Anal. Calcd for $Ce_3C_{40}H_{90}O_{11}$: Ce, 36.0. Found: Ce, 35.7. IR (KBr): 2900 s, 1450 m, 1350 s, 1170 s br, 930 s br, 760 m cm^{-1}. $Ce_2(OCMe_3)_9Na$ similarly transforms to **7**, but the reaction takes over 1 week.

Reactions of 1, 2, and 5 with $NaOCMe_3$. Complex **1** has been treated with 1, 2, 3, 3.5, and 5 equiv of $NaOCMe_3$ in THF to form **2**, **3**, **4**, **6**, and **5**, respectively, in good yield (80–95%). Similarly, **2** reacts with 1 and 2 equiv of $NaOCMe_3$ to form **3** and **4**, respectively, in good yield. Complex **5** has been treated with 0.5 equiv of $NaOCMe_3$ to form **6** in good yield. A typical procedure for these reactions follows.

Preparation of 4 from 1. In the glovebox, $NaOCMe_3$ (26.5 mg, 0.276 mmol) dissolved in 5 mL of THF was added to $Ce(OCMe_3)(NO_3)_3(THF)_2$ (50 mg, 0.072 mmol) in 5 mL of THF and a white precipitate formed. After it was stirred for 20 h, the reaction mixture was centrifuged and a white powder (23 mg, 100% if $NaNO_3$) was isolated. Removal of solvent from the centrifuged solution by rotary evaporation gave **4** as an orange powder (49 mg, 94%) identified by ^1H NMR spectroscopy.

Reaction of 5 with NH_4NO_3. $Ce(OCMe_3)_6Na_2(THF)_2$ (50 mg, 0.065 mmol) in 5 mL of THF was added to a Schlenk flask containing NH_4NO_3 (26 mg, 0.325 mmol) suspended in 5 mL of THF. After the mixture was stirred for 2 h, the solution was filtered to remove a pale yellow precipitate (12 mg, 109% yield if pure $NaNO_3$). Removal of solvent from the orange filtrate gave **1** (34 mg, 96%) identified by ^1H NMR spectroscopy.

Acknowledgment. We thank the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy for support of this research and the University of California, Irvine, CA, for a President's Undergraduate Fellowship (to T.J.D.). Funds for the purchase of the Nicolet R3m/V diffractometer system were made available from the National Science Foundation under Grant CHE-85-14495.

Registry No. **1**, 121314-35-0; **1′**, 122423-56-7; **2**, 121314-34-9; **2′**, 122423-65-8; **3**, 122423-57-8; **4**, 122423-58-9; **5**, 122423-59-0; **5′**, 122423-61-4; **6**, 122423-62-5; **7**, 122423-64-7; $(NH_4)_2Ce(NO_3)_6$, 16774-21-3; $Ce(NO_3)_4(THF)_2$, 122423-63-6.

Supplementary Material Available: Tables of crystal data, bond distances and angles, thermal parameters, and hydrogen atom coordinates (13 pages); tables of structure factor amplitudes (56 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of a Tetrameric Tantalum(III) Compound

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The tetrameric compound $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2{\cdot}2C_7H_8$ has been prepared from the reaction of $Ta_2Cl_4(SC_4H_8)_2(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)$ (**1**) with $Ph_2PCH_2CH_2PPh_2$ (dppe). The compound crystallizes in the space group *Bbcm*, which is the *bca* setting of space group No. 64, *Cmca*. The cell parameters are a = 12.706 (6) Å, b = 27.240 (7) Å, c = 25.93 (2) Å, V = 8976 (9) $Å^3$, and Z = 4. The structure consists of two confacial bioctahedral units of $Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)$ bridged by two $Ph_2PCH_2CH_2PPh_2$ ligands. The Ta=Ta double-bond distance within the bioctahedral units is 2.704 (2) Å with no metal–metal bonding between the separate dimeric units of the tetramer. To our knowledge this compound is the first tetrameric tantalum(III) compound reported in the literature. It is a deviation from the products previously reported for the reactions of analogous niobium or tantalum dimeric compounds with bidentate phosphine ligands, all of which result in the formation of edge-shared dimeric compounds of the type $M_2Cl_6(PP)_2$ (where PP = bidentate phosphine ligand). The fact that the bridging (SC_4H_8) ligand is not substituted in the tantalum tetramer suggests that the ligand is less labile in **1** than in its niobium analogue.

