Table IV. Selected Bond Angles (Deg)

Ru(1)-Ru(2)-Ru(3)	90.91 (3)	C(5)-Ru(3)-C(6)	96.7 (5)
Ru(2)-Ru(1)-Ru(3)	44.95 (3)	C(6)-Ru(3)-Ru(2)	92.8 (4)
Ru(2)-Ru(3)-Ru(1)	44.14 (3)	Ru(2)-Ru(3)-P(2)	71.95 (7)
C(1)-Ru(1)-C(8)	103.9 (4)	P(2)-Ru(3)-C(5)	97.4 (4)
C(8)-Ru(1)-Ru(2)	49.3 (3)	C(5)-Ru(3)-P(1)	109.5 (4)
Ru(2)-Ru(1)-C(2)	117.9 (3)	C(6)-Ru(3)-P(1)	88.2 (4)
C(2)-Ru(1)-C(1)	88.8 (5)	Ru(2)-Ru(3)-P(1)	53.34 (7)
C(1)-Ru(1)-P(1)	112.3 (4)	P(2)-Ru(3)-P(1)	81.57 (9)
C(8)-Ru(1)-P(1)	79.6 (3)	C(5)-Ru(3)-C(7)	99.9 (5)
Ru(2)-Ru(1)-P(1)	54.30 (7)	C(6)-Ru(3)-C(7)	91.1 (5)
C(2)-Ru(1)-P(1)	93.7 (3)	Ru(2)-Ru(3)-C(7)	97.3 (3)
C(1)-Ru(1)-P(3)	94.5 (4)	P(2)-Ru(3)-C(7)	92.3 (4)
C(8)-Ru(1)-P(3)	85.3 (3)	Ru(1)-P(1)-Ru(2)	74.67 (9)
Ru(2)-Ru(1)-P(3)	97.79 (7)	Ru(2)-P(1)-Ru(3)	75.14 (9)
C(2)-Ru(1)-P(3)	96.0 (3)	Ru(1)-P(1)-Ru(3)	123.7 (1)
C(3)-Ru(2)-C(4)	96.1 (5)	Ru(1)-P(1)-C(10)	120.2 (2)
C(4)-Ru(2)-C(8)	93.4 (4)	Ru(2)-P(1)-C(10)	128.0 (3)
C(8)-Ru(2)-Ru(1)	47.9 (2)	Ru(3)-P(1)-C(10)	115.8 (2)
Ru(1)-Ru(2)-C(3)	123.1 (3)	Ru(1)-C(1)-O(1)	177.5 (6)
C(3)-Ru(2)-Ru(3)	97.0 (3)	Ru(1)-C(2)-O(2)	176.4 (6)
C(4)-Ru(2)-Ru(3)	87.1 (3)	Ru(2)-C(3)-O(3)	177.2 (6)
C(8)-Ru(2)-Ru(3)	78.3 (2)	Ru(2)-C(4)-O(4)	177.0 (6)
C(3)-Ru(2)-P(1)	92.9 (3)	Ru(3)-C(5)-O(5)	177.7 (8)
C(4)-Ru(2)-P(1)	138.4 (3)	Ru(3)-C(6)-O(6)	175.9 (7)
C(8)-Ru(2)-P(1)	76.5 (2)	Ru(3)-C(7)-O(6)	176.6 (7)
Ru(1)-Ru(2)-P(1)	51.04 (7)		
C(3)-Ru(2)-P(4)	91.4 (3)		
C(4)-Ru(2)-P(4)	92.8 (3)		
C(8)-Ru(2)-P(4)	93.3 (2)		
Ru(1)-Ru(2)-P(4)	83.84 (7)		

this structure; this would suggest a bond order slightly higher than 1. The closely related organic fragment $CHP(Me)_2$ was previously derived[9] from the pyrolysis of $Os_3(CO)_{11}(PMe_3)_2$.]

(ii) The second is a phosphinidene ligand μ_3-$P(C_6H_5)$ linked to the three metal atoms in slightly asymmetric fashion [Ru(1)-P(1) 2.292 (3) Å, Ru(2)-P(1) 2.394 (3) Å Ru(3)-P(1) 2.336 (3) Å]. A salient feature is the distorted tetrahedral geometry of the phosphorus atom P(1), since this atom is only 0.05 Å out of the plane Ru(1)-Ru(3)-C(10). This distorsion has already been observed[10-12] and is sometimes assigned to a particular bonding sheme.[10] However, the observed geometry could be related to steric requirements about the open cluster.

