Inorganica Chimica Acta, *149* (1988) 105–110

Oxo-bridged Ta(+3) Dimers, $(TaCl_2L_2)_2(\mu\text{-}O)(\mu\text{-}SR_2)$, Revisited. Structural Differences between Isoelectronic μ-O and μ-OH Complexes

F. ALBERT COTTON*, MICHAEL P. DIEBOLD and WIESLAW J. ROTH

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Tex. 77843, U.S.A.

(Received January 13, 1988)

Abstract

The compounds $Ta_2Cl_4(dmpe)_2(\mu\text{-}Me_2S)(\mu\text{-}O)$ (**1**) and $Ta_2Cl_4(py)_4(\mu\text{-}THT)(\mu\text{-}O)$ (**2**) where dmpe = $Me_2PCH_2CH_2PMe_2$ and THT = tetrahydrothiophene, have been prepared and structurally characterized. They are authentic examples of μ-O bridged $Ta^{III}{=}Ta^{III}$ edge-sharing bioctahedral complexes. Their structures are virtually identical with respect to all of the bonds that they have in common. However, the structure of **1** differs significantly in its Ta–Ta, Ta–O and one type of Ta–Cl distance from the previously reported $Ta_2Cl_4(dmpe)_2(\mu\text{-}Me_2S)(\mu\text{-}O)\cdot HCl$ (**3**). These differences show that in **3** there is a μ-OH group hydrogen bonded to a Cl^- ion. The structural differences attendant upon the $\mu\text{-}OH \rightleftharpoons \mu\text{-}O$ change are of general interest and are discussed. The crystallographic data for the new compounds are as follows. **1**: monoclinic ($P2_1/c$) with $a = 10.412(2)$, $b = 14.749(2)$, $c = 22.177(3)$ Å, $\beta = 99.25(1)°$, $V = 3361(1)$ Å^3 and $Z = 4$. **2**: monoclinic ($P2_1/a$) with $a = 18.238(4)$, $b = 10.402(3)$, $c = 19.070(2)$ Å, $\beta = 95.37(2)$, $V = 3602(2)$ Å^3 and $Z = 4$.

Introduction

Several years ago we reported [1] the compound $Ta_2Cl_4(dmpe)_2(\mu\text{-}SMe_2)(\mu\text{-}X)$, where X was either $OH^+...Cl^-$ or O...HCl. While the presence of a hydrogen-bonded unit of one or the other type was clear from the O to Cl distance, 2.893(7) Å, as well as the overall composition, no conclusive evidence for one formulation or the other was available at that time. We report here the structure of $Ta_2Cl_4(dmpe)_2(\mu\text{-}SMe_2)(\mu\text{-}O)$ (**1**) and $Ta_2Cl_4(py)_4(\mu\text{-}THT)(\mu\text{-}O)$ (**2**). With this unambiguous example of μ-O bonding in hand we can now conclude that the previous compound is $[Ta_2Cl_4(dmpe)_2(\mu\text{-}SMe_2)(\mu\text{-}OH)]^+Cl^-$ (**3**). The comparison of **1** and **3** provides a clear picture of how deprotonation of a μ-OH group affects other aspects of the structure of a metal–metal bonded dimer.

Experimental

All manipulations were carried out by using standard double-manifold vacuum line techniques under an atmosphere of argon. $TaCl_5$ was purchased from Pressure Chemicals, Inc. $Ta_2Cl_6L_3$, L = SMe_2 and THT, were prepared according to literature methods [2] and they were used to make the $Ta_2Cl_6(THF)_2L$ adduct by dissolution in THF and isolation of the sparingly soluble precipitate. Dmpe [3] and $CH_2{=}C(PPh_2)_2$ [4] were synthesized by using published procedures. A stock solution of sodium amalgam (1 mmol/ml) was made by dissolving 0.48 g of Na in 20 ml of mercury. Pyridine was dried by storage over molecular sieves and subsequent distillation from BaO.

