Notes

Synthesis and X-ray Structure Analysis of [(η5-C5Me5)TaCl2]2(μ-O)(μ-OH)2

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Introduction

Recently we have reported the chemistry of some mid-valent, monocyclopentadienyl niobium and tantalum complexes.[2-7] These mono-Cp derivatives are of interest relative to the more thoroughly studied Cp2M type complexes, because the former present more coordination sites for ligand transformations.

During the course of these studies, we observed that solutions of Cp*Ta(CO)2(THF)[5] deposited yellow crystals when exposed to the atmosphere. These crystals analyzed well for Cp*TaOCl2. In view of the current interest in organometallic oxo complexes, we undertook an X-ray structure determination which showed that the oxidized complex was a dimer: [(η5-C5Me5)TaCl2]2-(μ-O)(μ-OH)2. This compound had been prepared previously by Geoffroy et al. by the controlled hydrolysis of Cp*TaCl4.[8] Here, we report the structure of the dimer.

Experimental Section

All operations were carried out under dinitrogen with the use of standard Schlenk techniques or in an inert-atmosphere box. Elemental analyses were carried out by the University of Michigan Microanalytical Service or by Galbraith Laboratories, Knoxville, TN. NMR spectra were obtained on a Bruker AM-300. TaCl5 was purchased from Pressure Chemicals Co. and stored in the glovebox. Solvents were dried by standard procedures and degassed prior to use. Cp*TaCl4 was prepared by the reaction of tantalum pentachloride with Cp*SnBu3 as described by Sanner[9] with the Bercaw modification.[10]

Synthesis of [(η5-C5Me5)TaCl2]2(μ-O)(μ-OH)2 (1). Solid Cp*Ta-(CO)2Cl2(THF) (2) (2 g, 3.88 mmol) was exposed to air for a few days, during which time the color turned to yellow. The product was extracted with 70 mL of CH2Cl2. The CH2Cl2 extract was filtered and then concentrated to give bright yellow crystals of [(η5-C5Me5)TaCl2]2(μ-O)(μ-OH)2 (1). Yield: 0.6 (38%). The best quality crystals were collected from an NMR tube where a benzene-d6 solution of 2 had slowly oxidized due to air diffusing through the rubber septum stopper. 1H NMR

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Table I. Crystallographic Data for [(η5-C5Me5TaCl2]2(μ-O)(μ-OH)2 (1)

formula	C20H32Cl4O3Ta2
fw	824.18
space group	*F2dd* (nonstandard *Fdd2*)
a, Å	8.953 (2)
b, Å	14.386 (4)
c, Å	39.617 (10)
V, Å³	5102 (2)
Z	8
μ(Mo Kα), cm⁻¹	94.7
ρ(calcd), g cm⁻³	2.15
T, K	293
I_{max}/I_{min}	0.064/0.050
$R(F)$,[a] %	3.63 (all data: 6.07)
$R_w(F)$,[b] %	3.85

[a] $R(F) = \sum |F_o - F_c|/\sum |F_o|$. [b] $R_w(F) = \sum [w^{1/2}|F_o - F_c|]/\sum [w^{1/2}F_o]$. $w^{-1} = \sigma^2(F_o) + gF_o^2$.
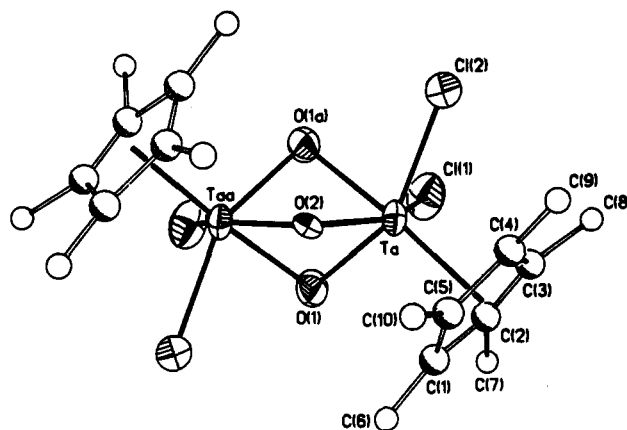
Figure 1. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of [(η5-C5Me5TaCl2]2(μ-O)(μ-OH)2 (1) with the numbering scheme.

(CDCl3): δ 2.30 (s, 30 H, C5*Me*5), 3.56 (s, 2 H, O*H*). Anal. Calcd for C20H32Cl4O3Ta2 (found): C, 29.15 (29.39); H, 3.91 (3.78).

Crystallographic Analysis. A yellow crystal for X-ray diffraction was selected from a crop of crystals obtained by slow evaporation of a benzene solution of 1. The crystal was mounted on a Nicolet R3m automated diffractometer. Data were collected with Mo Kα radiation (λ = 0.710 73 Å) monochromatized from a graphite crystal using the θ–2θ scan technique. Scanning rate was variable, depending on the peak intensity. Lattice parameters were obtained from least-squares analysis of 15 reflections, scattered in reciprocal space, obtained by the automatic centering routine. Intensities of three standard reflections were monitored after every 200 data points. Background was measured before and after each peak; the background to peak scan time ratio was about 1.0.

The solution and refinement of the structure were carried out with the SHELXTL package of crystallographic routines. The atomic scattering factors were taken from ref 11. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by standard least-squares and difference methods. Table I contains the crystallographic data.