The formation of this species from the parent complex 1 can be related to the known ability of transition-metal clusters to cleave P-C or As-C bonds,[12-17] sometimes leading to a naked phosphorus atom.[18] To our knowledge, the phosphinidene ligand has been rarely stabilized through a simple pyrolytic reaction[12,17] but through a different preparative route.[19-27]

At the present time, the precise nature of the mechanistic details of this oxidative addition remains uncertain. The first step of such a reaction could be the metalation of a CH bond;[28,29] as pointed out earlier,[30] the oxidative addition of a CH bond could be favored by a high electron density at the metal centers, which is precisely the case in the complex $Ru_3(CO)_8(dppm)_2$. A prerequisite for metalation is to bring a CH bond in close proximity to a metal center. In the present case, this could be achieved by rotation of a Ru-P bond from the equatorial plane to an axial position. Molecular models show that such a move brings a benzene ring close to a ruthenium center, thus favoring metalation. This is in agreement with the fact that the tripod ligand $((C_6H_5)_2P)_3CH$ does not undergo oxidative addition with $Ru_3(CO)_{12}$:[4] indeed, the rigid face-capped position of a tripod prevents any interaction between benzene rings and metal centers.

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Registry No. 1, 77611-27-9; **2**, 77611-28-0; $Ru_3(CO)_{12}$, 15243-33-1.

Supplementary Material Available: Listings of rigid-group positional and thermal parameters and of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[9] Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2727.
[10] Huttner, G.; Mohr, G.; Frank, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 682.
[11] Jacob, W.; Weiss, E. *J. Organomet. Chem.* **1977**, *131*, 263.
[12] Brown, S. C.; Evans, J.; Smart, L. E. *J. Chem. Soc., Chem. Commun.* **1980**, 1021.
[13] Cullen, W. R.; Harbourne, D. A.; Liengme, B. V.; Sams, J. R. *Inorg. Chem.* **1970**, *9*, 702.
[14] Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Dalton Trans.* **1973**, 529.
[15] Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1667.
[16] Carty, A. J.; Taylor, N. J.; Wayne, F. S.; Smith, W. F. *J. Chem. Soc., Chem. Commun.* **1979**, 750.
[17] Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1978**, 1015.
[18] Vidal, J. L.; Walker, W. E.; Pruett, R. L.; Shoening, R. C. *Inorg. Chem.* **1979**, *18*, 129.
[19] Treichel, P. M.; Dean, W. K.; Douglas, W. M. *Inorg. Chem.* **1972**, *11*, 1609.
[20] Marko, L.; Marko, B. *Inorg. Chim. Acta* **1975**, *14*, L 39.
[21] Huttner, G.; Müller, H.; Frank, A.; Lorentz, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 705.
[22] Huttner, G.; Frank, A.; Mohr, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *B31*, 1161.
[23] Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904.
[24] Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046.
[25] Richter, F.; Beurich, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1979**, *166*, C5.
[26] Beurich, H.; Madach, T.; Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 690.
[27] Rajib, Lal De; Von Seyerl, J.; Huttner, G. *J. Organomet. Chem.* **1979**, *178*, 319.
[28] Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499.
[29] Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183.
[30] Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742 and references therein.

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Binuclear Chloro Complexes of Tantalum(III) with Tantalum-Tantalum Double Bonds

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In the course of studying lower valent molecular compounds of the group 5 elements niobium and tantalum, we have investigated the structures of two binuclear tantalum compounds containing double bonds between the metal atoms. One of these is a compound first reported by McCarley and coworkers,[1] $Ta_2Cl_6(THT)_3$ (1), where THT = tetrahydrothiophene. As expected this compound forms crystals that are isotypic to those of $Ta_2Br_6(THT)_3$, the structure of which was recently reported by McCarley.[2] The reason for carrying out the structure analysis was to see how much the change from μ-Br ligands to μ-Cl ligands would affect the length of the Ta=Ta bond. We have also investigated the structure of the analogous compound $Ta_2Cl_6(Me_2S)_3$ (**2**). This is a new compound, although its niobium analogue has been reported before.[3] In this paper we report in detail these two structures

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[1] Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293.
[2] Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263.
[3] Allen, A. D.; Naito, S. *Can. J. Chem.* **1976**, *54*, 2948.