$Ta_2Cl_4O(SMe_2)(dmpe)_2$

A suspension of $Ta_2Cl_6(SMe_2)(THF)_2$ (0.36 g, 0.5 mmol) in 20 ml of THF was reacted with 1 eq. of Me_3CCO_2Li (0.054 g) producing a green solution of $Ta_2Cl_5(SMe_2)(Me_3CCO_2)(THF)_2$ within minutes. Addition of 1 mmol of Na/Hg and stirring gave a dark red solution, which was filtered through Celite and treated with 0.3 ml of dmpe. The color changed immediately to green and slow diffusion of hexane into this solution caused formation of dark green crystals.

$Ta_2Cl_4O(THT)py_4$

A mixture of $Ta_2Cl_6(THT)(THF)_2$ (0.4 g, 0.5 mmol) and $CH_2{=}C(PPh_2)_2$ (0.4 g, 1 mmol) in 20 ml of toluene was reacted with 1 mmol of Na/Hg. The resulting red solution was filtered and treated with 2 ml of pyridine. Slow diffusion of hexane into this solution produced dark red crystals in an estimated yield of 40%.

X-ray Crystallography

The unit cell determinations and collection of the intensity data were carried out by procedures which are routine to this laboratory and described elsewhere

---

*Author to whom correspondence shoud be addressed.

0020-1693/88/$3.50

TABLE I. Crystallographic Data for $Ta_2Cl_4O(SMe_2)(dmpe)_2 \cdot THF$ (1) and $Ta_2Cl_4O(THT)py_4 \cdot C_7H_8$ (2)

	1	2
Formula	$Ta_2Cl_4SP_4O_2C_{18}H_{46}$	$Ta_2Cl_4SON_4C_{31}H_{36}$
Formula weight	954.23	1016.47
Space group	$P2_1/c$	$P2_1/a$
Systematic absences	$h0l, l \neq 2n; 0k0, k \neq 2n$	$h0l, h \neq 2n; 0k0, k \neq 2n$
a (Å)	10.412(2)	18.238(4)
b (Å)	14.749(2)	10.402(3)
c (Å)	22.177(3)	19.070(2)
α (°)	90.0	90.0
β (°)	99.25(1)	95.37(2)
γ (°)	90.0	90.0
V (Å^3)	3361(1)	3602(2)
Z	4	4
D_{calc} (g cm^3)	1.885	1.874
Crystal size (mm)	0.10 × 0.30 × 0.20	0.10 × 0.50 × 0.60
μ(Mo Kα) (cm^{-1})	70.155	63.876
Data collection instrument	P3	Enraf-Nonius CAD-4
Radiation (monochromated in incident beam)	Mo Kα ($\lambda\bar{\alpha}$ = 0.71073 Å)	
Orientation reflections, number, range (2θ)	25; 20.3–30.5	25; 20.6–33.2
Temperature (°C)	22	22
Scan method	$\omega-2\theta$	ω
Data collection range, 2θ (°)	4–50	4.5–45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	4572, 2967	4059, 3368
No. parameters refined	255	349
Transmission factors, max., min.	1.0, 0.55	1.0, 0.4
R^a	0.033	0.034
$R_w{}^b$	0.045	0.045
Quality-of-fit indicator^c	0.966	1.292
Largest shift/e.s.d., final cycle	0.59	0.80
Largest peak (e Å^3)	0.625	0.999

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

in detail [5]. The structures were solved and refined by standard computational methods*. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections based upon azimuthal (ψ) scans were also applied. Crystallographic parameters and procedural data are given in Table I.

In each case the structure was solved by direct methods (program Multan 84), which revealed the location of the metal atoms. The remaining non-hydrogen atoms were located through a series of difference Fourier syntheses and least-squares refinements. Anisotropic displacement parameters were assigned to all atoms except those in the interstitial solvent molecules.

The pyridine derivative showed an interstitial benzene-like molecule, which could have been toluene with a disordered CH_3 group or pyridine. Since resolution of this ambiguity was not crucial it was simply treated as a benzene ring.

