3.97 (7)	O(5)	1.0666 (6)	0.7541 (6)	−0.0644 (4)	5.5 (2)
P(1)	0.3443 (2)	0.4922 (2)	0.3045 (2)	4.53 (8)	O(6)	1.1952 (6)	0.8029 (6)	0.0362 (5)	6.3 (2)
Cl(5)	0.4541 (3)	0.5124 (2)	0.1569 (2)	5.47 (8)	C(25)	0.886 (1)	0.496 (1)	0.2146 (8)	8.3 (5)
Cl(6)	0.5732 (2)	0.5397 (2)	0.2930 (2)	4.90 (7)	C(26)	0.958 (1)	0.437 (1)	0.2644 (9)	8.4 (5)
P(2)	0.7055 (3)	0.1542 (3)	0.4420 (2)	4.87 (8)	C(27)	0.952 (1)	0.494 (1)	0.3212 (8)	8.4 (5)
Cl(7)	0.7491 (2)	0.3672 (2)	0.3627 (2)	5.07 (8)	C(28)	0.896 (2)	0.593 (1)	0.2923 (8)	10.5 (6)
Cl(8)	0.8177 (2)	0.1768 (2)	0.2881 (2)	5.41 (8)	C(29)	0.6920 (9)	0.670 (1)	0.157 (1)	8.6 (5)
P(3)	0.4652 (2)	0.1037 (2)	0.1677 (2)	4.42 (8)	C(30)	0.597 (1)	0.726 (1)	0.127 (1)	9.9 (6)
Cl(9)	0.6988 (2)	0.1456 (2)	0.1559 (2)	5.26 (8)	C(31)	0.619 (1)	0.778 (1)	0.0629 (9)	9.8 (6)
Cl(10)	0.5168 (2)	0.3154 (2)	0.0881 (2)	4.81 (8)	C(32)	0.723 (1)	0.797 (1)	0.0621 (8)	8.3 (5)
C(1)	0.2337 (9)	0.4601 (9)	0.2752 (7)	5.9 (4)	C(33)	0.794 (1)	0.857 (1)	0.2209 (9)	12.1 (5)
C(2)	0.330 (1)	0.6261 (8)	0.2747 (8)	6.6 (4)	C(34)	0.814 (1)	0.915 (1)	0.2723 (8)	8.6 (5)
C(3)	0.3268 (9)	0.4746 (8)	0.3955 (6)	5.2 (3)	C(35)	0.911 (1)	0.933 (1)	0.262 (1)	10.4 (5)
C(4)	0.260 (1)	0.414 (1)	0.4296 (7)	6.8 (4)	C(36)	0.964 (1)	0.859 (1)	0.2259 (8)	9.6 (4)
C(5)	0.251 (1)	0.402 (1)	0.5019 (8)	8.6 (5)	C(37)	1.186 (1)	0.5053 (8)	0.0699 (7)	6.0 (4)
C(6)	0.306 (1)	0.446 (1)	0.5344 (9)	8.9 (5)	C(38)	1.267 (1)	0.4423 (9)	0.0454 (8)	6.5 (4)
C(7)	0.371 (1)	0.508 (1)	0.5017 (8)	8.5 (5)	C(39)	1.318 (1)	0.512 (1)	−0.0103 (8)	7.8 (4)
C(8)	0.384 (1)	0.521 (1)	0.4289 (7)	7.1 (4)	C(40)	1.256 (1)	0.601 (1)	−0.0256 (9)	10.8 (5)
C(9)	0.661 (1)	0.218 (1)	0.5087 (6)	6.4 (4)	C(41)	1.040 (1)	0.687 (1)	−0.1052 (8)	9.2 (5)
C(10)	0.8381 (9)	0.133 (1)	0.4560 (7)	6.9 (4)	C(42)	0.951 (1)	0.739 (1)	−0.137 (1)	12.1 (6)
C(11)	0.6723 (8)	0.0311 (8)	0.4697 (6)	4.9 (3)	C(43)	0.950 (1)	0.843 (1)	−0.1407 (9)	10.0 (6)
C(12)	0.707 (1)	−0.0355 (9)	0.4296 (7)	5.9 (4)	C(44)	1.038 (1)	0.852 (1)	−0.1045 (8)	7.0 (4)
C(13)	0.688 (1)	−0.133 (1)	0.4502 (8)	7.5 (5)	C(45)	1.284 (1)	0.766 (1)	0.068 (1)	12.5 (7)
C(14)	0.631 (1)	−0.159 (1)	0.5072 (9)	7.7 (5)	C(46)	1.314 (2)	0.845 (1)	0.095 (1)	13.3 (7)
C(15)	0.599 (1)	−0.095 (1)	0.5461 (9)	8.1 (5)	C(47)	1.262 (1)	0.934 (1)	0.055 (1)	11.1 (6)
C(16)	0.618 (1)	0.002 (1)	0.5291 (8)	7.2 (4)	C(48)	1.188 (1)	0.9077 (9)	0.0118 (9)	8.0 (5)
C(17)	0.3390 (8)	0.1506 (9)	0.1430 (7)	6.3 (4)	O(7)	0.168 (2)	0.085 (2)	0.311 (1)	26 (1)*
C(18)	0.517 (1)	0.0599 (9)	0.0927 (6)	6.0 (3)	C(49)	0.093 (2)	0.047 (2)	0.357 (2)	21 (1)*
C(19)	0.4574 (9)	−0.0103 (8)	0.2279 (6)	5.2 (3)	C(50)	0.095 (2)	0.107 (2)	0.404 (2)	19 (1)*
C(20)	0.370 (1)	−0.037 (1)	0.2549 (8)	8.6 (5)	C(51)	0.118 (2)	0.208 (2)	0.370 (2)	19 (1)*
C(21)	0.370 (1)	−0.130 (1)	0.3031 (9)	9.2 (5)	C(52)	0.177 (2)	0.188 (2)	0.319 (2)	19 (1)*
C(22)	0.453 (1)	−0.186 (1)	0.3206 (8)	9.1 (5)	O(8)	−0.020 (2)	0.757 (2)	0.441 (1)	24.2 (9)*
C(23)	0.543 (1)	−0.160 (1)	0.2931 (8)	9.1 (5)	C(53)	0.005 (2)	0.658 (2)	0.490 (2)	22 (1)*
C(24)	0.543 (1)	−0.0684 (9)	0.2458 (8)	7.5 (4)	C(54)	0.094 (2)	0.635 (2)	0.460 (2)	19 (1)*
Mg(1)	0.9106 (3)	0.7106 (3)	0.1434 (2)	4.10 (9)	C(55)	0.122 (2)	0.692 (2)	0.405 (1)	18 (1)*
Mg(2)	1.0829 (3)	0.7171 (3)	0.0386 (2)	4.21 (9)	C(56)	0.068 (2)	0.784 (2)	0.398 (1)	15.9 (9)*
Cl(11)	1.0869 (2)	0.6754 (2)	0.1648 (2)	5.13 (8)					

[a] Starred values denote that were refined isotropically. Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

polarization effects and empirical absorption corrections were made in each case by the method of Ψ scans for several reflections with χ angle close to 90°. A summary of the data collection parameters for all the crystal structures is listed in Table I.

$[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PMe_2Ph)_3]\cdot 2(THF)$ (1). The intensity data were also corrected for anisotropic decay because a total 15.7% intensity decrease was observed for the three standards during the data collection. The coordinates of the three Nb atoms were derived from a three-dimensional Patterson map, assuming that the space group was the centric $P\bar{1}$. Alternate least-squares refinements and difference Fourier syntheses located the rest of the non-hydrogen atoms successfully. Except for the interstitial THF molecules, all the non-hydrogen atoms were refined anisotropically in the final cycle of least-squares refinements. The three highest peaks in the final difference Fourier map were all in the vicinity of the Nb atoms. The final atomic positional and equivalent isotropic displacement parameters are listed in Table II.

$[HPEt_3][Nb_3Cl_{10}(PEt_3)_3]$ (2). Preliminary coordinates of all the non-hydrogen atoms were taken from the isomorphous tantalum structure $[HPEt_3][Ta_3Cl_{10}(PEt_3)_3]$.[3] All these atoms were successfully refined anisotropically in the final least-squares refinements. A final difference Fourier synthesis indicated possible positions for the phosphonium hydrogen atom and some of the hydrogen atoms from the ethyl groups. However, no further effort was made to locate or refine these hydrogen atoms. The final atomic positional and equivalent isotropic displacement parameters are listed in Table III.

$[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PEt_3)_3]\cdot 2THF$ (3). Crystal decay of 22.3% was observed during the data collection, and an appropriate correction for anisotropic decay was therefore applied to the intensity data. Direct methods (SHELXS-86) revealed positions of the three Nb atoms and their surrounding 13 ligands. The rest of the non-hydrogen atoms were located by alternate least-squares refinements and difference Fourier syntheses. Two carbon atoms, C(48) and C(50), from one of the two interstitial THF solvent molecules were found disordered on two sets of general positions, which were then assigned equal site occupancies. In the final least-squares refinement, these interstitial THF molecules were arbitrarily assigned site occupancies of 0.5, as they had too high isotropic displacement parameters (25–35), which, together with the crystal decay, was indicative of the escape of the solvent molecules from the crystal during data collection. In the final refinement, all the atoms except the carbon atoms from the THF ligands and the terminal carbon atoms from the PEt_3 ligands were refined anisotropically. There is little doubt that the relatively high *R* values are due to the messy state of the interstitial solvent molecules. The final atomic positional and equivalent isotropic displacement parameters are listed in Table IV.

$Ta_3Cl_9(THF)_4\cdot C_6H_6\cdot THF$ (4). Photographs along the axes and the diagonal ($a + b$) and also a preliminary data collection for $20 < 2\theta < 30°$ revealed systematic absences consistent with the *Cc* or *C*2/*c* space groups. The standard reflections showed no decay in the intensity.