Table I. Crystallographic Parameters

parameter	1	2
space group	$P\bar{1}$	$Pnma$
a, Å	11.723 (2)	13.575 (3)
b, Å	12.502 (3)	17.120 (4)
c, Å	8.969 (2)	8.629 (2)
α, deg	84.78 (3)	90.0
β, deg	113.37 (3)	90.0
γ, deg	105.51 (2)	90.0
V, Å^3	1162 (1)	2005 (1)
d_{calcd}, g/cm^3	2.14	2.539
Z	2	4
fw	845.13	767.02
cryst size, mm	0.27 × 0.30 × 0.41	0.20 × 0.24 × 0.31
μ(Mo Kα), cm^{-1}	108.580	125.656
range 2θ, deg	0-50	0-50
no. of unique data	3383	1216
no. of data with $F_o^2 > 3\sigma(F_o^2)$	3103	991
no. of variables	206	86
R_1	0.046	0.049
R_2	0.064	0.056
esd	1.965	1.419
largest shift[a]	0.08	0.16
largest peak[b]	0.89	0.92

[a] Largest parameter shift after final least-squares calculation.
[b] Largest peak in the final difference Fourier map.

and compare them with each other and with other structures containing Nb═Nb and Ta═Ta double bonds.

Experimental Section

All materials were handled under argon with use of Schlenk or vacuum line techniques. Solvents were distilled over sodium benzophenone ketal under argon. Tantalum pentachloride 99+% was purchased from the Alfa Division of Ventron Corp. $Ta_2Cl_6(SC_4H_8)_3$ (**1**) was prepared according to the literature method.[1] Dimethyl sulfide was dried and distilled before use. The infrared spectrum was recorded on a Nujol mull with use of a Unicam SP1100 spectrophotometer.

Preparation of $Ta_2Cl_6(SMe_2)_3$ (2). Dimethyl sulfide, SMe_2 (7.0 mL, 0.13 mol), was added to a suspension of $TaCl_5$ (10 g, 0.03 mol) in toluene (150 mL) at room temperature. Two equivalents of sodium amalgam (1.5%) was added to the stirred mixture. $TaCl_5$ was consumed over a 3 h period, yielding a yellow-brown solution. The solution was filtered and allowed to stand overnight. The solvent was removed under vacuum, and 2.94 g (28%) of a brown crystalline solid was obtained. Some of the crystals thus obtained were found to be suitable for X-ray analysis. IR (mull): 1434 (s), 1422 (m), 1330 (m), 1309 (m), 1266 (s), 1100 (br), 1030 (br), 982 (s), 699 (w), 682 (sh) cm^{-1}.

X-ray Crystallography. Data Collection. Crystals of **1** and **2** suitable for data collection were sealed in capillaries under nitrogen. Data were collected for both compounds on an Enraf-Nonius CAD-4F fully automated diffractometer at 25 ± 1 °C using Mo Kα radition (λ = 0.71073 Å) with a graphite-crystal monochromator in the incident beam. A summary of data collection and refinement parameters is presented in Table I. The standard CAD-4 centering, indexing, and data collection programs were used. Other details concerning collection and reduction of data have been described elsewhere.[4] Lorentz and polarization corrections were applied to the data as were empirical absorption corrections based on ψ scans at $\chi = 90°$.

During data collection, three intensity standards were measured after every hour of X-ray exposure for both compounds. No decay for the data of **1** was observed. However, the data for **2** exhibited a total decrease in intensity of 45% for all three reflections and a correction for anisotropic decay was made. This correction factor was obtained by interpolating between the two nearest (in terms of time) standard reflections, after those standards were corrected to zero time. The contribution of each standard toward determining the correction factor is weighted to account for the relative distance between reciprocal lattice points. The formulas used to convert measured intensities, I_u, to correct intensities, I_c, and the standard deviations of the latter were $I_c = I_u/C$, where $C = \sum_{i=1}^{N} P_i V_i / V_T$, $V_i = |hGh_i|/(hGh)^{1/2}$, and $V_T = \sum_{i=1}^{N} V_i$. $(100 - P_i)$ is the percent decomposition of standard i at the time of reflection h; h_i are the indices for standard i; N is the number of standards; G is the metric tensor.