Introduction

Several years ago, we explored the reactions of the dimeric niobium(III) and tantalum(III) compounds $M_2Cl_6L_3$ [L = tetrahydrothiophene (THT) or SMe_2] with a variety of bidentate ligands.[1] The starting compounds $M_2Cl_6L_3$ possess confacial bioctahedral geometry[2,3] (I) and were shown to undergo substitution of the L groups by various neutral ligands. Almost all reactions with neutral bidentate ligands have resulted in dimeric products of the formulation $M_2Cl_6(BB)_2$, where BB = 2,5-dithiahexane, 3,6-dithiaoctane, 2,2′-bipyridine, or ethylenebis(diphenylphosphine). In the case of the ligand $Ph_2PCH_2CH_2PPh_2$ (dppe), only the niobium dimer yielded a complex of the formulation $Nb_2Cl_6(dppe)_2$.[1,4] The structure of this compound has since been reported as an edge-shared bioctahedral dimer with the dppe ligands chelated trans to the bridging chlorines.[5] Repeated attempts to prepare the analogous $Ta_2Cl_6(dppe)_2$ dimer resulted in a compound approaching the stoichiometry $Ta_2Cl_6(dppe)$ rather than the expected $Ta_2Cl_6(dppe)_2$. Since our initial report, many niobium and tantalum dimers have been reported containing bidentate diphosphine ligands, PP (where PP = $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2CH_2PMe_2$ (dmpe), or $Me_2PCH_2PMe_2$ (dmpm).[5-8,16,17]

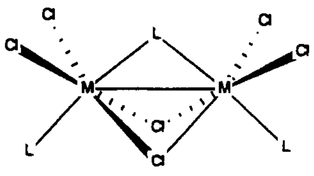

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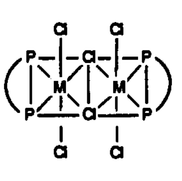
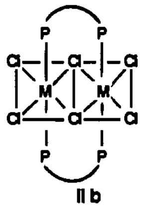
Table I. Crystallographic Parameters for $Ta_4Cl_{12}S_2P_4C_{60}H_{64}{\cdot}2C_7H_8$

$a = 12.706$ (6) Å	space group: *Bbcm* (No. 64 *bca* setting)
$b = 27.240$ (7) Å	$\lambda = 0.71073$ Å
$c = 25.93$ (2) Å	$\rho_{obsd} = 1.71$ g cm^{-3}; $\rho_{calcd} = 1.72$ g cm^{-3}
$V = 8976$ (9) Å^3	$\mu = 55.7$ cm^{-1}
$Z = 4$	transm coeff = 0.25–0.30
$T = 23$ °C	$R = 0.052$
fw: 2214.5	$R_w = 0.048$

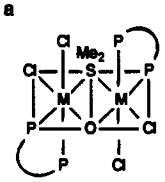
The structural geometries of these $M_2Cl_6(PP)_2$ complexes are all edge-shared bioctahedral dimers with the PP ligands in either chelating or bridging positions (IIa,b). Also of interest is the report of the compound $Ta_2(\mu\text{-}O)(\mu\text{-}SMe_2)Cl_4(dmpe)_2$ with the PP ligands chelating from axial to terminal positions as shown in IIc.[17]



IIa



IIb



IIc

Notably lacking in the series is the compound $Ta_2Cl_6(dppe)_2$, whose structure has not been reported to date. We now wish to report the synthesis and structure of the unusual tetrameric compound $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}THT)]_2(\mu\text{-}dppe)_2$. The previously observed stoichiometry of this compound is now explicable.

Experimental Section

Preparation. All manipulations were performed in a dry N_2 atmosphere, by using standard techniques. $Ta_2Cl_6(THT)_3$ was prepared according to the literature method.[9]

An excess of dppe (200 mg, 0.5 mmol) was dissolved in 5 mL of toluene and layered into the bottom of a test tube. A 1-in. layer of toluene was placed over the dppe solution. $Ta_2Cl_6(THT)_3$ (200 mg, 0.24 mmol) was dissolved in 5 mL of toluene and carefully syringed into the test tube, leaving three distinct layers. The tube was capped, and in 5–7 days dark red crystals having irregular shapes were harvested.

