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Half-Sandwich Pentamethylcyclopentadienyl Oxo and Alkoxo Complexes of Tantalum. Synthesis and Characterisation of $(\eta\text{-}C_5Me_5)Ta(O)Cl_2$†

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$(\eta\text{-}C_5Me_5)Ta(O)Cl_2$ has been isolated in 40% yield from the reaction of $(\eta\text{-}C_5Me_5)TaCl_2(PMe_3)_2$ with carbon dioxide; the mono-alkoxides $(\eta\text{-}C_5Me_5)TaCl_3(OR)$ (R = Me, Et) and the oxo-bridged dimer $[(\eta\text{-}C_5Me_5)TaCl_3]_2(O)$ are obtained by treatment of $(\eta\text{-}C_5Me_5)TaCl_4$ with Me_3SiOR (R = Me, Et) and $(Me_3Si)_2O$ respectively.

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There is much current interest in the reactivity of half-sandwich transition metal oxides and alkoxides since they provide soluble model species through which to probe the chemistry of metal–oxygen fragments relevant to heterogeneous oxidation catalysis. The first half-sandwich organometal oxide to be described was $(\eta\text{-}C_5H_5)V(O)Cl_2$, reported by Fischer[1] as long ago as 1958. Despite considerable recent progress in the synthesis of group 6 organometal oxides,[2] and extensive studies on the rhenium system Cp^*ReO_3[3] ($Cp^* = C_5Me_5$), half-sandwich oxo complexes of the heavier group 5 metals have proved particularly elusive.

Here, we describe the synthesis and characterisation of $Cp^*Ta(O)Cl_2$ (**1**), the first heavy metal analogue of Fischer's vanadium complex, along with half-sandwich mono-alkoxides of the type $Cp^*TaCl_3(OR)$ [R = Me, (**3**); Et, (**4**)] and the oxo-bridged dimer $[Cp^*TaCl_3]_2(O)$ (**5**). All products have been characterised by mass spectrometry, i.r. and n.m.r. spectroscopies,‡ and give satisfactory elemental analyses.

Treatment of the paramagnetic d^2 complex $Cp^*TaCl_2(PMe_3)_2$[4] with 1 atm. carbon dioxide in toluene at room temperature for 12 h gives yellow crystalline (**1**) in 40% yield (equation 1). Compound (**1**) arises by oxygen abstraction from CO_2 and precipitates from a red–brown supernatant solution which is found to contain $Cp^*TaCl_2(CO)_2(PMe_3)$ (**2**). Compound (**2**) is formed by reaction of $Cp^*TaCl_2(PMe_3)_2$ with the carbon monoxide by-product and has been characterised by comparison with data from an authentic sample.[4]

$$Cp^*TaCl_2(PMe_3)_2 \xrightarrow{CO_2\,(1\ atm)} Cp^*Ta(O)Cl_2\ (\mathbf{1})\ 40\% + Cp^*TaCl_2(CO)_2(PMe_3)\ (\mathbf{2})\ ca.\ 20\% \quad (1)$$

Compound (**1**) is moisture sensitive and sublimes at 180 °C (5×10^{-6} torr); it is partially soluble in aromatic solvent. Its poor solubility has prevented accurate molecular weight determinations. However, a low resolution mass spectrum gives an envelope at *m/z* 805 (^{35}Cl) consistent with a dimeric formulation (no higher mass fragments are observed) and the i.r. spectrum shows a strong band at 675 cm^{-1} indicating the presence of bridging oxo ligands. Thus, $Cp^*Ta(O)Cl_2$ (**1**) may be reasonably formulated as an oxo-bridged dimer (a representation with *trans* Cp* ligands is illustrated in Figure 1).

Compounds (**3**) and (**4**) have been prepared by exploiting the reaction between transition metal halides and silylethers[5] (equations 2 and 3). Thus, treatment of Cp^*TaCl_4 with Me_3SiOR (R = Me, Et) at 70 °C in dichloroethane affords the yellow crystalline monoalkoxides $Cp^*TaCl_3(OR)$ [R = Me, (**3**); Et, (**4**)] in high yield according to Scheme 1.

$$MCl_x + (Me_3Si)_2O \rightarrow M(O)Cl_{x-2} + 2Me_3SiCl \quad (2)$$

$$MCl_x + Me_3SiOR \rightarrow M(OR)Cl_{x-1} + Me_3SiCl \quad (3)$$

Compounds (**3**) and (**4**) may be heated at 100 °C for several hours without further elimination of RCl. However, upon warming Cp^*TaCl_4 with hexamethyldisiloxane at 70 °C in CH_3CN, elimination of two equivs. of Me_3SiCl occurs to afford the oxo-bridged dimer $[Cp^*TaCl_3]_2(O)$ (**5**). Compound (**5**) has been isolated previously in 8% yield by hydrolysis of