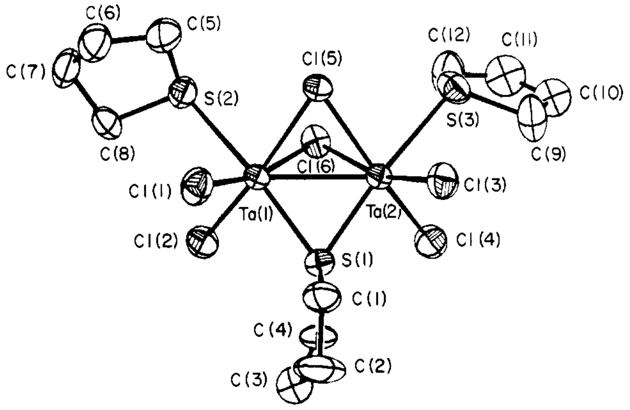

Figure 1. ORTEP drawing of the molecular structure of $Ta_2Cl_6(THT)_3$ (**1**). Atoms are numbered as in Tables II, IV, and V and are represented by ellipsoids of thermal vibration scaled to enclose 40% of the electron density. Atoms C(3), C(10), and C(11) were refined at half-occupancy isotropically, thus explaining their spherical figures of thermal vibration.

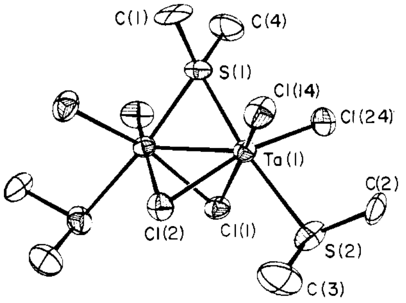

Figure 2. ORTEP drawing of the molecular structure of $Ta_2Cl_6(Me_2S)_3$ (**2**) with the atom numbering scheme of Tables III, VI, and VII shown. There is a plane of symmetry containing C(1), C(4), S(1), Cl(1), and Cl(2). Each atom is represented by its thermal ellipsoid scaled to enclose 40% of the electron density.

Solution and Refinement of Structures.[5] Crystals of $Ta_2Cl_6(SC_4H_8)_3$ (**1**) were found to be triclinic. The cell volume was consistent with $Z = 2$. Heavy-atom positions were obtained from a three-dimensional Patterson function. All other nonhydrogen atom positions were found in subsequent difference Fourier syntheses. The structure was refined by full-matrix least-squares methods in the space group $P\bar{1}$. High thermal parameters were found for several carbon atoms in two of the three THT rings suggesting a disorder problem. A difference Fourier map at this point revealed peaks at distances 1.1–0.6 Å from those atoms with high thermal parameters (C(3) of ring S(1) and C(10) and C(11) of ring S(3)). These peaks (C(33), C(20), and C(22), respectively) were refined isotropically as half-atoms as were the first three. All other nonhydrogen atoms were refined to convergence with use of anisotropic thermal parameters. The discrepancy indices $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ are listed in Table I.

Data for $Ta_2Cl_6(SMe_2)_3$ (**2**) were collected for the orthorhombic crystal system. The observed volume was consistent with $Z = 4$. Examination of the data revealed systematic absences for $0kl$, $k + l = 2n$, and $hk0$, $h = 2n$, which coincided with two possible space groups, $Pna2_1$ and $Pnma$. The centric space group $Pnma$ was chosen for data reduction and yielded a satisfactory solution. The heavy-atom positions were obtained by direct methods with the MULTAN program. Anisotropic temperature factors were assigned to all nonhydrogen atoms. Final residuals are given in Table I. The final difference maps of **1** and **2** showed no peaks of structural significance. Lists of the observed and calculated structure factors for **1** and **2** are available as supplementary material.