The Patterson interpretation of the SHELXS-86 program revealed the position of the atoms in the M_3X_{13} core, assuming *C*2/*c*. The remaining non-hydrogen atoms were located by a series of least-squares refinements and difference Fourier syntheses. All the atoms in $Ta_3Cl_9(THF)_4$ were refined anisotropically, and the interstitial benzene and THF molecules were refined isotropically in space group *C*2/*c*. The final difference Fourier map contained 11 peaks above 1 e/Å^3 within the vicinity of either the metal or chlorine atoms. The successful refinement, plus the fact that choice of *Cc* would mean two independent molecules in the asymmetric unit, led us to accept *C*2/*c* as the correct space group. The final atomic positional and equivalent isotropic displacement parameters are listed in Table V.

Table III. Positional and Equivalent Isotropic Displacement Parameters for $[HPEt_3][Nb_3Cl_{10}(PEt_3)_3]$ (**2**)

atom	*x*	*y*	*z*	B,[a] Å^2
Nb(1)	0.41882 (4)	0.12131 (3)	0.26448 (3)	3.14 (1)
Nb(2)	0.42746 (4)	0.23354 (3)	0.36407 (3)	3.33 (1)
Nb(3)	0.21333 (4)	0.15887 (3)	0.33042 (3)	3.61 (1)
Cl(1)	0.3983 (1)	0.11732 (8)	0.39494 (8)	3.99 (3)
Cl(2)	0.4710 (1)	0.23290 (7)	0.24030 (8)	3.59 (3)
Cl(3)	0.2412 (1)	0.27463 (8)	0.31456 (8)	3.91 (3)
Cl(4)	0.2297 (1)	0.14579 (8)	0.20256 (8)	3.90 (3)
Cl(5)	0.3746 (2)	0.00705 (8)	0.2604 (1)	5.42 (4)
Cl(6)	0.6178 (1)	0.09379 (9)	0.29548 (9)	4.67 (4)
Cl(7)	0.6290 (1)	0.22124 (9)	0.4057 (1)	4.87 (4)
Cl(8)	0.3983 (2)	0.2594 (1)	0.48472 (9)	5.92 (5)
Cl(9)	0.1534 (2)	0.1762 (1)	0.44715 (9)	6.03 (5)
Cl(10)	0.1388 (2)	0.04945 (9)	0.3343 (1)	6.07 (4)
P(1)	0.4716 (1)	0.10717 (9)	0.13233 (9)	3.99 (4)
P(2)	0.4826 (2)	0.3582 (1)	0.3583 (1)	5.20 (4)
P(3)	0.0024 (1)	0.1928 (1)	0.2775 (1)	4.49 (4)
C(11)	0.6043 (6)	0.1468 (4)	0.1180 (4)	5.4 (2)
C(12)	0.4914 (8)	0.0219 (4)	0.1038 (5)	7.4 (2)
C(13)	0.3683 (7)	0.1385 (5)	0.0571 (4)	6.4 (2)
C(14)	0.6461 (7)	0.1329 (5)	0.0444 (4)	7.5 (2)
C(15)	0.5923 (9)	−0.0120 (5)	0.1432 (6)	9.6 (3)
C(16)	0.3548 (8)	0.2086 (5)	0.0540 (5)	7.8 (2)
C(21)	0.549 (1)	0.3877 (5)	0.2781 (7)	13.4 (4)
C(22)	0.5780 (8)	0.3840 (4)	0.4388 (6)	8.6 (3)
C(23)	0.367 (1)	0.4182 (5)	0.3504 (8)	11.1 (4)
C(24)	0.648 (1)	0.3646 (9)	0.270 (1)	25.5 (6)
C(25)	0.617 (1)	0.4499 (6)	0.4459 (9)	13.4 (5)
C(26)	0.305 (1)	0.4213 (9)	0.4086 (8)	15.4 (5)
C(31)	−0.0107 (5)	0.2468 (4)	0.1984 (4)	5.3 (2)
C(32)	−0.0944 (7)	0.1245 (5)	0.2489 (7)	9.6 (3)
C(33)	−0.0788 (7)	0.2337 (5)	0.3409 (4)	7.0 (2)
C(34)	−0.1308 (7)	0.2694 (5)	0.1711 (4)	6.9 (2)
C(35)	−0.072 (1)	0.0933 (6)	0.1796 (8)	12.8 (4)
C(36)	−0.0390 (9)	0.3014 (5)	0.3627 (5)	9.9 (3)
P(4)	0.7209 (3)	0.0613 (1)	0.4893 (2)	8.31 (7)
C(41)	0.655 (1)	0.0641 (6)	0.5677 (6)	11.0 (3)
C(42)	0.740 (1)	−0.0217 (7)	0.4677 (8)	15.9 (5)
C(43)	0.852 (1)	0.1081 (7)	0.4917 (9)	16.4 (5)
C(44)	0.621 (1)	0.1284 (6)	0.5910 (7)	14.7 (4)
C(45)	0.716 (2)	−0.0459 (7)	0.4078 (9)	25.1 (8)
C(46)	0.931 (1)	0.0936 (9)	0.549 (1)	22.1 (7)

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

$Na[Ta_3Cl_{10}(THF)_3]$ (5). The preliminary examination of a green prismatic crystal of **5** revealed all three axes to be equal and $\alpha = \beta = \gamma = 90°$. The systematic absences are consistent with only one space group, $P2_13$, of the isometric system.

The position of the M_3M_{13} core was determined by using direct methods (SHELXS-86). The remaining non-hydrogen atoms were located by a series of least-squares refinements and difference Fourier syntheses. The trinuclear cluster is located about a 3-fold rotation axis and the capping Cl and the cationic Na atoms are located on the crystallographic 3-fold axis. Therefore, one-third of the trimer is unique and the other two-thirds is generated by the 3-fold rotation. In the final least-squares refinement, the atoms of the M_3X_{13} core and the sodium atom were refined anisotropically and the carbon atoms of the THF ring were refined isotropically. The final difference Fourier map contained a series of peaks located around a 3-fold axis. Attempts to model them as a possible interstitial solvent molecule of either toluene or THF failed. The final atomic positional and equivalent isotropic displacement parameters are listed in Table VI.

$Na[Nb_3Cl_{10}(THF)_3]\cdot 3THF$ (6). Positions of Nb and Cl atoms were located by the Patterson method (SHELXS-86). Subsequent alternate least-squares refinement and difference Fourier syntheses revealed the rest of the non-hydrogen atoms. No crystal decay was observed during the data collection. The six highest residual electron densities are located in the proximity of Nb atoms, but the final difference Fourier map was otherwise featureless. In the final cycle, all atoms were refined anisotropically. The final atomic positional and equivalent isotropic displacement parameters are listed in Table VII.

Results

Preparative Procedures. A principal objective of this work, in addition to that of obtaining and characterizing structurally some new triangular cluster compounds, was to learn more about the preparative reactions that can be used to make such compounds. As far as starting compounds from which the metal atoms are derived are concerned, we have continued to use the same ones, namely, $NbCl_4(THF)_2$ and $TaCl_5$.

The use of metallic magnesium as the reducing agent is new in this area. Compounds **1**–**3** were synthesized by reduction of $NbCl_4(THF)_2$ with magnesium turnings. In the cases of **1** and **3** this resulted in having the large cation $[Mg_2Cl_3(THF)_6]^+$ present in the product. This cation has been reported only twice previously,[7] but similar $[V_2Cl_3(THF)_6]^+$ cations are well established.[8]

A comparison of the preparative routes for **2** and **3** is instructive. The only important difference was in the solvents used. For **2**, the reaction medium was a 1:1 THF/toluene mixture while, for **3**, pure THF was used. This appears to be critical with respect to the formation of the $[Mg_2Cl_3(THF)_6]^+$ cation and its appearance in the product. Apparently when there is a deficit of THF, its place is taken by an alternative cation, $HPEt_3^+$. As before,[3b] we cannot account explicitly for the formation of this phosphonium ion in the reaction mixture.

Attempts to employ magnesium as the reducing agent for $TaCl_5$ have been unrewarding. All such reactions led consistently to the formation of oily products that we could not purify. Our experience is in accord with prior reports.[9]

Our final point concerns compound **2**, which is simply a different crystalline form of a previously reported compound. In our earlier work, it was formed in a pure toluene medium and the crystals contained interstitial toluene molecules.[3b]

The last three compounds reported here were obtained by using sodium amalgam as the reductant, but without adding any phosphine or other ligand to the reaction mixture. Thus THF was the only available donor molecule to fill coordination positions not occupied by chloride ions. In fact, for **4** and **5**, the reactions were conducted in two stages, during the first of which only benzene or toluene was present. The reduction of $TaCl_5$ with 2 equiv of Na/Hg gave a black precipitate, completely insoluble in the aromatic solvent but very reactive. We do not know what this precipitate is or what sort of bonds (e.g., Cl bridges, Ta–Ta) are present, but it can be said that the presence of double Ta–Ta bonds, as in the well-known $Ta_2Cl_6L_3$ molecules[10,11] is unlikely. It is well established that once formed these dimers are quite stable and their reactivity is mainly restricted to ligand-substitution reactions.

Attempts to prepare **4** by reduction of $TaCl_5$ in THF gave only oily, intractable products. Thus, initial use of an aromatic solvent during the reduction step and subsequent introduction of the THF is essential. The appearance of these oily materials may be due to the reaction of THF with intermediates formed during the reaction. Sattelberger[13] has previously noted a similar undesirable

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(7) (a) Sobota, P.; Utko, J.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1984**, 2077. (b) Sobota, P.; Pluzinski, T.; Lis, T. *Z. Anorg. Allg. Chem.* **1986**, *533*, 215. (c) Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990**, *29*, 508.

(8) (a) Cotton, F. A.; Duraj, S. A.; Manzer, L. E.; Roth, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 3850. (b) Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1987**, *6*, 1433. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913. (d) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulback, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377. (e) Canich, J. A. M.; Cotton, F. A.; Roth, W. J.; Duraj, S. A. *Polyhedron* **1988**, *7*, 737.

(9) Hovnanian, N.; Hubert-Pfalzgraf, L. G.; Le Borgne, G. *Inorg. Chem.* **1985**, *24*, 4647.

(10) (a) Maas, E. T.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1096. (b) Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263. (c) Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293.

(11) (a) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981**, *20*, 2716. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Acta Crystallogr.* **1985**, *C41*, 878.