A compound of similar properties and composition[15] has been obtained by using the batch preparation procedure as reported for $Nb_2Cl_6(dppe)_2$.[1,4]

X-ray Crystallography. A crystal having 12 faces approximately 0.3 mm on edge was selected and mounted in a 0.5-mm glass capillary and sealed under an N_2 atmosphere. Least-squares refinement of 15 reflections measured with a Syntex P$\bar{1}$ autodiffractometer at room temperature yielded the cell parameters, and axial photographs confirmed that the cell belonged to the orthorhombic system. The lattice and crystallographic parameters are listed in Table I. Standard Syntex P$\bar{1}$ centering, indexing, and data collection programs were used. Data were collected by ω-scan technique with a scan rate of 2°/min taking 1° on each side of peak. Four intensity standards were measured every 100 reflections, showing a linear decomposition of 2% over the collection time. Faces were indexed and measured, and analytical absorption corrections[10] were made by using the DDATA X-ray program. The structure was solved by using the CRYSTALS computing package.[11] All heavy atoms were refined with anisotropic temperature factors. Carbon atoms were refined isotropically, and hydrogen atoms were fixed at calculated positions. Final atomic coordinates and temperature factors are listed in Table II.

Results and Discussion

A three-dimensional Patterson synthesis provided the location of the tantalum atom in the asymmetric unit. Fourier synthesis using the tantalum atom position revealed the positions of all the non-hydrogen atoms. The structure was refined in both the centrosymmetric space group *Bbcm* and the acentric space group *Bba*2, since both space groups have identical extinction conditions. The *Bbcm* model gives a better result, $R = 5.2$ and $R_w = 4.8$ versus R and R_w values of 8.7 and 7.4 obtained for the *Bba*2 model, which required the use of considerable constraints.

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for All Non-Hydrogen Atoms in $[Ta_2Cl_6(THT)(dpp)]_2{\cdot}2C_7H_8$

atom	*x/a*	*y/b*	*z/c*	*U*(iso), Å^2
Ta(1)	0.39560 (7)	0.37419 (3)	0.05214 (3)	0.0425
Cl(1)	0.4008 (8)	0.4518 (2)	0	0.0534
Cl(2)	0.0585 (6)	0.1332 (3)	0	0.0503
S(1)	0.2738 (7)	0.3291 (3)	0	0.0551
Cl(11)	0.2514 (5)	0.4060 (3)	0.0994 (2)	0.0722
Cl(12)	0.4323 (5)	0.3013 (2)	0.0987 (2)	0.0614
P(1)	0.0313 (6)	0.0807 (2)	0.1200 (2)	0.0476
C(51)	0.1371 (28)	0.3382 (13)	0	0.074 (11)
C(54)	0.2621 (30)	0.2630 (14)	0	0.082 (12)
C(52)	0.0875 (40)	0.2898 (17)	0	0.116 (16)
C(53)	0.1556 (40)	0.2533 (20)	0.0228 (16)	0.086 (15)
C(1)	0.0585 (17)	0.0142 (8)	0.1143 (8)	0.0627 (69)
C(11)	0.1627 (17)	0.1048 (7)	0.1140 (8)	0.0484 (60)
C(12)	0.1851 (18)	0.1520 (8)	0.1352 (8)	0.0627 (67)
C(13)	0.2791 (22)	0.1752 (9)	0.1252 (11)	0.0830 (83)
C(14)	0.3519 (20)	0.1546 (9)	0.0945 (10)	0.0788 (79)
C(15)	0.3325 (19)	0.1095 (8)	0.0722 (9)	0.0706 (77)
C(16)	0.2382 (20)	0.0871 (9)	0.0835 (9)	0.0664 (74)
C(21)	0.0098 (19)	0.0853 (8)	0.1903 (8)	0.0589 (67)
C(22)	0.4170 (22)	0.3946 (9)	0.2076 (10)	0.0924 (92)
C(23)	0.3906 (27)	0.1068 (10)	0.2348 (12)	0.126 (11)
C(24)	0.4658 (27)	0.0854 (11)	0.2084 (12)	0.112 (11)
C(25)	0.0702 (29)	0.4306 (12)	0.2212 (14)	0.134 (13)
C(26)	0.0817 (23)	0.0664 (9)	0.2216 (11)	0.0902 (91)
C(100)	0.0971 (41)	0.4838 (15)	0	0.113 (15)
C(101)	0.0577 (24)	0.4900 (13)	0.0460 (12)	0.167 (13)
C(102)	0	0.5000	0.0903	0.0700[b]
C(200)	0.0684 (27)	0.2370 (16)	0.2681 (15)	0.176 (18)
C(201)	0.1429 (28)	0.2929 (12)	0.1955 (13)	0.143 (13)
C(202)	0.2346 (23)	0.2357 (12)	0.2692 (12)	0.129 (13)