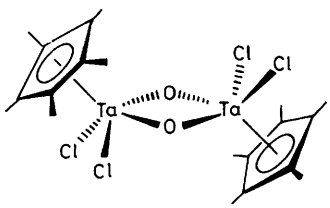
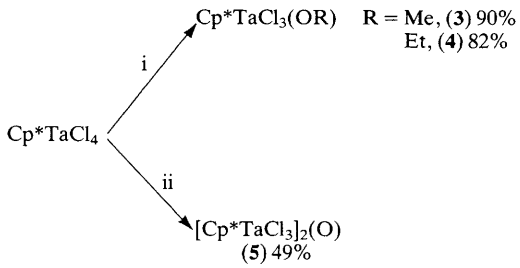


Figure 1



Scheme 1. *Reagents and conditions*: i, Me_3SiOR, $C_2H_4Cl_2$, 70 °C, 18 h, $-Me_3SiCl$; ii, $(Me_3Si)_2O$, CH_3CN, 70 °C, 3.5 h, $-2Me_3SiCl$.

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‡ *Selected spectroscopic data* for (**1**): ^1H n.m.r. (C_6D_6, 250 MHz, 298 K) δ 2.22 (s, C_5Me_5). I.r. (CsI, Nujol, cm^{-1}): 1430 (m), 1070 (w), 1025 (m), 803 (w), 675 (s, br), 610 (w), 598 (m), 550 (m), 436 (w), 387 (s), 330 (s), 310 (s), 291 (s). CI mass spec. (*m/z*, ^{35}Cl): 805 $[M_2-H]^+$, 403 $[M + H]^+$. For (**2**): ^1H n.m.r. ($CDCl_3$, 250 MHz, 298 K) δ 2.44 (s, 15H, C_5Me_5), 4.57 (s, 3H, OMe); $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$, 62.9 MHz, 298 K) δ 128.53 (s, C_5Me_5), 67.17 (s, OCH_3), 12.84 (s, C_5Me_5). I.r. (CsI, Nujol, cm^{-1}): 1483 (m), 1435 (m), 1127 (s, br), 1041 (m), 1025 (m), 963 (w), 805 (w), 683 (w), 523 (m), 381 (m), 335 (s), 290 (s). For (**3**): ^1H n.m.r. ($CDCl_3$, 250 MHz, 298 K) δ 1.37 [t, 3H, ^3J(HH) 7.0 Hz, OCH_2CH_3], 2.44 (s, 15H, C_5Me_5), 4.84 [q, 2H, ^3J(HH) 7.0 Hz, OCH_2CH_3]; ^{13}C n.m.r. ($CDCl_3$, 62.9 MHz, 298 K) δ 128.32 (s, C_5Me_5), 76.20 [t, ^1J(CH) 149.6 Hz, OCH_2CH_3], 17.27 [q, ^1J(CH) 127.2 Hz, OCH_3CH_3], 12.96 [q, ^1J(CH) 128.1 Hz, C_5Me_5]. I.r. (CsI, Nujol, cm^{-1}) 1115 (s, br), 1082 (s), 1030 (m), 1020 (m), 940 (m), 807 (w), 800 (w), 720 (w), 563 (m), 376 (m), 340 (s), 300 (m), 286 (m, sh).

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Cp^*TaCl_4.[6] $Cp^*Ta(O)Cl_2$ is not produced under these conditions, most probably due to its reactivity towards Me_3SiCl. For example a sample of (**1**) treated with two equivs. of Me_3SiCl at 70 °C in C_6D_6 deposits (**5**) and gives signals in the ^1H n.m.r. spectrum attributable to small amounts of two, as yet, uncharacterised siloxide species. $Cp^*Ta(O)Cl_2$ (**1**) is also surprisingly unstable in solution, slowly converting above room temperature to (**5**) and a species which gives a single Cp* proton resonance at δ 2.15 (C_6D_6).§ These observations may explain why the heavier group 5 derivatives have proved somewhat elusive, but nevertheless augurs well for the reactivity of oxygen atoms in these environments. Studies are now being directed towards assessing the influence of competitive metal–ligand π-interactions upon the nature of the bonding and reactivity of the oxo ligand in (**1**) and its analogues.

§ *Note added in proof.* A crystal structure (ref. 7) of this product (crystallised as a 1 : 1 toluene solvate) shows it to be the asymmetrically-bridged trinuclear cluster, $Cp^*_3Ta_3O_4Cl_4$ possessing a terminal chloride on each Ta, 3 edge-bridging oxo ligands, and a μ_3-oxo group capping the Ta_3 face. The remaining chloride ligand bridges two of the tantalum atoms. A partial structure determination on this compound has been reported in ref. 6. The single δ 2.15 resonance in C_6D_6 arises due to coincidental overlap of the Cp* methyl resonances.

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