(12) (a) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Inorg. Chim. Acta* **1982**, *63*, 107. (b) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* **1983**, *22*, 868. (c) Cotton, F. A.; Hall, W. *Inorg. Chem.* **1980**, *19*, 2354. (d) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 3323. (e) Cotton, F. A.; Diebold, M. P.; Matusz, M.; Roth, W. J. *Inorg. Chim. Acta* **1986**, *112*, 147. (f) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* **1983**, *22*, 3654.

Table IV. Positional and Equivalent Isotropic Displacement Parameters for $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PEt_3)_3]\cdot 2THF$ (**3**)

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
Nb(1)	0.6552 (3)	0.3210 (1)	0.3818 (3)	4.0 (1)	O(3)	0.692 (2)	0.1112 (9)	0.112 (2)	4.9 (9)
Nb(2)	0.4705 (3)	0.2915 (1)	0.4140 (3)	4.3 (1)	O(4)	0.846 (2)	−0.1619 (9)	0.180 (2)	6 (1)
Nb(3)	0.4304 (3)	0.3473 (1)	0.2033 (3)	4.3 (1)	O(5)	1.012 (2)	−0.1107 (9)	0.146 (2)	4.4 (8)
Cl(1)	0.5243 (8)	0.2478 (4)	0.2760 (8)	5.5 (4)	O(6)	0.790 (2)	−0.104 (1)	−0.031 (2)	5.5 (9)
Cl(2)	0.6126 (7)	0.3542 (4)	0.5288 (7)	4.2 (3)	C(19)	0.651 (3)	0.083 (2)	0.308 (3)	7 (1)*
Cl(3)	0.3563 (7)	0.3817 (4)	0.3266 (7)	4.3 (3)	C(20)	0.646 (4)	0.072 (2)	0.414 (4)	10 (1)*
Cl(4)	0.5697 (6)	0.4169 (3)	0.2934 (7)	3.8 (3)	C(21)	0.760 (3)	0.056 (2)	0.499 (3)	8 (1)*
Cl(5)	0.7330 (8)	0.3047 (5)	0.2580 (9)	6.8 (4)	C(22)	0.809 (3)	0.024 (2)	0.435 (3)	6.1 (9)*
Cl(6)	0.7788 (8)	0.2413 (4)	0.4938 (9)	6.3 (4)	C(23)	1.026 (4)	0.103 (2)	0.290 (4)	9 (1)*
Cl(7)	0.5720 (8)	0.2110 (4)	0.5365 (9)	6.3 (4)	C(24)	1.070 (4)	0.162 (2)	0.346 (4)	10 (1)*
Cl(8)	0.3163 (8)	0.2355 (5)	0.3322 (9)	7.2 (5)	C(25)	0.998 (3)	0.193 (2)	0.390 (3)	8 (1)*
Cl(9)	0.2669 (8)	0.3008 (4)	0.0944 (9)	6.9 (4)	C(26)	0.926 (4)	0.141 (2)	0.388 (4)	9 (1)*
Cl(10)	0.4775 (9)	0.3349 (5)	0.0555 (8)	7.3 (5)	C(27)	0.728 (4)	0.168 (2)	0.098 (4)	12 (2)*
P(1)	0.8210 (8)	0.3837 (4)	0.4956 (8)	4.7 (4)	C(28)	0.626 (4)	0.195 (2)	−0.002 (4)	10 (1)*
P(2)	0.4087 (9)	0.3180 (4)	0.5666 (9)	5.5 (5)	C(29)	0.542 (5)	0.161 (3)	−0.020 (5)	14 (2)*
P(3)	0.3156 (8)	0.4450 (5)	0.0869 (8)	5.4 (4)	C(30)	0.589 (4)	0.096 (2)	0.007 (4)	11 (2)*
C(1)	0.938 (3)	0.349 (2)	0.622 (3)	7 (2)	C(31)	0.880 (3)	−0.178 (2)	0.304 (3)	7 (1)*
C(2)	0.900 (3)	0.343 (2)	0.712 (3)	5.6 (9)*	C(32)	0.821 (5)	−0.230 (3)	0.290 (5)	14 (2)*
C(3)	0.783 (3)	0.459 (1)	0.537 (3)	6 (1)	C(33)	0.767 (5)	−0.249 (3)	0.185 (6)	14 (2)*
C(4)	0.881 (3)	0.494 (1)	0.604 (3)	5.5 (9)*	C(34)	0.763 (5)	−0.197 (3)	0.116 (6)	16 (2)*
C(5)	0.904 (3)	0.402 (2)	0.429 (4)	8 (2)	C(35)	1.092 (3)	−0.074 (2)	0.167 (3)	5.5 (9)*
C(6)	0.837 (3)	0.439 (2)	0.322 (4)	8 (1)*	C(36)	1.200 (3)	−0.112 (2)	0.206 (3)	8 (1)*
C(7)	0.400 (3)	0.399 (1)	0.596 (3)	5 (1)	C(37)	1.155 (4)	−0.171 (2)	0.155 (4)	12 (2)*
C(8)	0.371 (3)	0.414 (1)	0.689 (3)	5.0 (8)*	C(38)	1.058 (4)	−0.169 (2)	0.173 (4)	11 (2)*
C(9)	0.494 (4)	0.278 (1)	0.703 (4)	9 (2)	C(39)	0.847 (3)	−0.110 (2)	−0.098 (3)	6 (1)*
C(10)	0.613 (4)	0.303 (2)	0.761 (4)	8 (1)*	C(40)	0.764 (4)	−0.088 (2)	−0.214 (4)	10 (1)*
C(11)	0.275 (3)	0.292 (1)	0.535 (3)	7 (2)	C(41)	0.660 (4)	−0.079 (2)	−0.202 (4)	10 (1)*
C(12)	0.174 (4)	0.331 (2)	0.439 (4)	10 (1)*	C(42)	0.674 (5)	−0.112 (3)	−0.111 (5)	14 (2)*
C(13)	0.406 (3)	0.486 (2)	0.049 (4)	11 (2)	C(7)	0.509 (3)	0.065 (2)	0.600 (4)	15 (1)*
C(14)	0.348 (4)	0.543 (2)	−0.020 (4)	12 (2)*	C(43)	0.388 (5)	0.085 (2)	0.504 (4)	12 (2)*
C(15)	0.248 (4)	0.495 (2)	0.153 (4)	10 (2)	C(44)	0.340 (5)	0.113 (3)	0.561 (6)	14 (2)*
C(16)	0.331 (4)	0.529 (2)	0.242 (4)	10 (1)*	C(45)	0.395 (6)	0.121 (3)	0.676 (6)	18 (2)*
C(17)	0.193 (4)	0.432 (3)	−0.047 (5)	16 (3)	C(46)	0.497 (4)	0.080 (2)	0.708 (4)	13 (2)*
C(18)	0.220 (4)	0.401 (2)	−0.132 (4)	11 (2)*	O(8)	0.932 (5)	0.288 (2)	0.035 (6)	16 (3)*
Mg(1)	0.8077 (8)	0.0465 (4)	0.2138 (9)	3.6 (4)	C(47)	0.936 (5)	0.344 (3)	−0.011 (3)	10 (3)*
Mg(2)	0.8601 (9)	−0.0759 (5)	0.1296 (9)	4.0 (4)	C(48)	0.956 (5)	0.387 (2)	0.076 (5)	12 (9)*
Cl(11)	0.8685 (7)	0.0250 (4)	0.0697 (7)	4.6 (3)	C(49)	0.953 (6)	0.357 (3)	0.168 (4)	12 (3)*
Cl(12)	0.6880 (7)	−0.0352 (4)	0.1268 (7)	5.0 (3)	C(50)	0.888 (5)	0.308 (3)	0.112 (6)	14 (4)*
Cl(13)	0.9487 (7)	−0.0358 (4)	0.3191 (7)	5.1 (3)	C(48)′	0.971 (5)	0.384 (2)	0.083 (5)	18 (2)*
O(1)	0.757 (2)	0.0584 (9)	0.331 (2)	4.4 (8)	C(50)′	0.994 (5)	0.296 (3)	0.156 (5)	14 (4)*
O(2)	0.921 (2)	0.1068 (9)	0.295 (2)	6 (1)					

[a] Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

effect when THF was present during the reduction of tantalum. It is known that the breaking of the carbon oxygen bond(s) and the conversion of THF to 1,4-dihalobutane by metal halides can occur.[14]

The relationship between **4** and **5** is such that it is possible to control which one is formed and to interconvert them. Compound **4** is formed by decanting as much of the aromatic solvent as possible from the reaction mixture and dissolving the black precipitate in THF. Crystals of **4** are then obtained by slow diffusion of hexane isomers into this solution. Compound **5** is formed when a smaller fraction of the aromatic solvent is replaced by THF. One can tell at this stage whether **4** or **5** is going to appear by noting whether a precipitate of NaCl is present. In principle, it should be possible to obtain a mixture, but it is hard to see why this would be desirable, and in any case, we have not done so. Compound **5** can be converted to **4** by dissolving **5** in THF, which affords a green solution of **4** and a solid residue of NaCl:

$$Na[Ta_3Cl_{10}(THF)_3] \xrightarrow{THF} Ta_3Cl_9(THF)_4 + NaCl(s)$$

Compound **4** can also be prepared by the reduction of $TaCl_5$ with $Bu^n{}_3SnH$. When $TaCl_5$ is reduced with 1 equiv of $Bu^n{}_3SnH$ in benzene, a green solution and a green precipitate result. Dissolving the precipitate in THF and layering it with hexane produces crystals of **4**. Another product isolated from this reaction is $Sn[Ta_2Cl_9]_2\cdot C_6H_6$ which was reported earlier separately.[15] The reduction of $TaCl_5$ with $Bu^n{}_3SnH$ was originally carried out in an attempt to prepare simple THF adducts of Ta(IV). However, the reduction seems to proceed further and the major product isolated is **4**, where the metal atoms are in the oxidation state III.