Results and Discussion

Molecular Structures

The atomic coordinates for the two structures are listed in Tables II and III for 1 and 2, respectively. ORTEP drawings of the dinuclear molecules are shown in Figs. 1 and 2. Both of these molecules, like the one in 3, have effective C_2 symmetry, with the C_2 axis passing through the μ-S and μ-O atoms.

Table IV gives the principal dimensions of 1 and 2 (see also 'Supplementary Material') and for comparison, those of 3. It is clear that all comparable dimensions of 1 and 2 are closely similar and in some cases identical within the experimental uncertainties. On the other hand a comparison of the dimensions of 1

---

*Calculations were done on the VAX-11/780 computer at Department of Chemistry, Texas A&M University, College Station, Texas, with the VAX-SDP software package.

TABLE II. Positional and Isotropic Equivalent Displacement Parameters for $Ta_2Cl_4O(SMe_2)(dmpe)_2 \cdot THF$ (1)

Atom	x	y	z	B (Å^2)[a]
Ta(1)	0.18617(5)	0.15228(3)	0.34801(2)	2.757(9)
Ta(2)	0.36845(5)	0.21836(3)	0.28914(2)	3.05(1)
Cl(1)	0.0113(3)	0.2064(3)	0.4057(2)	5.19(8)
Cl(2)	0.0251(3)	0.0741(2)	0.2741(2)	4.23(7)
Cl(3)	0.4947(4)	0.3278(2)	0.3557(2)	5.07(8)
Cl(4)	0.3851(4)	0.3138(3)	0.1961(2)	5.61(9)
S	0.1651(3)	0.2933(2)	0.2943(2)	3.84(7)
P(1)	0.3129(4)	0.1943(3)	0.4564(2)	4.07(8)
P(2)	0.1869(4)	0.0027(2)	0.4117(2)	4.00(8)
P(3)	0.5966(3)	0.1497(3)	0.2762(2)	4.42(8)
P(4)	0.3174(4)	0.1012(3)	0.1993(2)	4.25(8)
O(1)	0.3586(7)	0.1079(5)	0.3370(3)	3.1(2)
C(1)	0.045(1)	0.314(1)	0.2254(7)	5.7(4)
C(2)	0.144(2)	0.401(1)	0.3351(8)	6.3(4)
C(3)	0.299(2)	0.307(1)	0.4891(7)	6.0(4)
C(4)	0.490(1)	0.172(1)	0.4694(7)	5.3(4)
C(5)	0.255(2)	0.118(1)	0.5127(6)	6.0(4)
C(6)	0.272(2)	0.018(1)	0.4910(6)	6.1(4)
C(7)	0.266(1)	−0.096(1)	0.3843(7)	5.2(4)
C(8)	0.026(1)	−0.040(1)	0.4222(7)	5.7(4)
C(9)	0.714(1)	0.233(1)	0.2586(8)	6.8(4)
C(10)	0.683(1)	0.084(1)	0.3404(7)	5.7(4)
C(11)	0.581(1)	0.070(1)	0.2121(7)	5.7(4)
C(12)	0.463(1)	0.090(1)	0.1623(6)	5.5(3)
C(13)	0.291(2)	−0.018(1)	0.2189(7)	5.3(4)
C(14)	0.187(2)	0.124(1)	0.1347(7)	6.7(5)
O(2)	0.249(3)	0.552(3)	0.505(2)	26(1)*
C(15)	0.143(5)	0.616(3)	0.513(2)	24(2)*
C(16)	0.168(4)	0.692(3)	0.475(2)	18(1)*
C(17)	0.215(4)	0.651(3)	0.425(2)	18(1)*
C(18)	0.312(4)	0.594(3)	0.459(2)	19(1)*

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

TABLE III. Positional and Isotropic Equivalent Displacement Parameters for $Ta_2Cl_4O(THT)py_4 \cdot C_7H_8$ (2)

