A Novel Tantalum Butterfly Oxo Cluster

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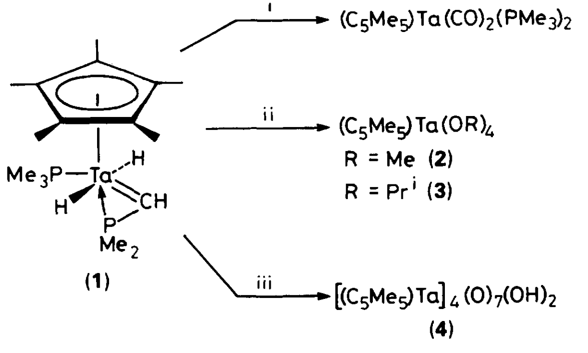
$(\eta^5\text{-}C_5Me_5)Ta(H)_2(\eta^2\text{-}CHPMe_2)(PMe_3)$ reacts with deoxygenated water in benzene to give the novel tetranuclear butterfly oxo cluster $[(\eta^5\text{-}C_5Me_5)Ta]_4(\mu_2\text{-}O)_4(\mu_3\text{-}O)_2(\mu_4\text{-}O)(OH)_2$ containing doubly, triply, and quadruply bridging oxo ligands, the *X*-ray crystal structure of which has been determined.

Half-sandwich poly-oxides are of considerable interest as hydrocarbon-soluble models for heterogeneous oxide catalysts. A variety of early transition metal cluster oxides benefiting from highly solubilizing pentamethylcyclopentadienyl ligands have been isolated, including $[(C_5Me_5)Ti]_4O_6$[1] and $[(C_5Me_5)TiMe(\mu_2\text{-}O)]_3$,[2] which are formed upon hydrolysis of $(C_5Me_5)TiCl_3$ and $(C_5Me_5)TiMe_3$, respectively, and trimeric $(C_5Me_5)VO_2$, obtained by treatment of $(C_5Me_5)V(O)Cl_2$ with Ag_2CO_3.[3] In general, hydrolyses of second and third row half-sandwich halides invariably lead to retention of halide groups within the cluster products; for example, hydrolyses of the half-sandwich zirconium and hafnium chlorides, $(C_5Me_5)MCl_3$ (M = Zr, Hf), give the cluster compounds $[(C_5Me_5)MCl]_3(O)(OH)_3Cl$ and $[(C_5Me_5)MCl]_3(O)(OH)_4$ (M = Zr, Hf),[4] while $(C_5Me_5)TaCl_4$ may be hydrolysed in stepwise fashion to $(C_5Me_5)_3Ta_3O_4Cl_4$ and $[(C_5Me_5)_3Ta_3O_5Cl(H_2O)]Cl$.[5] Here, we describe an alternative 'non-halide' approach to the synthesis of pentamethylcyclopentadienyl oxides of tantalum which has allowed the preparation of a unique high-valent tantalum butterfly oxo cluster containing a μ_4-oxo ligand. Only one other butterfly compound containing the μ_4-oxo group has been reported; the low valent carbonyl complex, $[Fe_3Mn(CO)_{12}(\mu_4\text{-}O)]$, prepared by Shriver and co-workers.[6]

The compound $(C_5Me_5)Ta(PMe_3)_2$[7] has been shown to exist in the unusual cyclometallated form (**1**) (Scheme 1); it reacts with π-acids such as carbon monoxide to regenerate the classical PMe_3 group and retain both PMe_3 molecules within the metal co-ordination sphere.[7] When the oxophilic metal centre of (**1**) is exposed to substrates containing acidic hydroxy functionalities such as alcohols and water, displacement of the PMe_3 ligands and liberation of dihydrogen results, leading to preferential binding of hard, π-basic OR or oxo groups. Thus, treatment of (**1**) with 4 equiv. of ROH (R = Me, Pr^i) in toluene at room temperature affords the known tetra-alkoxides $(C_5Me_5)Ta(OR)_4$ [R = Me (**2**), Pr^i (**3**)][8] (>95% by ^{1}H NMR).



Scheme 1. *Reagents and conditions*: i, CO (g), 1 atm., toluene, 25 °C, 3 days; ii, 4ROH, 25 °C, 30 min; iii, H_2O, 3—5 equiv., C_6H_6, 25 °C.

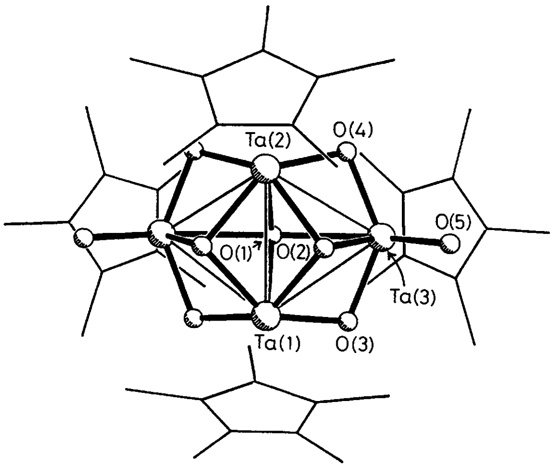


Figure 1. Molecular structure of (**4**), with independent Ta and O atoms labelled. The mirror plane passes through Ta(1), Ta(2), and O(1). Key dimensions: Ta(1)–Ta(2) 3.089(1), Ta(1)–Ta(3) 3.022(1), Ta(2)–Ta(3) 3.013(1), Ta(1)–O(1) 2.103(5), Ta(1)–O(2) 2.096(4), Ta(1)–O(3) 1.951(4), Ta(2)–O(1) 2.128(7), Ta(2)–O(2) 2.083(4), Ta(2)–O(4) 1.940(4), Ta(3)–O(1) 2.358(1), Ta(3)–O(2) 2.126(4), Ta(3)–O(3) 1.957(5), Ta(3)–O(4) 1.956(5), Ta(3)–O(5) 1.950(5) Å.