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(4) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.
(5) All refinement was done with the use of a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX, equipped with the Enraf-Nonius structure determination package.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for **1**[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Ta(1)	−0.31491 (4)	0.28618 (4)	0.26539 (6)	2.31 (2)	2.60 (2)	3.25 (2)	0.33 (1)	1.04 (1)	−0.25 (2)
Ta(2)	−0.14245 (4)	0.20685 (4)	0.21370 (6)	2.42 (2)	2.68 (2)	3.45 (2)	0.31 (1)	1.19 (1)	−0.37 (2)
Cl(1)	−0.3135 (3)	0.2987 (3)	0.5279 (4)	5.4 (1)	4.5 (1)	4.0 (1)	1.8 (1)	2.3 (1)	0.2 (1)
Cl(2)	−0.5383 (3)	0.2206 (3)	0.1129 (5)	2.4 (1)	4.5 (1)	6.5 (2)	0.1 (1)	0.9 (1)	−1.5 (1)
Cl(3)	0.0247 (3)	0.1509 (3)	0.4322 (5)	3.6 (1)	4.6 (1)	5.3 (2)	1.73 (9)	1.6 (1)	0.6 (1)
Cl(4)	−0.2079 (4)	0.0656 (3)	0.0177 (5)	4.6 (1)	4.5 (1)	6.1 (2)	−0.0 (1)	2.5 (1)	−2.4 (1)
Cl(5)	−0.0849 (3)	0.3895 (2)	0.3545 (4)	2.5 (1)	2.9 (1)	3.8 (1)	0.10 (8)	0.99 (9)	−0.6 (1)
Cl(6)	−0.2761 (3)	0.3192 (3)	0.0070 (4)	3.5 (1)	4.8 (1)	3.3 (1)	1.21 (9)	1.23 (9)	0.0 (1)
S(1)	−0.2944 (3)	0.1001 (3)	0.3201 (4)	3.3 (1)	2.7 (1)	4.2 (1)	0.47 (9)	1.4 (1)	−0.2 (1)
S(2)	−0.3525 (3)	0.4861 (3)	0.2145 (4)	4.3 (1)	3.5 (1)	3.8 (1)	1.27 (9)	1.88 (9)	0.1 (1)
S(3)	0.0446 (3)	0.3107 (3)	0.1195 (4)	3.8 (1)	5.0 (2)	4.4 (1)	0.2 (1)	2.2 (1)	−0.5 (1)
C(1)	−0.249 (1)	0.039 (1)	0.527 (2)	5.0 (6)	3.6 (6)	5.1 (6)	0.9 (5)	2.5 (5)	1.3 (5)
C(2)	−0.340 (2)	−0.075 (1)	0.509 (3)	6.0 (9)	3.9 (7)	9 (1)	−0.5 (7)	2.6 (8)	2.2 (7)
C(4)	−0.423 (1)	−0.023 (1)	0.219 (2)	4.1 (6)	2.6 (5)	7.4 (8)	−0.8 (5)	2.2 (5)	−1.0 (5)
C(5)	−0.247 (1)	0.578 (1)	0.393 (2)	4.3 (6)	4.4 (6)	6.5 (7)	0.3 (5)	1.6 (5)	−2.1 (5)
C(6)	−0.336 (1)	0.606 (1)	0.460 (2)	5.2 (6)	5.0 (6)	5.3 (6)	1.4 (4)	2.0 (5)	−1.3 (5)
C(7)	−0.464 (1)	0.598 (1)	0.324 (2)	5.3 (5)	4.7 (5)	5.8 (6)	2.2 (4)	2.5 (4)	−0.8 (5)
C(8)	−0.500 (1)	0.485 (1)	0.237 (2)	2.7 (4)	4.9 (6)	5.4 (6)	0.5 (4)	1.7 (4)	−0.5 (5)
C(9)	0.122 (1)	0.207 (1)	0.093 (2)	5.5 (5)	8.3 (8)	6.6 (8)	3.8 (5)	3.2 (5)	1.4 (7)
C(12)	−0.015 (2)	0.348 (2)	−0.090 (2)	8.1 (6)	8.0 (8)	5.9 (6)	4.4 (5)	4.8 (5)	2.7 (6)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(3)	−0.463 (3)	−0.087 (3)	0.348 (4)	5.0 (7)	C20	0.072 (3)	0.186 (3)	−0.092 (4)	5.0 (7)
C(10)	0.124 (3)	0.234 (3)	−0.081 (4)	5.9 (8)	C22	0.009 (4)	0.271 (3)	−0.187 (5)	7.1 (10)
C(11)	0.052 (4)	0.309 (3)	−0.164 (5)	6.9 (9)	C33	−0.403 (5)	−0.117 (4)	0.341 (6)	9.0 (13)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$, where *a*, *b*, and *c* are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for 2[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Ta(1)	0.18236 (6)	0.17139 (4)	0.01646 (8)	1.84 (3)	2.59 (2)	2.45 (2)	−0.01 (4)	−0.11 (4)	−0.06 (3)
Cl(1)	0.0292 (5)	0.2500 (0)	0.0111 (8)	2.0 (3)	3.6 (3)	3.5 (3)	0	0.0 (3)	0
Cl(2)	0.1896 (7)	0.2500 (0)	0.2629 (7)	3.4 (4)	3.4 (3)	2.5 (2)	0	−0.7 (3)	0
Cl(14)	0.3248 (4)	0.3975 (3)	0.0990 (7)	2.5 (3)	3.6 (2)	6.2 (3)	−0.3 (2)	−0.5 (3)	−0.5 (2)
Cl(24)	0.1329 (5)	0.4004 (3)	−0.2043 (6)	4.3 (3)	4.4 (2)	4.0 (2)	1.2 (2)	0.1 (3)	1.6 (2)
S(1)	0.2838 (6)	0.2500 (0)	−0.1452 (8)	2.4 (4)	3.9 (3)	2.4 (3)	0	0.6 (3)	0
S(2)	0.0771 (5)	0.0689 (3)	0.1687 (7)	2.9 (3)	3.7 (2)	5.2 (3)	−0.3 (3)	−0.1 (3)	1.3 (2)
C(1)	0.424 (2)	0.250 (0)	−0.123 (5)	1 (1)	7 (2)	8 (2)	0	2 (2)	0
C(2)	0.128 (2)	−0.029 (1)	0.126 (3)	3 (1)	1.4 (7)	10 (2)	−0.5 (8)	2 (1)	−0.5 (9)
C(3)	0.107 (2)	0.071 (1)	0.377 (3)	9 (2)	7 (1)	4 (1)	2 (2)	1 (1)	1 (1)
C(4)	0.271 (3)	0.250 (0)	−0.362 (3)	6 (2)	6 (2)	3 (1)	0	1 (2)	0