[a] Atoms having *U* values without esd's were refined anisotropically. [b] The methyl carbon was placed.

Table III. Selected Bond Distances (Å) for $[Ta_2Cl_6(THT)(dppe)]_2$

Ta(1)–Ta(1)	2.704 (2)	S(1)–C(54)	1.754 (35)
Ta(1)–Cl(1)	2.510 (6)	C(51)–C(52)	1.462 (48)
Ta(1)–Cl(2)	2.480 (6)	C(52)–C(53)	1.444 (57)
Ta(1)–Cl(11)	2.369 (6)	C(53)–C(54)	1.500 (49)
Ta(1)–Cl(12)	2.369 (5)	P(1)–C(1)	1.848 (21)
Ta(1)–P(1)	2.753 (7)	P(1)–C(11)	1.801 (21)
Ta(1)–S(1)	2.395 (7)	P(1)–C(21)	1.848 (21)
S(1)–C(51)	1.806 (38)	C(1)–C(1)	1.679 (41)

The bridging chlorines [Cl(1) and Cl(2)], sulfur, three of the THT carbon atoms (C(51), C(52), C(54)) and C(100) of one of the solvent molecules are located at special positions ($x, y, 0$) and were assigned occupancies of $^1/_2$. The fourth THT carbon atom C(53) is disordered and was located and refined as a half-atom on each side of the mirror plane. Only one position of the disordered C(53) is shown in the ORTEP drawing for clarity (Figure 1). The atoms of the two toluene solvent molecules, C(100), C(101), and C(102) and C(200), C(201), and C(202), were located on a difference Fourier map. They displayed an expected high degree of disorder and could be only partially refined. The solvent molecules are not in close contact distance with any of the tetramer atoms (ca. 3.59 Å for C(100)–C(15)) and are not included in the ORTEP drawing. Selected bond lengths and angles found in the tantalum tetramer are listed in Tables III and IV.

A compilation of selected bond lengths and angles found in other related compounds is listed in Table V. The Ta=Ta double-bond length of 2.704 (2) Å is well within the range for double-bonded Ta=Ta compounds. It is 0.023 Å longer than the Ta=Ta double bond found in the starting material, which also has a confacial structure,[2] and falls within the range of M=M bond lengths found in the edge-shared phosphine-containing dimers. It therefore

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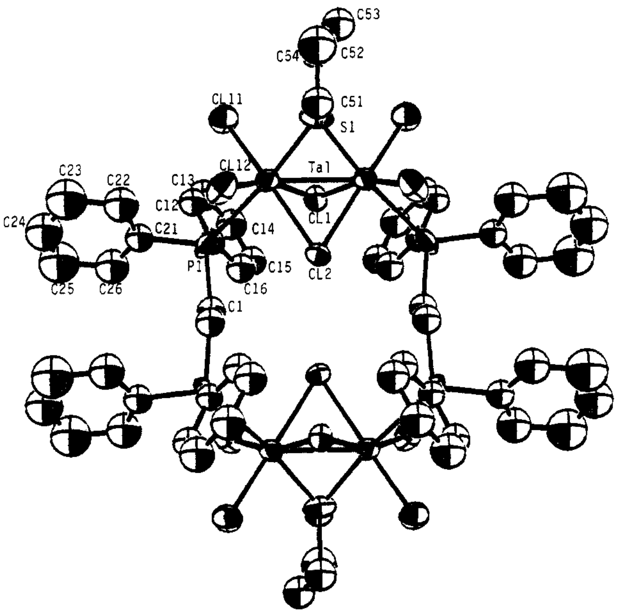


Figure 1. ORTEP plot of $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2$. Thermal ellipsoids are drawn at 50% probability level, and hydrogens have been omitted for clarity.