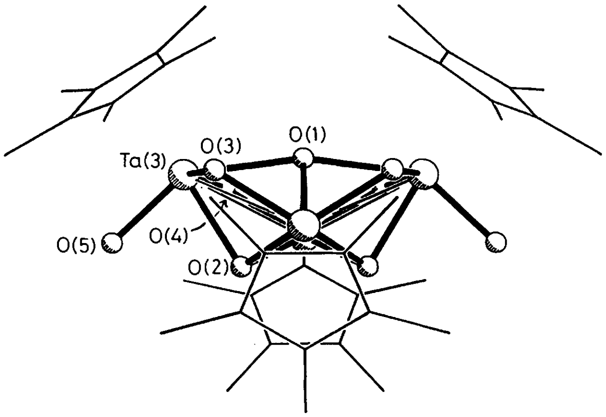


Figure 2. A side view of (**4**) along the Ta(1)–Ta(2) vector showing the butterfly geometry.

When an excess of water (typically 3—5 equiv.) is added to (**1**) in benzene at room temperature, a white solid forms immediately with concomitant evolution of dihydrogen. Extraction of the solid with benzene, followed by standing of this solution for several days at room temperature resulted in large colourless prisms of the title complex in *ca.* 50% yield. The crystal structure† shows a butterfly core of four tantalum atoms with a crystallographic mirror plane containing the hinge atoms Ta(1) and Ta(2) (Figures 1 and 2).

The tetranuclear core is surrounded by seven bridging oxo ligands; four doubly bridging [O(3), O(3′), O(4), and O(4′)], two triply bridging oxygens [O(2), O(2′)] which cap the triangular faces of each wing, and a unique quadruply bridging oxygen atom attached to the hinge and wing-tip tantalums. The co-ordination sphere is completed by two terminal hydroxide ligands, one on each Ta(3) atom. The metal atoms are pentavalent and consequently direct metal–metal bonds are not required to interpret the structure; the metal–metal distances of 3.089(1) [Ta(1)–Ta(2)], 3.022(1) [Ta(1)–Ta(3)], and 3.013(1) Å [Ta(2)–Ta(3)] are significantly longer than those normally found in Ta–Ta bonded systems (typically *ca.* 2.6—2.8 Å[12]). The unique μ_4-oxide ligand possesses relatively short distances to Ta(1) and Ta(2) [2.103(5) and 2.128(7) Å, respectively] and an elongated bond [2.358(1) Å] to the symmetry related Ta(3) and Ta(3′). The latter is more consistent with a dative covalent bond (for comparison, the Ta–O distances of tetrahydrofuran ligands lie in the range 2.22—2.31 Å[13]). Although the hydrogens of the terminal hydroxide ligands were not located in the *X*-ray structure determination, their presence was confirmed by an O–H stretch at 3545 cm^{-1} in the IR spectrum and a singlet resonance at δ 6.00 in the ^{1}H NMR spectrum. The methyl hydrogens of the C_5Me_5 ligands occur as singlets at δ 2.12 and δ 2.13 respectively.

The mode of assembly of the butterfly cluster is unknown. However, an intriguing alternative representation for (**4**) is $[(C_5Me_5)TaO_2]_4(H_2O)$ which may be viewed as a hydrated form of $(C_5Me_5)TaO_2$; this could suggest that (**4**) arises from the reaction of the presently unknown $(C_5Me_5)TaO_2$ with water. However, an attempt to dehydrate (**4**) by azeotropic distillation with benzene failed to give a tractable product.[14]

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14 A. Shaw and V. C. Gibson, unpublished observations.

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† *Crystal data*: $C_{40}H_{62}O_9Ta_4 \cdot 1/2C_6H_6$, $M = 1149.8$, monoclinic, $C2/m$, $a = 18.809(4)$, $b = 16.066(3)$, $c = 14.884(3)$ Å, $\beta = 100.50(2)°$, $U = 4422.4$ Å^3, $Z = 4$ (molecule has crystallographic mirror symmetry), $D_c = 2.178$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu = 9.80$ mm^{-1}, $F(000) = 2748$, $T = 295$ K. The structure was determined by Patterson methods and refined[9] to a minimum of $\Sigma w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 82 + 2235G + 1484G^2 - 485H + 557H^2 - 3817GH$, $G = F_o/F_{max.}$, $H = \sin\theta/\sin\theta_{max.}$]^{10} from 3502 reflections with $2\theta < 50°$ and $F > 4\sigma_c(F)$ (σ_c from counting statistics only), measured with a Stoe-Siemens diffractometer and on-line profile fitting.[11] Anisotropic thermal parameters were refined for all non-H atoms, H atoms were not included. Final $R = 0.036$, $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2} = 0.033$, for 269 parameters. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.