[a] The form of the anisotropic thermal parameter is $\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$, where *a*, *b*, and *c* are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses.

Results and Discussion

The positional and thermal parameters for $Ta_2Cl_6(THT)_3$ (**1**) and $Ta_2Cl_6(Me_2S)_3$ (**2**) are listed in Tables II and III, respectively, and the molecular structures are shown in Figures 1 and 2, respectively. Three of the carbon atoms of **1** were each refined as two half-atoms to take account of disorder in the arrangement of these puckered rings, but Figure 1 shows only one of each pair of half-atoms, i.e., C(3) but not C(33), C(10) but not C(20), and C(11) but not C(22).

The structure of **1** is essentially identical with that previously reported for its bromo analogue[2] as is to be expected. The Ta–Cl(t) distances are shorter by an average of 0.17 Å than the Ta–Br(t) distances, which compares well with the generally accepted difference of 0.15 Å in the single-bond covalent radii of these two halogens. The Ta–Cl(b) distances are on the average 0.13 Å shorter than the Ta–Br(b) distances. The Ta–Cl–Ta angles are slightly larger (64.9°, 64.6°) than the Ta–Br–Ta angles (62.3°, 61.6°), which may be attributed primarily to the greater length of the Ta–Br bonds. The distances and angle to the bridging sulfur atom are very similar in the two compounds.

Table IV. Bond Distances (Å) in Compound **1**[a]

Ta(1)–Ta(2)	2.681 (1)	S(3)–C(9)	1.848 (13)
–Cl(1)	2.367 (3)	S(3)–C(12)	1.794 (13)
–Cl(2)	2.369 (3)	C(1)–C(2)	1.51 (2)
–Cl(5)	2.489 (2)	C(2)–C(3)	1.56 (3)
–Cl(6)	2.512 (3)	C(2)–C(33)	1.46 (4)
–S(1)	2.391 (2)	C(3)–C(4)	1.50 (3)
–S(2)	2.622 (3)	C(33)–C(4)	1.53 (4)
Ta(2)–Cl(3)	2.368 (2)	C(5)–C(6)	1.51 (2)
–Cl(4)	2.360 (3)	C(6)–C(7)	1.50 (2)
–Cl(5)	2.507 (3)	C(7)–C(8)	1.554 (15)
–Cl(6)	2.503 (2)	C(9)–C(10)	1.58 (3)
–S(1)	2.389 (3)	C(9)–C(20)	1.55 (3)
–S(3)	2.635 (3)	C(10)–C(11)	1.40 (5)
S(1)–C(1)	1.864 (11)	C(11)–C(12)	1.40 (4)
S(1)–C(4)	1.841 (11)	C(11)–C(20)	1.65 (5)
S(2)–C(5)	1.848 (12)	C(12)–C(22)	1.51 (4)
S(2)–C(8)	1.812 (11)	C(20)–C(22)	1.46 (4)

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

The only difference of note is in the Ta–Ta distance, which is 2.681(1) Å in $Ta_2Cl_6(THT)_3$ whereas it is 2.710 (2) Å in the bromo analogue. We believe that this difference is primarily due to the greater size of the bridging Br atoms. If the Ta–Ta distance in the Br compound were to remain as short as it is in the Cl compound, the angle at the bridging