We have not yet succeeded in the preparation of Nb analogues of **4** and **5** by the direct reduction of $NbCl_5$. However, $Na[Nb_3Cl_{10}(THF)_3]\cdot 3THF$ (**6**) was synthesized by the reduction of $NbCl_4(THF)_2$. Upon addition of sodium amalgam to a THF solution of $NbCl_4(THF)_2$, the reaction mixture immediately changes color from yellow to brown-red. When a portion of this solution is layered with hexane, slow diffusion of these two layers precipitates crystals of **6**. Preparation of $Nb_3Cl_9(THF)_4$ by this method was not successful. Even addition of hexane to the reaction mixture did not remove the NaCl byproduct completely, and the only isolated product was compound **6**.

Since **4** could also be prepared by the reduction of $TaCl_5$ with $Bu^n{}_3SnH$, analogous reaction of $NbCl_5$ with this reducing agent was carried out. Reduction of $NbCl_5$ with 1 equiv of $Bu^n{}_3SnH$ gives the well-known $NbCl_4(THF)_2$ monomer as the major product and $Nb_3Cl_9(THF)_4$ as the minor product. Due to the extreme air and moisture sensitivity of $Nb_3Cl_9(THF)_4$, the characterization of this compound was limited to a unit cell determination. A crystal of $Nb_3Cl_9(THF)_4$ was shown to be isostructural with

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(13) Luetkens, M. L.; Hopkins, M. D.; Schultz, A. J.; Williams, J. M.; Fair, C. K.; Koss, F. K.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1987**, *26*, 2430.

(14) (a) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* **1983**, *22*, 868. (b) Cotton, F. A.; Shang, M. *J. Am. Chem. Soc.* **1990**, *112*, 1584.

(15) Cotton, F. A.; Babain-Kibala, E.; Falvello, L. R.; Shang, M. *Inorg. Chem.* **1990**, *29*, 2591.

Table V. Atomic Positional and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $Ta_3Cl_9(THF)_4 \cdot C_6H_6 \cdot THF$ (**4**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eqv},[a] Å^2
Ta(1)	0.35807 (1)	0.36008 (2)	0.22255 (3)	1.644 (8)
Ta(2)	0.28147 (1)	0.40568 (2)	0.00774 (3)	1.767 (8)
Ta(3)	0.37310 (1)	0.35028 (2)	0.00445 (3)	1.706 (8)
Cl(1)	0.30631 (8)	0.3000 (1)	0.0505 (2)	1.97 (5)
Cl(2)	0.43081 (8)	0.3948 (1)	0.1875 (2)	1.96 (5)
Cl(3)	0.33986 (9)	0.4493 (1)	−0.0719 (2)	2.17 (5)
Cl(4)	0.32648 (9)	0.4622 (1)	0.1906 (2)	2.16 (5)
Cl(5)	0.30026 (9)	0.3301 (1)	0.3115 (2)	2.55 (5)
Cl(6)	0.21222 (9)	0.3829 (1)	0.0608 (2)	2.92 (6)
Cl(7)	0.43908 (9)	0.3792 (1)	−0.0693 (2)	2.62 (6)
Cl(8)	0.2314 (1)	0.3741 (1)	−0.1953 (2)	2.69 (6)
Cl(9)	0.4155 (1)	0.2547 (1)	0.0528 (2)	2.84 (6)
O(1)	0.4041 (2)	0.3952 (3)	0.4066 (6)	2.1 (1)
O(2)	0.3960 (2)	0.2763 (3)	0.2943 (6)	2.3 (2)
O(3)	0.2441 (3)	0.4946 (3)	−0.0450 (6)	2.4 (2)
O(4)	0.3344 (3)	0.3135 (3)	−0.1716 (6)	2.4 (2)
C(11)	0.4405 (4)	0.4465 (5)	0.4359 (9)	2.5 (2)
C(12)	0.4529 (4)	0.4595 (5)	0.5687 (9)	2.5 (2)
C(13)	0.4426 (5)	0.3998 (6)	0.616 (1)	3.9 (3)
C(14)	0.3981 (5)	0.3747 (7)	0.5152 (9)	4.2 (3)
C(21)	0.4516 (4)	0.2714 (5)	0.363 (1)	3.1 (3)
C(22)	0.4600 (5)	0.2024 (6)	0.386 (1)	4.7 (4)
C(23)	0.4092 (6)	0.1800 (6)	0.377 (1)	4.9 (4)
C(24)	0.3711 (4)	0.2169 (5)	0.276 (1)	3.1 (3)
C(31)	0.2213 (4)	0.5293 (5)	0.024 (1)	3.5 (3)
C(32)	0.2003 (6)	0.5853 (7)	−0.047 (1)	5.6 (4)
C(33)	0.1913 (5)	0.5701 (6)	−0.174 (1)	4.5 (3)
C(34)	0.2330 (5)	0.5248 (6)	−0.1621 (9)	3.9 (3)
C(41)	0.3091 (4)	0.2540 (6)	−0.200 (1)	3.4 (3)
C(42)	0.3022 (6)	0.2434 (8)	−0.328 (1)	8.1 (4)
C(43)	0.3134 (9)	0.2954 (8)	−0.375 (1)	9.1 (6)
C(44)	0.3321 (51)	0.3432 (6)	−0.2837 (9)	3.9 (3)
O(5)	0.0779 (8)	0.496 (1)	0.363 (2)	15.2 (2)*
C(51)	0.0796 (9)	0.559 (1)	0.342 (2)	10.2 (7)*
C(52)	0.067 (1)	0.584 (1)	0.436 (2)	12.1 (8)*
C(53)	0.074 (1)	0.542 (2)	0.530 (3)	15 (4)*
C(54)	0.0717 (9)	0.484 (1)	0.473 (2)	11.3 (8)*
C(61)	0.0211 (7)	0.254 (1)	0.238 (2)	9.4 (6)*
C(62)	0.044 (1)	0.308 (1)	0.224 (2)	13.0 (9)*
C(63)	0.0195 (9)	0.356 (1)	0.236 (3)	13 (1)*

[a] The equivalent isotropic displacement parameter, B_{eqv}, is calculated as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos \gamma)a^*b^*B_{12} + 2ac(\cos \beta)a^*c^*B_{13} + 2bc(\cos \alpha)b^*c^*B_{23}]$.

Table VI. Atomic Positional and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $Na[Ta_3Cl_{10}(THF)_3]$ (**5**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eqv},[a] Å^2
Ta	0.5981 (1)	0.73300 (9)	0.6019 (1)	3.18 (3)
Cl(1)	0.5761 (5)	0.576	0.576	3.21 (9)
Cl(2)	0.7535 (5)	0.7581 (6)	0.5966 (6)	4.0 (2)
Cl(3)	0.5928 (6)	0.8964 (5)	0.5985 (6)	4.2 (2)
Cl(4)	0.4397 (5)	0.7375 (6)	0.5962 (7)	4.2 (2)
Na	−0.9171 (8)	−0.917	−0.917	3.8 (1)
O	0.590 (2)	0.740 (2)	0.459 (2)	5.3 (6)
C(1)	0.536 (2)	0.683 (2)	0.403 (3)	4.1 (7)*
C(2)	0.553 (3)	0.716 (3)	0.313 (3)	7 (1)*
C(3)	0.609 (4)	0.782 (4)	0.314 (4)	10 (2)*
C(4)	0.641 (3)	0.813 (3)	0.420 (3)	8 (1)*

[a] Starred values denote atoms that were refined isotropically. The equivalent isotropic displacement parameter, B_{eqv}, is calculated as $^1/_3$-$[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos \gamma)a^*B^*B_{12} + 2ac(\cos \beta)$-$a^*c^*B_{13} + 2bc(\cos \alpha)b^*c^*B_{23}]$.

Table VII. Atomic Positional and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $Na[Nb_3Cl_{10}(THF)_4] \cdot 3THF$ (**6**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eqv},[a] Å^2
Nb(1)	0.25426 (6)	0.07387 (5)	0.11398 (3)	2.15 (1)
Nb(2)	0.12859 (5)	0.06244 (5)	0.21935 (3)	1.99 (1)
Nb(3)	0.07162 (5)	0.20238 (5)	0.12849 (3)	1.89 (1)
Cl(1)	0.0593 (1)	0.0349 (1)	0.11449 (9)	2.07 (4)
Cl(2)	0.3259 (2)	0.0846 (2)	0.21949 (9)	2.77 (4)
Cl(3)	0.2605 (2)	0.2421 (1)	0.11158 (9)	2.56 (4)
Cl(4)	0.1110 (2)	0.2263 (1)	0.23448 (9)	2.56 (4)
Cl(5)	0.2194 (2)	0.0707 (2)	0.00602 (9)	3.03 (5)
Cl(6)	0.2970 (2)	−0.0865 (2)	0.1127 (1)	3.24 (5)
Cl(7)	0.1686 (2)	0.0632 (2)	0.33112 (9)	2.97 (4)
Cl(8)	0.1387 (2)	−0.1030 (2)	0.22831 (9)	2.79 (4)
Cl(9)	0.0461 (2)	0.3731 (1)	0.1288 (1)	2.77 (4)
Cl(10)	−0.1261 (2)	0.1928 (1)	0.13565 (9)	2.53 (4)
Na	0.1757 (3)	−0.1206 (2)	0.3565 (2)	2.99 (7)
O(1)	0.4329 (4)	0.0925 (4)	0.0998 (3)	3.1 (1)
O(2)	−0.0430 (4)	0.0466 (4)	0.2377 (2)	2.6 (1)
O(3)	0.0305 (4)	0.2131 (4)	0.0323 (2)	2.3 (1)
O(4)	0.3660 (5)	−0.1478 (5)	0.3512 (4)	5.2 (2)
O(5)	0.2155 (6)	−0.0934 (5)	0.4601 (3)	5.5 (2)
C(1)	0.5242 (7)	0.0456 (8)	0.1340 (5)	4.9 (2)
C(2)	0.6175 (8)	0.0510 (9)	0.0976 (5)	5.2 (3)
C(3)	0.5939 (7)	0.1229 (8)	0.0512 (5)	5.3 (3)
C(4)	0.4741 (7)	0.1447 (8)	0.0512 (5)	4.4 (2)
C(5)	−0.1208 (7)	−0.0211 (6)	0.2083 (4)	3.3 (2)
C(6)	−0.2200 (7)	−0.0205 (8)	0.2453 (4)	4.2 (2)
C(7)	−0.2179 (7)	0.0764 (7)	0.2721 (5)	4.0 (2)
C(8)	−0.0958 (7)	0.0975 (7)	0.2848 (4)	3.5 (2)
C(9)	−0.0465 (7)	0.1536 (6)	−0.0063 (4)	3.2 (2)
C(10)	−0.0287 (9)	0.1871 (7)	−0.0696 (4)	4.7 (2)
C(11)	0.0057 (9)	0.2825 (8)	−0.0636 (4)	5.1 (3)
C(12)	0.0753 (8)	0.2864 (7)	−0.0037 (4)	3.4 (2)
C(13)	0.4444 (9)	−0.0777 (9)	0.3722 (6)	7.2 (3)
C(14)	0.520 (1)	−0.0666 (9)	0.3256 (6)	6.6 (3)
C(15)	0.491 (1)	−0.136 (1)	0.2794 (6)	8.7 (4)
C(16)	0.409 (1)	−0.1946 (9)	0.3004 (6)	6.7 (3)
C(17)	0.7063 (9)	0.1386 (8)	0.4982 (5)	5.6 (3)
C(18)	0.677 (1)	0.070 (1)	0.4529 (7)	14.7 (4)
C(19)	0.745 (1)	−0.008 (1)	0.4610 (7)	8.4 (4)
C(20)	0.8287 (8)	0.0136 (7)	0.5137 (5)	4.8 (2)
O(6)	0.463 (1)	0.205 (1)	0.4284 (6)	14.2 (5)
C(21)	0.480 (1)	0.232 (1)	0.3655 (7)	9.9 (5)
C(22)	0.386 (1)	0.294 (1)	0.3483 (7)	9.9 (5)
C(23)	0.302 (1)	0.271 (1)	0.3876 (7)	8.8 (4)
C(24)	0.346 (1)	0.209 (1)	0.4325 (7)	9.1 (4)