Table IV. Selected Bond Angles (deg) for $[Ta_2Cl_6(THT)(dppe)]_2$

Ta(1)–Ta(1)–Cl(1)	57.40 (9)	Cl(12)–Ta(1)–S(1)	89.13 (23)
Ta(1)–Ta(1)–Cl(2)	56.96 (9)	P(1)–Ta(1)–S(1)	174.17 (18)
Ta(1)–Ta(1)–Cl(11)	121.18 (16)	Ta(1)–Cl(1)–Ta(2)	65.20 (17)
Ta(1)–Ta(1)–Cl(12)	120.60 (14)	Ta(1)–Cl(2)–Ta(2)	66.07 (19)
Ta(1)–Ta(1)–P(1)	129.71 (12)	Ta(1)–S(1)–Ta(2)	68.75 (23)
Ta(1)–Ta(1)–S(1)	55.6 (12)	C(51)–S(1)–C(54)	93.5 (1.6)
Cl(1)–Ta(1)–Cl(2)	75.70 (27)	S–C(51)–C(52)	107.4 (2.9)
Cl(1)–Ta(1)–Cl(11)	89.51 (26)	C(51)–C(52)–C(53)	111.6 (3.7)
Cl(1)–Ta(1)–Cl(12)	167.08 (29)	C(52)–C(53)–C(54)	104.9 (4.0)
Cl(1)–Ta(1)–P(1)	87.23 (20)	C(53)–C(54)–S(1)	104.4 (3.1)
Cl(1)–Ta(1)–S(1)	98.32 (24)	C(53)–C(52)–C(53′)	48.4 (3.9)
Cl(2)–Ta(1)–Cl(11)	163.22 (25)	C(53)–C(54)–C(53′)	46.5 (3.3)
Cl(2)–Ta(1)–Cl(12)	92.58 (22)	Ta(1)–P(1)–C(1)	120.27 (70)
Cl(2)–Ta(1)–P(1)	82.08 (18)	Ta(1)–P(1)–C(11)	111.26 (67)
Cl(2)–Ta(1)–S(1)	100.94 (21)	Ta(1)–P(1)–C(21)	120.47 (83)
Cl(11)–Ta(1)–Cl(12)	101.24 (22)	C(1)–P(1)–(C11)	100.18 (98)
Cl(11)–Ta(1)–P(1)	89.45 (22)	C(1)–P(1)–C(21)	99.9 (1.0)
Cl(11)–Ta(1)–S(1)	88.84 (26)	C(11)–P(1)–C(21)	101.4 (1.1)
Cl(12)–Ta(1)–P(1)	85.75 (19)	P(1)–C(1)–C(1′)	106.7 (1.8)

Table V. Selected Bond Lengths (Å) and Angles (deg) in Related M–M-Bonded Complexes

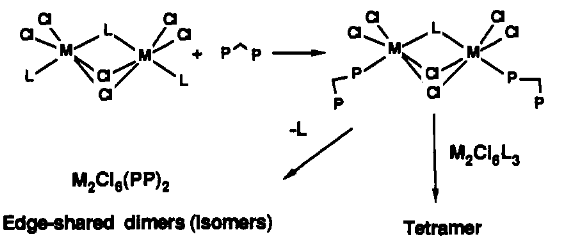
compd	M–M bond	M–P bond	M–M–P angle	ref
$Ta_2Cl_6(THT)_3$	2.681 (1)			2
$Nb_2Cl_6(dppm)_2$	2.696 (1)	2.662 (av)	146.2 (av)	7
$Nb_2Cl_6(dppe)_2$	2.721 (2)	2.678 (av)	142.3	5
$Nb_2Cl_6(dmpm)_2$	2.711 (3)	2.630 (av)	93.0 (av)[a]	8
$Ta_2Cl_6(dmpm)_2$	2.692 (2)	2.619 (av)	93.5 (av)[a]	16
$Ta_2Cl_6(dmpe)_2$	2.710 (1)	2.630 (av)	140.7 (av)	6
$Ta_2Cl_6[P(CH_3)_3]_4$	2.721 (1)	2.63 (av)	130.6 (av)[b] 97.6	14
$Ta_2(\mu\text{-}O)(\mu\text{-}SMe_2)Cl_4(dmpe)_2$	2.726 (3)	2.627 (3)	134.47 (7)[c] 93.53 (7)	17
$[Ta_2Cl_6(THT)(dppe)]_2$	2.704 (2)	2.753 (7)	129.7	*d*