Table V. Bond Angles (Deg) in Compound **1**

Ta(1)–Cl(5)–Ta(2)	64.90 (6)	C(1)–S(1)–C(4)	94.9 (6)
–Cl(6)–Ta(2)	64.63 (6)	Ta(1)–S(2)–C(5)	110.6 (4)
–S(1)–Ta(2)	68.21 (7)	–C(8)	109.0 (4)
Cl(1)–Ta(2)–Cl(2)	100.5 (1)	C(5)–S(2)–C(8)	94.6 (6)
–Cl(5)	92.2 (1)	Ta(2)–S(3)–C(9)	108.1 (5)
–Cl(6)	165.6 (1)	–C(12)	112.1 (6)
–S(1)	89.19 (9)	C(9)–S(3)–C(12)	95.6 (6)
–S(2)	87.64 (9)	S(1)–C(1)–C(2)	106.4 (9)
Cl(2)–Ta(1)–Cl(5)	163.2 (1)	C(1)–C(2)–C(3)	112 (1)
–Cl(6)	90.1 (1)	C(1)–C(2)–C(33)	113 (2)
–S(1)	90.9 (1)	C(2)–C(3)–C(4)	108 (2)
–S(2)	86.20 (9)	C(2)–C(33)–C(4)	112 (3)
Cl(5)–Ta(1)–Cl(6)	75.69 (8)	S(1)–C(4)–C(3)	107 (1)
–S(1)	100.38 (8)	S(1)–C(4)–C(33)	106 (2)
–S(2)	83.25 (8)	S(2)–C(5)–C(6)	105.9 (8)
Cl(6)–Ta(1)–S(1)	100.44 (9)	C(5)–C(6)–C(7)	109 (1)
–S(2)	83.33 (9)	C(6)–C(7)–C(8)	105.7 (9)
S(1)–Ta(1)–S(2)	175.28 (9)	S(2)–C(8)–C(7)	102.2 (7)
Cl(3)–Ta(2)–Cl(4)	102.1 (1)	S(3)–C(9)–C(10)	102 (1)
–Cl(5)	90.47 (9)	S(3)–C(9)–C(20)	106 (1)
–Cl(6)	163.7 (1)	C(9)–C(10)–C(11)	113 (3)
–S(1)	89.7 (1)	C(9)–C(20)–C(11)	102 (2)
–S(3)	83.6 (1)	C(9)–C(10)–C(22)	110 (3)
Cl(4)–Ta(2)–Cl(5)	164.3 (1)	C(9)–C(20)–C(22)	113 (2)
–Cl(6)	90.5 (1)	C(10)–C(11)–C(12)	119 (3)
–S(1)	89.6 (1)	C(10)–C(22)–C(12)	108 (3)
–S(3)	89.8 (1)	C(12)–C(11)–C(20)	110 (3)
Cl(5)–Ta(2)–Cl(6)	75.52 (8)	C(12)–C(22)–C(20)	115 (3)
–S(1)	99.95 (9)	S(3)–C(12)–C(11)	107 (2)
–S(3)	82.17 (9)	S(3)–C(12)–C(22)	109 (2)
Cl(6)–Ta(2)–S(1)	100.73 (9)	C(3)–C(2)–C(33)	35 (2)
–S(3)	86.25 (9)	C(3)–C(4)–C(33)	35 (2)
S(1)–Ta(2)–S(3)	173.00 (9)	C(10)–C(9)–C(20)	26 (1)
Ta(1)–S(1)–C(1)	123.9 (4)	C(10)–C(11)–C(20)	25 (2)
–C(4)	124.0 (4)	C(10)–C(22)–C(20)	28 (2)
Ta(2)–S(1)–C(1)	123.6 (4)	C(11)–C(10)–C(22)	23 (2)
–C(4)	125.2 (5)	C(11)–C(20)–C(22)	20 (2)
		C(11)–C(12)–C(22)	22 (2)

Table VI. Bond Distances (Å) in Compound **2**[a]

Ta(1)–Ta(1)′	2.691 (1)	Ta(1)–Cl(24)	2.865 (4)
–Cl(1)	2.478 (5)	S(1)–C(1)	1.91 (3)
–Cl(2)	2.519 (5)	–C(4)	1.88 (3)
–S(1)	2.378 (5)	S(2)–C(2)	1.85 (2)
–Cl(14)	2.378 (5)	–C(3)	1.84 (2)
–S(2)	2.618 (5)		