[a] The equivalent isotropic displacement parameter, B_{eqv}, is calculated as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos \gamma)a^*b^*B_{12} + 2ac(\cos \beta)a^*b^*B_{13} + 2bc(\cos \alpha)b^*c^*B_{23}]$.

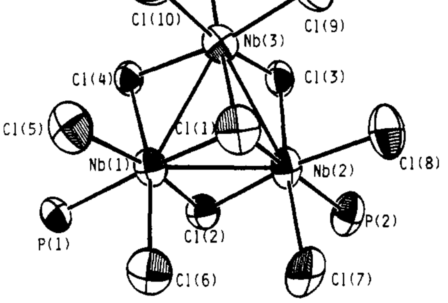

Figure 1. ORTEP drawing of the $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_3P_3$ core for compounds **1**–**3**. The thermal ellipsoids are drawn at the 50% probability level.

$Ta_3Cl_9(THF)_4 \cdot C_6H_6 \cdot THF$ (**4**). Thus, in contrast to the reduction of $TaCl_5$ with $Bu^n{}_3SnH$, the reduction of $NbCl_5$ with $Bu^n{}_3SnH$ results in the isolation of only small amounts of the product with the III oxidation state.

Reduction of both Nb and Ta pentachlorides with 2 equiv of $Bu^n{}_3SnH$ in aromatic solvents was also carried out. However, we have not been able to characterize the products. After the reduction of MCl_5 with $Bu^n{}_3SnH$ a precipitate is formed that is only partially soluble in THF. The remaining precipitate which did not dissolve in THF is also insoluble in methylene chloride, pyridine, and methanol.

Crystal Structures. An ORTEP drawing of the M_3X_{13} core common to compounds **1**–**3** is shown in Figure 1. Important bond

Table VIII. Important Bond Distances (Å) and Angles (deg) for $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PMe_2Ph)_3]\cdot 2THF$ (**1**)[a]

Distances			
Nb(1)–Nb(2)	2.956 (1)	Nb(3)–Cl(4)	2.445 (3)
Nb(1)–Nb(3)	2.963 (2)	Nb(3)–P(3)	2.653 (4)
Nb(1)–Cl(1)	2.488 (3)	Nb(3)–Cl(9)	2.419 (3)
Nb(1)–Cl(2)	2.442 (3)	Nb(3)–Cl(10)	2.418 (3)
Nb(1)–Cl(4)	2.450 (3)	Mg(1)–Cl(11)	2.497 (5)
Nb(1)–P(1)	2.650 (3)	Mg(1)–Cl(12)	2.467 (5)
Nb(1)–Cl(5)	2.407 (3)	Mg(1)–Cl(13)	2.502 (5)
Nb(1)–Cl(6)	2.427 (3)	Mg(1)–O(1)	2.088 (8)
Nb(2)–Nb(3)	2.962 (2)	Mg(1)–O(2)	2.103 (8)
Nb(2)–Cl(1)	2.504 (3)	Mg(1)–O(3)	2.095 (10)
Nb(2)–Cl(2)	2.448 (3)	Mg(2)–Cl(11)	2.525 (5)
Nb(2)–Cl(3)	2.429 (3)	Mg(2)–Cl(12)	2.529 (5)
Nb(2)–P(2)	2.659 (3)	Mg(2)–Cl(13)	2.531 (5)
Nb(2)–Cl(7)	2.421 (4)	Mg(2)–O(4)	2.063 (8)
Nb(2)–Cl(8)	2.421 (3)	Mg(2)–O(5)	2.075 (9)
Nb(3)–Cl(1)	2.491 (3)	Mg(2)–O(6)	2.108 (10)
Nb(3)–Cl(3)	2.442 (3)		
Angles			
Nb(2)–Nb(1)–Nb(3)	60.05 (3)	Cl(3)–Nb(2)–Cl(7)	163.7 (1)
Cl(1)–Nb(1)–Cl(2)	106.45 (9)	Cl(3)–Nb(2)–Cl(8)	91.8 (1)
Cl(1)–Nb(1)–Cl(4)	105.8 (1)	P(2)–Nb(2)–Cl(7)	78.8 (1)
Cl(1)–Nb(1)–P(1)	167.0 (1)	P(2)–Nb(2)–Cl(8)	84.8 (1)
Cl(1)–Nb(1)–Cl(5)	88.6 (1)	Cl(7)–Nb(2)–Cl(8)	88.9 (1)
Cl(1)–Nb(1)–Cl(6)	89.0 (1)	Nb(1)–Nb(3)–Nb(2)	59.86 (3)
Cl(2)–Nb(1)–Cl(4)	85.9 (1)	Cl(1)–Nb(3)–Cl(3)	105.7 (1)
Cl(2)–Nb(1)–P(1)	83.7 (1)	Cl(1)–Nb(3)–Cl(4)	105.9 (1)
Cl(2)–Nb(1)–Cl(5)	165.0 (1)	Cl(1)–Nb(3)–P(3)	167.1 (1)
Cl(2)–Nb(1)–Cl(6)	90.1 (1)	Cl(1)–Nb(3)–Cl(9)	88.8 (1)
Cl(4)–Nb(1)–P(1)	82.7 (1)	Cl(1)–Nb(3)–Cl(10)	89.5 (1)
Cl(4)–Nb(1)–Cl(5)	90.0 (1)	Cl(3)–Nb(3)–Cl(4)	86.38 (9)
Cl(4)–Nb(1)–Cl(6)	165.2 (1)	Cl(3)–Nb(3)–P(3)	85.0 (1)
P(1)–Nb(1)–Cl(5)	81.5 (1)	Cl(3)–Nb(3)–Cl(9)	89.8 (1)
P(1)–Nb(1)–Cl(6)	82.7 (1)	Cl(3)–Nb(3)–Cl(10)	164.6 (1)
Cl(5)–Nb(1)–Cl(6)	90.2 (1)	Cl(4)–Nb(3)–P(3)	81.6 (1)
Nb(1)–Nb(2)–Nb(3)	60.09 (3)	Cl(4)–Nb(3)–Cl(9)	165.3 (1)
Cl(1)–Nb(2)–Cl(2)	105.75 (9)	Cl(4)–Nb(3)–Cl(10)	91.0 (1)
Cl(1)–Nb(2)–Cl(3)	105.7 (1)	P(3)–Nb(3)–Cl(9)	84.0 (1)
Cl(1)–Nb(2)–P(2)	166.8 (1)	P(3)–Nb(3)–Cl(10)	79.6 (1)
Cl(1)–Nb(2)–Cl(7)	90.6 (1)	Cl(9)–Nb(3)–Cl(10)	88.9 (1)
Cl(1)–Nb(2)–Cl(8)	87.1 (1)	Nb(1)–Cl(1)–Nb(2)	72.61 (8)
Cl(2)–Nb(2)–Cl(3)	87.0 (1)	Nb(1)–Cl(1)–Nb(3)	73.03 (8)
Cl(2)–Nb(2)–P(2)	82.1 (1)	Nb(2)–Cl(1)–Nb(3)	72.72 (8)
Cl(2)–Nb(2)–Cl(7)	88.6 (1)	Nb(1)–Cl(2)–Nb(2)	74.39 (8)
Cl(2)–Nb(2)–Cl(8)	166.9 (1)	Nb(2)–Cl(3)–Nb(3)	74.90 (8)
Cl(3)–Nb(2)–P(2)	85.0 (1)	Nb(1)–Cl(4)–Nb(3)	74.50 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IX. Important Bond Distances (Å) and Angles (deg) for $[HPEt_3][Nb_3Cl_{10}(PEt_3)_3]$ (**2**)[a]