Atom	x	y	z	B (Å^2)[a]
Ta(1)	0.12501(2)	0.04347(4)	0.34620(2)	3.463(9)
Ta(2)	0.07368(2)	−0.06423(4)	0.22531(2)	3.285(9)
Cl(1)	0.1095(2)	0.0412(3)	0.4755(2)	5.36(7)
Cl(2)	0.2448(1)	−0.0554(3)	0.3691(2)	4.88(7)
Cl(3)	−0.0516(1)	0.0175(3)	0.2095(2)	4.66(7)
Cl(4)	0.0309(2)	−0.2768(3)	0.1709(2)	5.31(7)
S(1)	0.0577(2)	−0.1525(3)	0.3376(2)	4.49(6)
O(1)	0.1269(3)	0.0946(6)	0.2475(4)	3.5(1)
N(1)	0.0288(4)	0.1888(9)	0.3435(5)	4.5(2)
N(2)	0.1887(4)	0.2354(9)	0.3623(5)	4.5(2)
N(3)	0.0823(4)	0.0151(8)	0.1133(4)	3.9(2)
N(4)	0.1866(4)	−0.1472(8)	0.2082(4)	3.8(2)
C(1)	0.0292(7)	0.287(1)	0.2960(7)	5.7(3)
C(2)	−0.0275(7)	0.381(1)	0.2914(8)	7.1(4)
C(3)	−0.0837(6)	0.363(1)	0.3391(8)	8.0(4)
C(4)	−0.0826(7)	0.267(1)	0.3854(8)	7.1(4)
C(5)	−0.0255(6)	0.177(1)	0.3874(6)	5.3(3)
C(6)	0.2315(6)	0.276(1)	0.3116(7)	4.9(3)

(continued)

TABLE III. *(continued)*

Atom	x	y	z	B (Å^2)^a
C(7)	0.2703(7)	0.390(1)	0.3195(7)	6.1(3)
C(8)	0.2672(8)	0.465(1)	0.3804(8)	6.7(4)
C(9)	0.2266(7)	0.422(1)	0.4313(8)	6.4(4)
C(10)	0.1864(7)	0.306(1)	0.4219(7)	6.0(3)
C(11)	0.0977(5)	−0.062(1)	0.0587(6)	4.8(3)
C(12)	0.0990(6)	−0.014(1)	−0.0087(6)	5.4(3)
C(13)	0.0833(6)	0.111(1)	−0.0245(7)	5.8(3)
C(14)	0.0671(7)	0.192(1)	0.0330(7)	7.0(4)
C(15)	0.0682(6)	0.140(1)	0.1014(6)	4.9(3)
C(16)	0.2388(6)	−0.065(1)	0.1892(6)	4.5(3)
C(17)	0.3104(6)	−0.106(1)	0.1802(6)	5.1(3)
C(18)	0.3310(6)	−0.231(1)	0.1939(7)	5.8(3)
C(19)	0.2764(7)	−0.315(1)	0.2118(7)	6.8(3)
C(20)	0.2054(6)	−0.271(1)	0.2200(6)	5.2(3)
C(21)	−0.0338(6)	−0.172(1)	0.3723(7)	6.2(3)
C(22)	−0.0399(9)	−0.306(2)	0.390(1)	12.5(5)
C(23)	0.039(1)	−0.353(2)	0.4232(9)	10.6(5)
C(24)	0.0929(8)	−0.310(1)	0.3697(7)	7.0(4)
C(1S)	0.866(1)	0.310(2)	0.111(1)	12.0(6)*
C(2S)	0.791(1)	0.247(3)	0.101(1)	16.2(8)*
C(3S)	0.782(1)	0.311(2)	0.025(1)	11.9(6)*
C(4S)	0.820(1)	0.399(3)	−0.019(1)	16.6(9)*
C(5S)	0.890(1)	0.436(2)	0.012(1)	15.2(8)*
C(6S)	0.914(1)	0.384(2)	0.081(1)	14.3(7)*

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

TABLE IV. Average Values of Bond Distances (Å) and Angles (°) in 1, 2 and 3[a]