[a] Phosphine ligand is bridging. [b] Monodentate phosphate ligands in equatorial and axial positions. [c] Phosphine ligand is chelating from axial to equatorial sites. [d] This work.

appears the difference between the two bioctahedral geometries has little effect on the length of the metal–metal bond.

The phosphine ligands are trans to the bridging THT, having a P–Ta–S angle of ~174.2°. It is interesting to note the Ta–P bond length of 2.753 (7) Å is ~0.1 Å longer than the M–P bonds of related compounds. The Ta–Ta–P bond angle of 129.7 (1)° is very close to the 130.6° (av) value for the equatorial phosphine ligands found in $Ta_2Cl_6[P(CH_3)_3]_4$,[14] in which the phosphine ligands are monocoordinate and therefore less strained. This angle is probably more favorable than the 140–146° M–M–P angles found in similar compounds in which the phosphine ligands are chelating or the ~93° angle formed by the bridging phosphine groups in $M_2Cl_6(dmpm)_2$. The constrained P–M–P angle of 67–78° found in edge-shared binuclear compounds with chelating phosphines is also avoided in the tetramer.

Scheme I



It was previously reported that the substitution reaction of $M_2Cl_6L_3$ with the monodentate ligand tetrahydrofuran (THF) results in the product $M_2Cl_6(THF)_2(\mu\text{-}L)$, demonstrating that the terminal L ligands are more labile than the bridging ligands.[11,12] The fact that the bridging THT ligand remains intact during the substitution reaction of the tantalum dimer with dppe further indicates that the bridging ligand is less labile than the terminal THT ligands and less labile in the tantalum dimer than in the niobium dimer.

The tetrameric structure consisting of two confacial dimers is somewhat unexpected since analogous reactions using $Nb_2Cl_6L_3$ and either dppe or dppm or the reaction of $Ta_2Cl_6L_3$ with dmpe yield dimers having edge-shared bioctahedral structures with the bidentate ligands in chelating positions as in IIa.[5-7] The compounds $Nb_2Cl_6(dmpm)_2$[8] and $Ta_2Cl_6(dmpm)_2$[16] have also been synthesized and have been reported as dimers having edge-shared bioctahedral structures with the phosphine ligands occupying bridging positions as in IIb. It is interesting to note that Cotton et al. did not find tetramers in the synthesis of $Nb_2Cl_6(SMe_2)(MeSCH_2SMe)_2$ and $Ta_2Cl_6(SMe_2)(dppm)_2$ in which the $MeSCH_2SMe$ and dppm ligands are reported to be dangling.[18] In our synthesis of $[Ta_2Cl_6(THT)(dppe)]_2$, even with the variation of the dppe:Ta dimer ratio from 1:1 to 3:1, the reaction went on to form the reported tetramer. It is possible that the two ligands, $Me_2SCH_2SMe_2$ and dppm, which have only methylene bridges, do not have large enough bites to form tetramers. Thus it appears there are at least two reaction pathways possible for these dimers with bidentate ligands (Scheme I). The structural geometry obtained most likely is a result of solubility, ligand-bite size, ligand lability, solid-state packing, and reaction conditions. In principle, under the proper conditions, other tetramers should be obtainable. We are currently investigating the possibility that at a higher temperature the tantalum substitution reaction will proceed to $Ta_2Cl_6(dppe)_2$ having an edge-shared bioctahedral dimeric structure. It is also conceivable that the reaction of $Nb_2Cl_6(THT)_3$ with dppe at lower temperatures may produce the tetrameric structure reported here.

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Supplementary Material Available: Tables SI–SV, listing experimental details for the structure determination, thermal parameters, derived hydrogen positions, and complete bond distances and angles (6 pages); a table of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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[18] Canich, J. M.; Cotton, F. A. *Inorg. Chem.* **1987**, *26*, 3473.