Distances			
Nb(1)–Nb(2)	2.9620 (8)	Nb(2)–Cl(3)	2.438 (2)
Nb(1)–Nb(3)	2.9777 (8)	Nb(2)–Cl(7)	2.435 (2)
Nb(1)–Cl(1)	2.487 (2)	Nb(2)–Cl(8)	2.389 (2)
Nb(1)–Cl(2)	2.437 (2)	Nb(2)–P(2)	2.654 (2)
Nb(1)–Cl(4)	2.445 (1)	Nb(3)–Cl(1)	2.518 (2)
Nb(1)–Cl(5)	2.409 (2)	Nb(3)–Cl(3)	2.429 (2)
Nb(1)–Cl(6)	2.428 (2)	Nb(3)–Cl(4)	2.441 (2)
Nb(1)–P(1)	2.645 (2)	Nb(3)–Cl(9)	2.410 (2)
Nb(2)–Nb(3)	2.9705 (8)	Nb(3)–Cl(10)	2.425 (2)
Nb(2)–Cl(1)	2.496 (2)	Nb(3)–P(3)	2.668 (2)
Nb(2)–Cl(2)	2.439 (2)		
Angles			
Nb(2)–Nb(1)–Nb(3)	60.02 (2)	Cl(3)–Nb(2)–Cl(8)	92.67 (7)
Cl(1)–Nb(1)–Cl(2)	105.86 (5)	Cl(3)–Nb(2)–P(2)	82.31 (6)
Cl(1)–Nb(1)–Cl(4)	105.75 (5)	Cl(7)–Nb(2)–Cl(8)	88.72 (7)
Cl(1)–Nb(1)–Cl(5)	87.13 (6)	Cl(7)–Nb(2)–P(2)	82.84 (6)
Cl(1)–Nb(1)–Cl(6)	88.49 (6)	Cl(8)–Nb(2)–P(2)	83.69 (7)
Cl(1)–Nb(1)–P(1)	168.47 (6)	Nb(1)–Nb(3)–Nb(2)	59.73 (2)
Cl(2)–Nb(1)–Cl(4)	87.62 (5)	Cl(1)–Nb(3)–Cl(3)	105.51 (5)
Cl(2)–Nb(1)–Cl(5)	166.95 (6)	Cl(1)–Nb(3)–Cl(4)	104.94 (5)
Cl(2)–Nb(1)–Cl(6)	90.04 (6)	Cl(1)–Nb(3)–Cl(9)	87.55 (6)
Cl(2)–Nb(1)–P(1)	80.39 (6)	Cl(1)–Nb(3)–Cl(10)	88.29 (6)
Cl(4)–Nb(1)–Cl(5)	90.15 (6)	Cl(1)–Nb(3)–P(3)	171.10 (6)
Cl(4)–Nb(1)–Cl(6)	165.67 (6)	Cl(3)–Nb(3)–Cl(4)	87.64 (6)
Cl(4)–Nb(1)–P(1)	83.93 (5)	Cl(3)–Nb(3)–Cl(9)	91.53 (7)
Cl(5)–Nb(1)–Cl(6)	88.95 (6)	Cl(3)–Nb(3)–Cl(10)	166.14 (6)
Cl(5)–Nb(1)–P(1)	86.58 (6)	Cl(3)–Nb(3)–P(3)	80.44 (6)
Cl(6)–Nb(1)–P(1)	81.75 (6)	Cl(4)–Nb(3)–Cl(9)	167.25 (6)
Nb(1)–Nb(2)–Nb(3)	60.25 (2)	Cl(4)–Nb(3)–Cl(10)	90.16 (7)
Cl(1)–Nb(2)–Cl(2)	105.52 (5)	Cl(4)–Nb(3)–P(3)	81.66 (6)
Cl(1)–Nb(2)–Cl(3)	105.90 (5)	Cl(9)–Nb(3)–Cl(10)	87.61 (8)
Cl(1)–Nb(2)–Cl(7)	89.24 (6)	Cl(9)–Nb(3)–P(3)	85.65 (6)
Cl(1)–Nb(2)–Cl(8)	87.31 (7)	Cl(10)–Nb(3)–P(3)	85.70 (6)
Cl(1)–Nb(2)–P(2)	168.12 (6)	Nb(1)–Cl(1)–Nb(2)	72.95 (5)
Cl(2)–Nb(2)–Cl(3)	86.25 (5)	Nb(1)–Cl(1)–Nb(3)	73.03 (4)
Cl(2)–Nb(2)–Cl(7)	88.99 (6)	Nb(2)–Cl(1)–Nb(3)	72.67 (5)
Cl(2)–Nb(2)–Cl(8)	166.93 (7)	Nb(1)–Cl(2)–Nb(2)	74.82 (5)
Cl(2)–Nb(2)–P(2)	83.26 (6)	Nb(2)–Cl(3)–Nb(3)	75.22 (5)
Cl(3)–Nb(2)–Cl(7)	164.84 (6)	Nb(1)–Cl(4)–Nb(3)	75.09 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

distances and angles for these compounds are listed in Tables VIII–X. This core is very similar to that found in the d^6 trimers of Nb and Ta reported earlier.[3] The capping chlorine atom is symmetrically bonded to the three metal atoms, within the experimental errors. The terminal phosphine ligands are all located trans to the capping chlorine atom. The $[Nb_3Cl_{10}(PEt_3)_3]^-$ anion in **2**, **3**, and the previously[3b] reported $(HPEt_3)[Nb_3Cl_{10}(PEt_3)_3]\cdot 1.25C_7H_8$ are identical. The mean Nb–Nb distances are 2.970 [5], 2.969 [10], and 2.976 [6] Å, respectively.

In compounds **4**–**6**, the THF ligands are found in either cis or trans positions to the capping chlorine atoms. An ORTEP drawing of compound **4**, Figure 2, shows that the four THF ligands are so oriented that two of them coordinate to the Ta(1) atom and one to each remaining tantalum atom. The metal–metal distances in this cluster show much greater variation than in any other case. The metal–metal distance between the two Ta atoms opposite to Ta(1), namely Ta(2)–Ta(3), is the longest, 2.932 (1) Å, while the two nearly equal Ta(1)–Ta(3) and Ta(1)–Ta(2) distances are much shorter (2.850 (1) and 2.868 (1) Å, respectively). Important bond distances and angles for **4** are listed in Table XI.

Although both compound **5** and compound **6** contain an anion of the same general formula $[M_3Cl_{10}(THF)_3]^-$, there are differences in the orientation of the THF ligands about the metal atoms. In compound **5**, as shown in Figure 3, three THF ligands are cis to the capping chlorine, and arranged in accord with crystallographic C_3 symmetry. Compound **6** has two of the THF ligands trans and the third cis to the capping chlorine. An ORTEP drawing of this anion is shown in Figure 4.

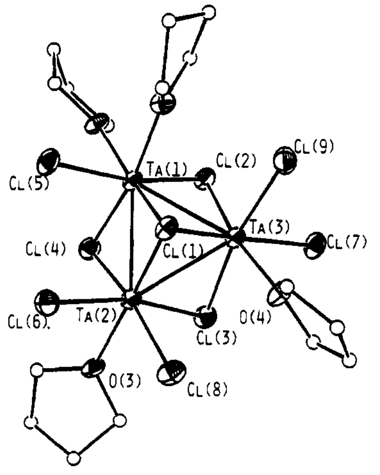

Figure 2. ORTEP drawing of $Ta_3Cl_9(THF)_4$ (**4**), with the thermal ellipsoids drawn at 50% probability level and carbon atoms assigned arbitrarily small radii.

In compounds **5** and **6**, where Na is the counterion, there are interesting solid-state interactions between some of the terminal chlorine atoms and the sodium atoms. In compound **5**, the Na cation, which is located on a 3-fold symmetry axis, interacts with

Table X. Important Bond Distances (Å) and Angles (deg) for $[Mg_2Cl_3(THF)_6][Nb_3Cl_{10}(PEt_3)_3]\cdot 2THF$ (**3**)[a]

Distances			
Nb(1)–Nb(2)	2.954 (6)	Nb(3)–Cl(4)	2.467 (9)
Nb(1)–Nb(3)	2.967 (4)	Nb(3)–Cl(9)	2.403 (10)
Nb(1)–Cl(1)	2.495 (9)	Nb(3)–Cl(10)	2.410 (14)
Nb(1)–Cl(2)	2.438 (11)	Nb(3)–P(3)	2.705 (10)
Nb(1)–Cl(4)	2.463 (8)	Mg(1)–Cl(11)	2.51 (2)
Nb(1)–Cl(5)	2.411 (15)	Mg(1)–Cl(12)	2.515 (13)
Nb(1)–Cl(6)	2.408 (9)	Mg(1)–Cl(13)	2.520 (12)
Nb(1)–P(1)	2.645 (10)	Mg(1)–O(1)	2.05 (3)
Nb(2)–Nb(3)	2.987 (6)	Mg(1)–O(2)	2.08 (2)
Nb(2)–Cl(1)	2.493 (13)	Mg(1)–O(3)	2.09 (2)
Nb(2)–Cl(2)	2.446 (8)	Mg(2)–Cl(11)	2.514 (14)
Nb(2)–Cl(3)	2.454 (8)	Mg(2)–Cl(12)	2.48 (2)
Nb(2)–Cl(7)	2.395 (9)	Mg(2)–Cl(13)	2.492 (13)
Nb(2)–Cl(8)	2.394 (11)	Mg(2)–O(4)	2.17 (3)
Nb(2)–P(2)	2.648 (15)	Mg(2)–O(5)	2.10 (3)
Nb(3)–Cl(1)	2.507 (8)	Mg(2)–O(6)	2.07 (2)
Nb(3)–Cl(3)	2.438 (12)		