	3	1	2
Ta–Ta	2.726(1)	2.6557(7)	2.6537(6)
Ta–Cl$_e$(*trans* O)	2.447[5]	2.522[4]	2.521[13]
Ta–Cl$_a$(*trans* L)	2.407[4]	2.432[5]	2.423[7]
Ta–L	2.631[3]	2.628[5]	2.305[8]
Ta–S	2.397[3]	2.399[10]	2.375[2]
Ta–O	2.033[9]	1.960[4]	1.951[9]
Cl$_e$–Ta–Cl$_a$	95.0[2]	91.2[3]	90.2[1]
Cl$_e$–Ta–L(*trans* Cl)	77.4[1]	76.6[6]	82.3[4]
Cl$_e$–Ta–L(*trans* S)	86.6[3]	86.5[4]	88.8[1]
Cl$_e$–Ta–S	85.4[1]	87.8[1]	87.9[5]
Cl$_e$–Ta–O	155.7[1]	157.2[3]	163.8[1]
Cl$_a$–Ta–L(*trans* Cl)	157.2[3]	157.0[4]	163.6[12]
Cl$_a$–Ta–L(*trans* S)	81.9[1]	84.8[2]	84.6[2]
Cl$_a$–Ta–S	92.5[4]	94.0[6]	94.4[13]
Cl$_a$–Ta–O	107.2[5]	107.4[2]	100.6[6]
L(*trans* Cl)–Ta–L(*trans* S)	76.2[2]	75.2[2]	80.6[16]
L(*trans* Cl)–Ta–S	108.1[5]	104.8[7]	100.0[1]
L(*trans* Cl)–Ta–O	78.3[1]	81.4[5]	84.2[10]
L(*trans* S)–Ta–S	169.74[2]	174.0[2]	176.2[1]
L(*trans* S)–Ta–O	86.7[3]	82.2[1]	80.2[6]
S–Ta–O	103.3[4]	103.8[3]	103.2[4]
Ta–S–Ta	69.32(7)	67.23(9)	67.92(8)
Ta–O–Ta	84.2(2)	85.3(3)	85.7(3)

[a] Numbers in square brackets are variances, obtained from the expression $[(\Sigma\Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the ith value from the arithmetic mean and n is the total number of values averaged.

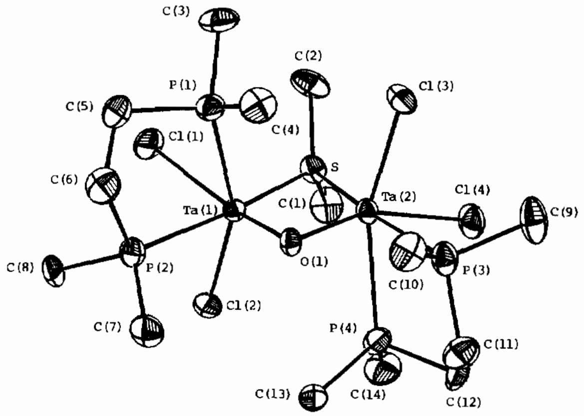

Fig. 1. ORTEP drawing of the $Ta_2Cl_4O(SMe_2)(dmpe)_2$ (**1**) molecule with thermal ellipsoids drawn at 30% probability level.

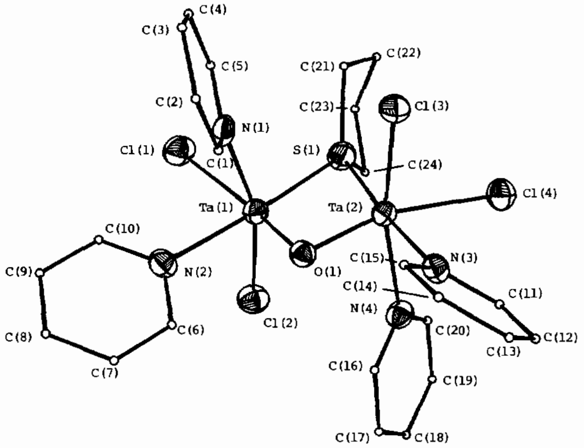

Fig. 2. ORTEP drawing of the $Ta_2Cl_4O(THT)py_4$ (**2**) molecule. Thermal ellipsoids enclose 30% of electron density while the carbon atoms are represented by spheres with arbitrarily small radius for the sake of clarity.