Results and Discussion

Air oxidation of Cp*Ta(CO)2Cl2(THF) (2) in the solid state or in benzene solution afforded yellow dimer 1 (eq 1). Geoffroy
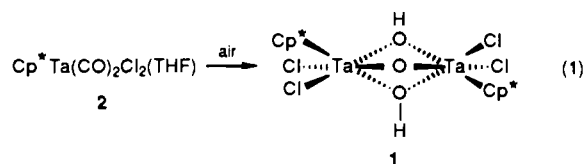
Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U^a
Ta	5000	20 (1)	382.1 (1)	31.8 (3)
Cl(1)	2428 (11)	−122 (5)	568 (2)	61 (2)
Cl(2)	5577 (13)	−1497 (4)	604 (2)	59 (3)
O(1)	4079 (22)	900 (11)	4 (4)	48 (5)
O(2)	6336 (25)	0	0	33 (6)
C(1)	5884 (58)	1672 (26)	517 (7)	100 (18)
C(2)	4886 (34)	1276 (18)	770 (8)	59 (10)
C(3)	5359 (45)	615 (26)	958 (9)	94 (13)
C(4)	6900 (42)	348 (24)	830 (8)	88 (14)
C(5)	7144 (38)	1015 (29)	559 (10)	91 (15)
C(6)	5792 (99)	2371 (24)	304 (13)	257 (51)
C(7)	3539 (47)	1967 (33)	802 (14)	196 (32)
C(8)	4664 (69)	146 (31)	1263 (7)	126 (30)
C(9)	7955 (77)	−254 (22)	996 (13)	186 (36)
C(10)	8646 (57)	908 (49)	391 (15)	295 (49)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

et al. prepared this complex by systematic hydrolysis of Cp*TaCl₄ but did not report its structure.[8] The molecular structure of **1** is shown in Figure 1. Fractional coordinates for the non-hydrogen atoms are listed in Table II, and selected bond lengths and angles are shown in Table III.

The molecule consists of two Cp*TaCl₂ groupings bridged by one oxo and two hydroxo ligands such that the molecule has crystallographically imposed C_2 symmetry. The 2-fold rotation axis passes through the oxo ligand and the midpoint of the Ta–Ta vector. The operator for the symmetry related atoms is (x, y, z; x, $-y$, $-z$). Each Ta atom has pseudooctahedral coordination if the Cp* centroid is taken to occupy a single coordination site. The overall geometry is very similar to that found in the dimer, [(Cp*TaCl₂)₂(μ-Cl₃)]⁺.[12] The Ta···Ta distance (3.028 (1) Å) is very short for a nonbonded metal–metal distance and is in the range often observed in compounds with Ta–Ta bonds.[6] This effect is due to the presence of the three small bridging ligands.

Table III. Selected Bond Lengths and Angles for [(η^5-C₅Me₅TaCl₂]₂(μ-O)(μ-OH)₂ (**1**)

Distances (Å)			
Ta–Cl(1)	2.426 (9)	Ta–Cl(2)	2.409 (7)
Ta–O(1)	2.13 (2)	Ta–O(2)	1.93 (1)
Ta···Ta(A)	3.028 (1)	Ta(A)-O(2)	1.93 (1)
Ta–O(1A)	2.18 (2)	Ta(A)–O(1)	2.18 (2)

Angles (deg)			
Ta–O(1)–Ta(A)	89.2 (6)	O(2)–Ta–O(1)	72.3 (6)
Ta–O(1)–Ta(A)	103.4 (10)	O(2)–Ta–O(1A)	71.1 (6)
O(1)–Ta–O(1A)	73.8 (7)	Cl(2)–Ta–Cl(1)	91.0 (3)
Cl(2)–Ta–O(1)	151.6 (5)	Cl(1)–Ta–O(1)	84.0 (5)
Cl(2)–Ta–O(2)	98.0 (3)	O(2)–Ta–Cl(1)	145.6 (5)
Ta–O(2)–Ta(A)	103.0 (1)		

Similar short Ta–Ta distances are also seen in the compound [Cp*₃Ta₃(μ-O)₃(μ_3-O)₂(H₂O)₂Cl]Cl (**3**).[8]

The Ta–O(2) distance (1.93 (1) Å) is 0.2–0.3 Å shorter than the Ta–O(1) or Ta–O(1A) distances, 2.13 and 2.18 Å, respectively. Thus, O(2) is implicated as the oxo ligand, and the other two oxygen atoms are implicated as belonging to the hydroxo groups. It is interesting to note that the Ta–O(2)–Ta(A) angle (103°) is ca. 14° larger than the Ta–O(1)–Ta(A) angle. The increased π-donation, relative to the hydroxo ligand, of the oxo (O2) ligand to the two tanatalum atoms causes the angle to open up. A linear M–O–M arrangement allows for maximum π-bonding with both oxygen p_π-orbitals. The Ta–Cl(1) bond, trans to the oxo ligand, appears to be somewhat shorter than the Ta–Cl bond trans to the hydroxo ligands, 2.426 (9) vs 2.496 (7) Å. This order is unexpected based on π-bonding arguments.

Supplementary Material Available: Tables IVS–VIIIS (crystallographic data, thermal parameters, bond distances, bond angles, and H atom positions) (4 pages). Ordering information is given on any current masthead page.