Angles			
Nb(2)–Nb(1)–Nb(3)	60.6 (1)	Cl(3)–Nb(2)–Cl(8)	91.1 (3)
Cl(1)–Nb(1)–Cl(2)	106.2 (4)	Cl(3)–Nb(2)–P(2)	82.8 (4)
Cl(1)–Nb(1)–Cl(4)	106.4 (3)	Cl(7)–Nb(2)–Cl(8)	89.4 (4)
Cl(1)–Nb(1)–Cl(5)	88.3 (4)	Cl(7)–Nb(2)–P(2)	82.8 (4)
Cl(1)–Nb(1)–Cl(6)	88.2 (3)	Cl(8)–Nb(2)–P(2)	85.8 (4)
Cl(1)–Nb(1)–P(1)	169.7 (4)	Nb(1)–Nb(3)–Nb(2)	59.5 (1)
Cl(2)–Nb(1)–Cl(4)	86.2 (3)	Cl(1)–Nb(3)–Cl(3)	105.1 (4)
Cl(2)–Nb(1)–Cl(5)	165.4 (4)	Cl(1)–Nb(3)–Cl(4)	106.0 (3)
Cl(2)–Nb(1)–Cl(6)	92.0 (4)	Cl(1)–Nb(3)–Cl(9)	88.0 (3)
Cl(2)–Nb(1)–P(1)	80.3 (4)	Cl(1)–Nb(3)–Cl(10)	89.1 (4)
Cl(4)–Nb(1)–Cl(5)	90.1 (4)	Cl(1)–Nb(3)–P(3)	169.1 (4)
Cl(4)–Nb(1)–Cl(6)	165.2 (3)	Cl(3)–Nb(3)–Cl(4)	87.4 (3)
Cl(4)–Nb(1)–P(1)	81.6 (3)	Cl(3)–Nb(3)–Cl(9)	89.0 (4)
Cl(5)–Nb(1)–Cl(6)	88.1 (4)	Cl(3)–Nb(3)–Cl(10)	165.7 (3)
Cl(5)–Nb(1)–P(1)	85.2 (4)	Cl(3)–Nb(3)–P(3)	83.1 (4)
Cl(6)–Nb(1)–P(1)	83.6 (3)	Cl(4)–Nb(3)–Cl(9)	166.0 (3)
Nb(1)–Nb(2)–Nb(3)	59.9 (1)	Cl(4)–Nb(3)–Cl(10)	90.6 (4)
Cl(1)–Nb(2)–Cl(2)	106.0 (4)	Cl(4)–Nb(3)–P(3)	81.2 (3)
Cl(1)–Nb(2)–Cl(3)	105.1 (4)	Cl(9)–Nb(3)–Cl(10)	89.6 (4)
Cl(1)–Nb(2)–Cl(7)	89.4 (4)	Cl(9)–Nb(3)–P(3)	85.0 (3)
Cl(1)–Nb(2)–Cl(8)	87.3 (4)	Cl(10)–Nb(3)–P(3)	82.6 (4)
Cl(1)–Nb(2)–P(2)	169.6 (4)	Nb(1)–Cl(1)–Nb(2)	72.6 (3)
Cl(2)–Nb(2)–Cl(3)	86.9 (3)	Nb(1)–Cl(1)–Nb(3)	72.8 (2)
Cl(2)–Nb(2)–Cl(7)	89.3 (3)	Nb(2)–Cl(1)–Nb(3)	73.4 (3)
Cl(2)–Nb(2)–Cl(8)	166.6 (5)	Nb(1)–Cl(2)–Nb(2)	74.4 (3)
Cl(2)–Nb(2)–P(2)	80.8 (4)	Nb(2)–Cl(3)–Nb(3)	75.3 (3)
Cl(3)–Nb(2)–Cl(7)	165.5 (5)	Nb(1)–Cl(4)–Nb(3)	74.0 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

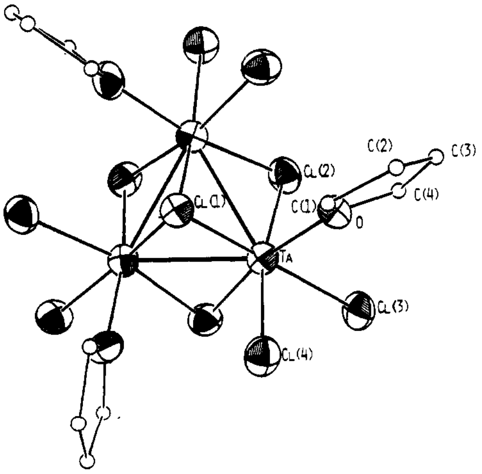

Figure 3. ORTEP drawing of $[Ta_3Cl_{10}(THF)_3]^-$ (anion of **5**), with the thermal ellipsoids drawn at 50% probability level and carbon atoms assigned arbitrarily small radii.

Table XI. Selected Bond Distances (Å) and Angles (deg) for $Ta_3Cl_9(THF)_4\cdot C_6H_6\cdot THF$ (**4**)[a]

Distances			
Ta(1)–Ta(2)	2.868 (1)	Ta(2)–Cl(4)	2.439 (2)
Ta(1)–Ta(3)	2.850 (1)	Ta(2)–Cl(6)	2.380 (3)
Ta(1)–Cl(1)	2.439 (2)	Ta(2)–Cl(8)	2.425 (2)
Ta(1)–Cl(2)	2.425 (3)	Ta(2)–O(3)	2.226 (7)
Ta(1)–Cl(4)	2.423 (3)	Ta(3)–Cl(1)	2.473 (3)
Ta(1)–Cl(5)	2.407 (3)	Ta(3)–Cl(2)	2.410 (2)
Ta(1)–O(1)	2.248 (6)	Ta(3)–Cl(3)	2.438 (3)
Ta(1)–O(2)	2.166 (7)	Ta(3)–Cl(7)	2.483 (3)
Ta(2)–Ta(3)	2.932 (1)	Ta(3)–Cl(9)	2.410 (3)
Ta(2)–Cl(1)	2.454 (3)	Ta(3)–O(4)	2.150 (6)
Ta(2)–Cl(3)	2.445 (3)		

Angles			
Ta(2)–Ta(1)–Ta(3)	61.70 (1)	Cl(4)–Ta(2)–Cl(8)	165.81 (9)
Cl(1)–Ta(1)–Cl(2)	108.00 (9)	Cl(4)–Ta(2)–O(3)	80.2 (2)
Cl(1)–Ta(1)–Cl(4)	108.05 (7)	Cl(6)–Ta(2)–Cl(8)	88.9 (1)
Cl(1)–Ta(1)–Cl(5)	86.01 (9)	Cl(6)–Ta(2)–O(3)	84.4 (2)
Cl(1)–Ta(1)–O(1)	165.7 (2)	Cl(8)–Ta(2)–O(3)	86.3 (2)
Cl(1)–Ta(1)–O(2)	85.3 (2)	Ta(1)–Ta(3)–Ta(2)	59.46 (1)
Cl(2)–Ta(1)–Cl(4)	88.34 (9)	Cl(1)–Ta(3)–Cl(2)	107.36 (9)
Cl(2)–Ta(1)–Cl(5)	164.86 (7)	Cl(1)–Ta(3)–Cl(3)	105.56 (9)
Cl(2)–Ta(1)–O(1)	81.1 (2)	Cl(1)–Ta(3)–Cl(7)	166.65 (9)
Cl(2)–Ta(1)–O(2)	90.4 (2)	Cl(1)–Ta(3)–Cl(9)	85.0 (1)
Cl(4)–Ta(1)–Cl(5)	92.8 (1)	Cl(1)–Ta(3)–O(4)	84.4 (2)
Cl(4)–Ta(1)–O(1)	82.7 (2)	Cl(2)–Ta(3)–Cl(3)	90.44 (8)
Cl(4)–Ta(1)–O(2)	166.3 (2)	Cl(2)–Ta(3)–Cl(7)	82.67 (9)
Cl(5)–Ta(1)–O(1)	84.1 (2)	Cl(2)–Ta(3)–Cl(9)	91.98 (8)
Cl(5)–Ta(1)–O(2)	84.9 (2)	Cl(2)–Ta(3)–O(4)	167.8 (2)
O(1)–Ta(1)–O(2)	83.6 (2)	Cl(3)–Ta(3)–Cl(7)	82.67 (9)
Ta(1)–Ta(2)–Ta(3)	58.84 (1)	Cl(3)–Ta(3)–Cl(9)	167.9 (1)
Cl(1)–Ta(2)–Cl(3)	105.91 (9)	Cl(3)–Ta(3)–O(4)	89.5 (2)
Cl(1)–Ta(2)–Cl(4)	107.06 (8)	Cl(7)–Ta(3)–Cl(9)	85.9 (1)
Cl(1)–Ta(2)–Cl(6)	86.9 (1)	Cl(7)–Ta(3)–O(4)	85.2 (2)
Cl(1)–Ta(2)–Cl(8)	86.95 (8)	Cl(9)–Ta(3)–O(4)	85.6 (2)
Cl(1)–Ta(2)–O(3)	169.1 (2)	Ta(1)–Cl(1)–Ta(2)	71.77 (7)
Cl(3)–Ta(2)–Cl(4)	87.08 (9)	Ta(1)–Cl(1)–Ta(3)	70.91 (6)
Cl(3)–Ta(2)–Cl(6)	166.22 (9)	Ta(2)–Cl(1)–Ta(3)	73.04 (7)
Cl(3)–Ta(2)–Cl(8)	86.82 (9)	Ta(1)–Cl(2)–Ta(3)	72.23 (6)
Cl(3)–Ta(2)–O(3)	82.3 (2)	Ta(2)–Cl(3)–Ta(3)	73.81 (8)
Cl(4)–Ta(2)–Cl(6)	94.0 (1)	Ta(1)–Cl(4)–Ta(2)	73.20 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table XII. Selected Bond Distances (Å) and Angles (deg) for $Na[Ta_3Cl_{10}(THF)_3]$ (**5**)[a]

Distances			
Ta–Ta	2.875 (2)	Ta–Cl(4)	2.423 (8)
Ta–Cl(1)	2.453 (2)	Ta–O	2.18 (2)
Ta–Cl(2)	2.408 (8)	Na–Cl(3)	2.714 (9)
Ta–Cl(3)	2.499 (8)	Na–Cl(4)	2.774 (9)

Angles			
Ta–Ta–Ta	60.00 (5)	Ta–Cl(1)–Ta	71.73 (6)
Cl(1)–Ta–Cl(2)	106.6 (3)	Ta–Cl(2)–Ta	73.3 (2)
Cl(1)–Ta–Cl(3)	165.7 (3)	Cl(3)–Na–Cl(3)	101.1 (3)
Cl(1)–Ta–Cl(4)	83.4 (3)	Cl(3)–Na–Cl(4)	75.8 (3)
Cl(2)–Ta–Cl(2)	91.2 (3)	Cl(3)–Na–Cl(4)	168.9 (3)
Cl(2)–Ta–Cl(3)	82.6 (3)	Cl(3)–Na–Cl(4)	90.0 (3)
Cl(2)–Ta–Cl(4)	168.5 (3)	Cl(4)–Na–Cl(4)	93.4 (4)
Cl(3)–Ta–Cl(4)	86.5 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

two terminal Cl_t atoms from each of the three different trimers, with an average distance of 2.74 [3] Å between the Cl_t and Na atoms.[16] Chlorine atoms are arranged in an approximately octahedral geometry about the Na atom. Important bond distances and angles for compound **5** are listed in Table XII.