and **3**, which are of identical composition except for the oxygen containing bridge, shows some large differences. While the Ta–X, where X = P, S and $Cl_{\mathit{trans}\ \mathrm{to\ P}}$, bond lengths in **1** and **3** show a good match, the Ta–Ta, Ta–O and $Ta–Cl_{\mathit{trans}\ \mathrm{to\ O}}$ differ by about 0.07 Å. These effects can be directly associated with the bridging oxygen ligand. In fact, one is led to the conclusion that 'μ-O' in **3** is protonated, *i.e.* it is a μ-hydroxyl group. Based on the values in Table IV it is evident that deprotonation of the μ-hydroxo group, thereby converting it to an oxo bridge, results in shortening of the Ta–Ta and Ta–O bonds and enhances the *trans* influence of the coordinated O atom. In the μ-OH species the M–M distance is in the range typically observed for a double Ta=Ta bond when the bridging ligands are from the third period [6]. The M–M bond lengths in the μ-O complex described here are the shortest reported for a $Ta^{III}=Ta^{III}$ dimer without hydride ligands [7].

We are not aware of any other such closely related pair involving oxo and hydroxo bridged dimers with a metal to metal bond. Consequently we are not able to assess how general the trend observed for Ta might be. Because of relatively large atomic radii for the group 5 elements both Nb and Ta usually have long M=M bonds, which are quite sensitive to the radius of the bridging atom. Electronic effects, namely strengthening of the M–M interaction, if it in fact takes place, is probably a secondary process. Based on that it may be expected that elements from groups 6 and higher would show less pronounced differences in such cases.

Chemistry

Compound **3**, which we now recognize as $\{[TaCl_2(dmpe)]_2(\mu\text{-}SMe_2)(\mu\text{-}OH)\}^+Cl^-$ was obtained as a minor product when $Ta_2Cl_6(SMe_2)_3$ in dichloromethane was treated with dmpe. This reaction afforded sparingly soluble $Ta_2Cl_6(dmpe)_2$ in over 80% yield and a green solution from which **3** was crystallized out. There is little doubt that this μ-OH derivative resulted from hydrolysis rather than by action of O_2. In the latter case the oxidation state of the metal would have increased while, in fact it remains unchanged. The presence of water can be attributed to the fact that CH_2Cl_2 is notoriously difficult to make completely anhydrous.

The two new complexes reported here were obtained when, following the discovery of the first triply M–M bonded complexes of Nb and Ta [8], which were prepared by reduction of $M^{III}=M^{III}$ dimers in THF, we have investigated this general reaction route in the presence of various ligands. With Nb some interesting new materials were prepared, for example compounds of the formula $Nb_3Cl_7(PR_3)_6$ [9]. We have been less successful with tantalum, where there are indications of considerable interference from side reactions and even failure to achieve reduction. Such conclusions stemmed from lower yields of $Ta_2Cl_6(THT)_3{}^{2-}$ species, frequent intractability of products and isolation of Ta^{III} compounds [10] when ligands like phosphines were used.

Compound **1** was obtained according to the following reaction sequence

$$\underset{\text{brown solid}}{Ta_2Cl_6(SMe_2)(THF)_2} \xrightarrow{\text{THF, }Me_3CCO_2Li}$$

$$\underset{\text{green solution}}{Ta_2Cl_5(SMe_2)(Me_3CCO_2)(THF)_2} \xrightarrow{2Na/Hg}$$

$$\underset{\text{red solution}}{[Ta(+2\text{ or }+3)\text{ dimer}]?} \xrightarrow{\text{dmpe}}$$