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

Table VII. Bond Angles (Deg) in Compound **2**

Cl(1)–Ta(1)–Cl(2)	76.0 (2)	Cl(14)–Ta(1)–Cl(24)	102.4 (2)
Cl(1)–Ta(1)–Cl(14)	163.5 (2)	–S(1)	89.1 (2)
–Cl(24)	91.6 (2)	–S(2)	87.8 (2)
–S(1)	99.7 (2)	Cl(24)–Ta(1)–S(1)	89.2 (2)
–S(2)	85.1 (2)	–S(2)	84.3 (2)
Cl(2)–Ta(1)–Cl(14)	88.9 (2)	S(1)–Ta(1)–S(2)	172.1 (2)
–Cl(24)	165.7 (2)	Ta(1)–Cl(1)–Ta(1)	65.8 (2)
–S(1)	99.8 (2)	–Cl(2)–Ta(1)	64.6 (1)
–S(2)	87.4 (2)	Ta(1)–S(1)–Ta(1)	68.9 (2)
		C(1)–S(1)–C(4)	101 (2)
		C(2)–S(2)–C(3)	97 (1)

Br atoms would be even smaller. Presumably, this is energetically unfavorable and beyond a certain point Ta–Ta bond stretching becomes energetically as feasible as further compression of the Ta–X–Ta angle.

Compound **1** is of particular interest for comparison with $Ta_2Cl_6(THF)_2(\mu$-*t*-BuCC-*t*-Bu)] (**3**) whose structure has recently been reported.[6] The Ta–Ta bond length in **3**, 2.677 (1) Å, is shorter than that reported for any other Ta–Ta bond (or Nb–Nb bond, for that matter). The results presented here for **1** suggest that this is at least partly due to the presence of bridging Cl atoms in place of bridging Br atoms, since the previously reported structures were of the $M_2Br_6(THT)_3$ (M = Nb, Ta) compounds. There are, however, two other features of **3** that may influence the bond length. One is the replacement of the bridging THT by a bridging alkyne, *t*-BuCC-*t*-Bu, and the other is replacement of the terminal THT's by THF's. It is not possible to say anything with certainty about the role played by these two features.

On comparison of the structures of **1** and **2**, it is clear that they are virtually identical, as would certainly be expected. Their Ta–Ta bonds do not differ in length to a statistically significant extent.

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Registry No. 1, 66758-43-8; **2**, 77827-59-9; Ta, 7440-25-7.

Supplementary Material Available: Tables of structure factors (19 pages) for both structures. Ordering information is given on any current masthead page.

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(6) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354.

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Crystal and Molecular Structure of Triiodo(η^5-methylcyclopentadienyl)dicarbonylmolybdenum(IV), (η^5-$CH_3C_5H_4$)Mo$(CO)_2I_3$

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Organometallic complexes in exceptionally high oxidation states are expected to have low-energy ligand-to-metal charge-transfer (LMCT) excited states.[1] The photochemical reactivity of these states is of considerable interest. We have therefore been studying the photochemical reactivity of the complexes $CpM(CO)_2X_3$ (Cp = η^5-C_5H_5; M = Mo, W; X = Cl, Br, I).[2,3] The metal atom formal oxidation state of IV is exceptionally high for metal carbonyl compounds. To facilitate interpretation of the photochemical behavior and electronic spectroscopic properties of this series of complexes, we investigated the molecular structure of a representative member. Attempts to prepare crystals of the $CpM(CO)_2X_3$ complexes suitable for an X-ray diffraction study were unsuccessful and invariably resulted in crystals that were twinned. Suitable single crystals of the methyl-substituted cyclopentadienyl complex (MeCp)Mo$(CO)_2I_3$ (MeCp = η^5-$CH_3C_5H_4$)[4] were obtained, however. This paper reports the results of an X-ray study of this derivative.

Experimental Section

Synthesis of (MeCp)Mo$(CO)_2I_3$. Preparative work was carried out under an atmosphere of nitrogen with use of Schlenk techniques or in a Vacuum Atmospheres drybox. A solution of iodine (0.2 g, 0.79 mmol) in degassed benzene (30 mL) was added dropwise to a stirred solution of 0.1 g (0.19 mmol) of [(MeCp)Mo$(CO)_3]_2$ (Strem Chemical Co.) in degassed benzene (50 mL). The mixture was then irradiated (λ > 320 nm) for 15 min with use of a 200-W high-pressure

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(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; p 667.

(2) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1966**, 1606–1607.

(3) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1967**, 686–688.

(4) Dineen, J. A.; Pauson, P. L. *J. Organomet. Chem.* **1974**, *71*, 91–96.