In compound **6**, the trinuclear cluster units are connected together by Na–Cl_t bonds to form infinite spiral chains along the *b* axis. The coordination of the Na counterion consists of two

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(16) Throughout this document, the estimated standard deviation of a measurement is reported in parentheses. When more than one measurement is averaged, the variance, defined as $[\sum \Delta_i^2/n(n-1)]^{0.5}$ where Δ_i is the deviation of the *i*th value from the arithmetic mean and n is the total number of values averaged, is reported in square brackets.

Table XIII. Selected Bond Distances (Å) and Angles (deg) for $Na[Nb_3Cl_{10}(THF)_3]\cdot 3THF$ (**6**)[a]

Distances			
Nb(1)-Nb(2)	2.926 (1)	Nb(2)-O(2)	2.182 (5)
Nb(1)-Nb(3)	2.953 (1)	Nb(3)-Cl(1)	2.467 (2)
Nb(1)-Cl(1)	2.448 (2)	Nb(3)-Cl(3)	2.440 (2)
Nb(1)-Cl(2)	2.448 (2)	Nb(3)-Cl(4)	2.401 (2)
Nb(1)-Cl(3)	2.458 (2)	Nb(3)-Cl(9)	2.511 (2)
Nb(1)-Cl(5)	2.413 (2)	Nb(3)-Cl(10)	2.437 (2)
Nb(1)-Cl(6)	2.398 (2)	Nb(3)-O(3)	2.170 (5)
Nb(1)-O(1)	2.248 (5)	Cl(7)-Na	2.741 (4)
Nb(2)-Nb(3)	2.921 (1)	Cl(8)-Na	2.872 (4)
Nb(2)-Cl(1)	2.454 (2)	Cl(9)-Na	2.757 (4)
Nb(2)-Cl(2)	2.431 (2)	Cl(10)-Na	2.798 (4)
Nb(2)-Cl(4)	2.427 (2)	Na-O(4)	2.371 (7)
Nb(2)-Cl(7)	2.503 (2)	Na-O(5)	2.358 (8)
Nb(2)-Cl(8)	2.425 (2)		
Angles			
Nb(2)-Nb(1)-Nb(3)	59.58 (2)	Nb(1)-Nb(3)-Nb(2)	59.74 (2)
Cl(1)-Nb(1)-Cl(2)	106.04 (7)	Cl(1)-Nb(3)-Cl(3)	105.30 (7)
Cl(1)-Nb(1)-Cl(3)	105.33 (7)	Cl(1)-Nb(3)-Cl(4)	105.88 (7)
Cl(1)-Nb(1)-Cl(5)	85.05 (7)	Cl(1)-Nb(3)-Cl(9)	167.74 (7)
Cl(1)-Nb(1)-Cl(6)	89.18 (7)	Cl(1)-Nb(3)-Cl(10)	84.37 (7)
Cl(1)-Nb(1)-O(1)	169.9 (2)	Cl(1)-Nb(3)-O(3)	86.5 (2)
Cl(2)-Nb(1)-Cl(3)	87.02 (7)	Cl(3)-Nb(3)-Cl(4)	90.45 (7)
Cl(2)-Nb(1)-Cl(5)	168.91 (8)	Cl(3)-Nb(3)-Cl(9)	83.33 (7)
Cl(2)-Nb(1)-Cl(6)	90.78 (8)	Cl(3)-Nb(3)-Cl(10)	168.25 (8)
Cl(2)-Nb(1)-O(1)	81.8 (2)	Cl(3)-Nb(3)-O(3)	88.3 (1)
Cl(3)-Nb(1)-Cl(5)	90.02 (8)	Cl(4)-Nb(3)-Cl(9)	82.38 (7)
Cl(3)-Nb(1)-Cl(6)	165.37 (8)	Cl(4)-Nb(3)-Cl(10)	93.30 (7)
Cl(3)-Nb(1)-O(1)	81.0 (2)	Cl(4)-Nb(3)-O(3)	167.4 (2)
Cl(5)-Nb(1)-Cl(6)	89.39 (8)	Cl(9)-Nb(3)-Cl(10)	86.13 (7)
Cl(5)-Nb(1)-O(1)	87.1 (2)	Cl(9)-Nb(3)-O(3)	85.0 (2)
Cl(6)-Nb(1)-O(1)	84.4 (2)	Cl(10)-Nb(3)-O(3)	85.7 (1)
Nb(1)-Nb(2)-Nb(3)	60.68 (2)	Cl(7)-Na-Cl(8)	73.0 (1)
Cl(1)-Nb(2)-Cl(2)	106.37 (7)	Cl(7)-Na-Cl(9)	92.5 (1)
Cl(1)-Nb(2)-Cl(4)	105.49 (7)	Cl(7)-Na-Cl(10)	164.2 (1)
Cl(1)-Nb(2)-Cl(7)	167.08 (7)	Cl(7)-Na-O(4)	99.6 (2)
Cl(1)-Nb(2)-Cl(8)	85.78 (7)	Cl(7)-Na-O(5)	92.2 (2)
Cl(1)-Nb(2)-O(2)	84.6 (2)	Cl(8)-Na-Cl(9)	92.9 (1)
Cl(2)-Nb(2)-Cl(4)	88.21 (7)	Cl(8)-Na-Cl(10)	97.7 (1)
Cl(2)-Nb(2)-Cl(7)	83.73 (7)	Cl(8)-Na-O(4)	92.0 (2)
Cl(2)-Nb(2)-Cl(8)	95.11 (8)	Cl(8)-Na-O(5)	164.9 (2)
Cl(2)-Nb(2)-O(2)	169.0 (2)	Cl(9)-Na-Cl(10)	74.9 (1)
Cl(4)-Nb(2)-Cl(7)	82.45 (7)	Cl(9)-Na-O(4)	167.8 (3)
Cl(4)-Nb(2)-Cl(8)	166.88 (8)	Cl(9)-Na-O(5)	90.5 (2)
Cl(4)-Nb(2)-O(2)	88.9 (2)	Cl(10)-Na-O(4)	93.4 (2)
Cl(7)-Nb(2)-Cl(8)	85.29 (7)	Cl(10)-Na-O(5)	97.4 (2)
Cl(7)-Nb(2)-O(2)	85.4 (2)	O(4)-Na-O(5)	87.6 (3)
Cl(8)-Nb(2)-O(2)	85.5 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

oxygen atoms from two THF solvent molecules and four terminal chlorine atoms from two trimer units. The average Na–O distance is 2.365 Å, while the average Na–Cl_t distance is 2.79 [3] Å. The selected bond distances and angles for **6** are listed in Table XIII.

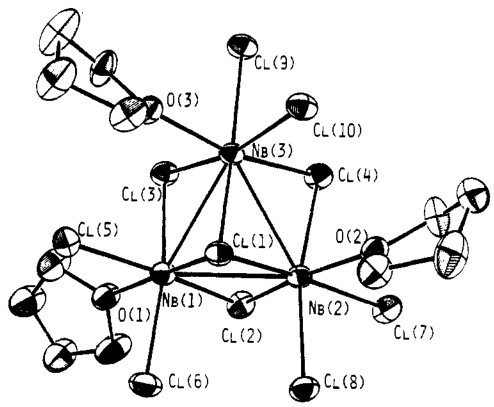

Figure 4. ORTEP drawing of $[Nb_3Cl_{10}(THF)_3]^-$ (anion of **6**), with the thermal ellipsoids drawn at 50% probability level and carbon atoms assigned arbitrarily small radii.

The coordination of chlorine atoms and THF molecules around the sodium cation was also observed in $[Na(THF)_3][Nb_2X_5(\mu\text{-}THT)_3]_2$[17] where the Na atoms adopt two types of coordination. One, similar to that in **4**, comprises six chlorine atoms while the other consists of four chlorine atoms and one THF molecule.

Discussion

The results reported here show that the preparation of triangular cluster species of the type with an M_3Cl_4 core, where M is Nb or Ta can be accomplished in several ways, whereby some control over the type of ligands present and the countercations (where appropriate) can be exercised. It must be noted that the results presented here are only exploratory from a preparative point of view. In general, the yields were low, but there is no doubt that they could be improved. Some ways of doing this are obvious. The deliberate addition of $MgCl_2$, to take account of the fact that more $[Mg_2Cl_3(THF)_6]^+$ ions are required in **1** and **3** than can be provided by the Mg metal that is oxidized, would clearly be worthwhile. Similarly, instead of relying on the adventitious formation of $[HPEt_3]^+$ in making **2**, one could deliberately add this cation or a similar one. However, a critical problem with no obvious solution is that the reactions are generally not "clean". Large quantities of unidentified precipitates or oils are often formed. What we have done is to show that interesting compounds exist and to structurally characterize them. What remains to be done is to optimize and better understand the reactions that produce them.

It is not clear why the products in these reactions are the trinuclear species rather than dinuclear ones with M=M bonds, since the M^{III} atoms can do either one of these things.

Another phase of this chemistry that still requires work is the further reduction of the clusters to give seven- and eight-electron clusters. One discrete example of the latter is known, $Nb_3Cl_7(PMe_2Ph)_6$, but none of the seven-electron type. It has been found that such reduced species have a strong tendency to abstract oxygen atoms from neighboring oxygen-containing molecules and replace the μ_3-Cl atom by μ_3-O.

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Supplementary Material Available: Full ORTEP drawings of compounds 1–3 and, for all six structures, complete tables of the crystallographic data and full listings of bond distances and bond angles and anisotropic displacement parameters (53 pages); tables of observed and calculated structure factors (144 pages). Ordering information is given on any current masthead page.

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(17) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5506.

(18) Cotton, F. A.; Diebold, M. P.; Roth, W. J. Unpublished results, 1987.