$$\underset{\text{green solution}}{Ta_2Cl_4(SMe_2)(O)(dmpe)_2}$$

The first product with bridging carboxylate has been isolated and characterized previously [11]. In the last step the addition of dmpe caused an immediate color change to green. This suggests that the $Ta_2(\mu\text{-}O)$ moiety might have been already present in the solution. In a similar system containing free THT the reduction of a mono-tert-butylcarboxylate complex (prepared *in situ* from $Ta_2Cl_6(THT)_3$) did afford some Ta^{II} species as it was the first system from which the triply bonded $Ta_2Cl_6(THT)_2{}^{2-}$ was isolated, although in small yield. From the above we conclude that either THF or the pivalate may be not entirely passive in this system and provide oxygen for the strongly oxophilic tantalum. The detrimental effect of THF in the reaction involving the reduction of Ta was reported by Sattelberger *et al.* [12]. Thus no desirable product was obtained when $TaH_2Cl_2(PMe_3)_3$ was reduced with Na/Hg in neat THF while a high yield of $TaClH_2(PMe_3)_3$ was isolated when 6:1 Et_2O/THF was used as the medium.

The pyridine adduct 2 was obtained after the following sequence

$$Ta_2Cl_6(THT)(THF)_2 \xrightarrow{CH_2{=}C(PPh_2)_2,\ Na/Hg} \xrightarrow{py} Ta_2Cl_4O(THT)py_4$$

As was observed in other cases [10] the presence of phosphine, which substituted the weakly coordinated THF ligands, seemed to prevent reduction of Ta^{III}. By analogy to 3 the hydroxo species would be formed initially due to hydrolysis, but the presence of a base, namely pyridine, causes deprotonation.

The above rationalizations are based upon the assumption that no contamination of the reaction systems occurred and this is justified by apparent complete conversion at every stage. However, since no appropriate tests were carried out we cannot, with certainty, rule out such possibilities. On the other hand, the compounds we described have marginal synthetic utility and are of interest mainly because of their structure. In view of that, an effort to prove rigorously the mechanism of their formation, which, because of the extreme sensitivity of Ta compounds to protic and oxidizing media would be a lengthy and tedious process, does not seem to be worth pursuing.

Supplementary Material

Tables of bond distances, bond angles and anisotropic displacement parameters (12 pages); and calculated and observed structure factors (33 pages) for compounds 1 and 2 may be obtained from author F.A.C.

Acknowledgements

We are grateful to the Robert A. Welch Foundation for support under Grant No. A-494. M.P.D. thanks Texaco/I.U.C.C.P and the National Science Foundation for Predoctoral Fellowship support.

References

1 F. A. Cotton and W. J. Roth, *Inorg. Chem., 22,* 868 (1983).
2 F. A. Cotton and R. C. Najjar, *Inorg. Chem., 20,* 2716 (1981).
3 R. J. Burt, J. Chatt, W. Hussain and G. J. Leigh, *J. Organomet. Chem., 182,* 203 (1979).
4 I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1915 (1982).
5 (a) A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem., 18,* 3558 (1979); (b) F. A. Cotton, B. A. Frenz, G. Deganello and A. Shaver, *J. Organomet. Chem., 50,* 227 (1973).
6 F. A. Cotton, *Polyhedron, 6,* 667 (1987).
7 C. E. Holloway and M. Melnik, *Rev. Inorg. Chem., 7,* 161 (1985).
8 F. A. Cotton, M. P. Diebold and W. J. Roth, *J. Am. Chem. Soc., 108,* 3538 (1986); *109,* 5506 (1987).
9 F. A. Cotton, M. P. Diebold and W. J. Roth, *J. Am. Chem. Soc., 109,* 2833 (1987).
10 F. A. Cotton, M. P. Diebold and W. J. Roth, *Inorg. Chem., 26,* 4130 (1987).
11 F. A. Cotton, M. P. Diebold, S. A. Duraj and W. J. Roth, *Polyhedron, 4,* 1479 (1985).
12 M. L. Luetkens, M. D. Hopkins, A. J. Schultz, J. M. Williams, C. K. Fair, F. K. Ross, J. C. Huffman and A. P. Sattelberger, *Inorg. Chem., 26,* 2430 (1987).