# Preparation and Crystal Structure of Tris(2-methylphenyl)silanolatotantalum Tetrachloride–1.5 Diethyl Ether and Isolation of the Novel Tantalum(IV) Derivative Hexamethylbis[tris(2-methylphenyl)silanolato]ditantalum

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The tantalum(V) compound tris(2-methylphenyl)silanolatotantalum tetrachloride–1.5-diethyl ether [$(2\text{-MeC}_6H_4)_3SiOTaCl_4 \cdot 1.5\ (Et_2O)$] (**1**) has been prepared and structurally characterised; on treatment with methylmagnesium chloride (4 equiv.) (**1**) gave solutions containing the apparently unstable tetramethyl derivative [$(2\text{-MeC}_6H_4)_3\ SiOTaMe_4$] **A** and its decomposition product hexamethylbis[tris(2-methylphenyl)silanolato]ditantalum, [$(2\text{-MeC}_6H_4)_3\ SiOTaMe_3]_2$ (**2**), from which pure (**2**) was isolated.

There has been much recent interest in the chemistry of tantalum(V) diaryloxy and di- or tri-siloxy compounds, for example, $Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(CH_2R)_3$,[1] $Ta(OSiBu^t_3)_2Cl_3$ or $Ta(OSiBu^t_3)_3Cl_2$,[2] but studies on related mono-alkoxy or siloxy species are relatively rare. Only two examples of the latter class have been reported, namely $Ta(OPh)Cl_4$[3] and $Ta[OSiMe_2\{C(SiMe_3)\}_3]Cl_4$,[4] but neither has been structurally characterised. We now report the synthesis and structural characterisation of the monosiloxytantalum(V) compound $Ta[OSi(C_6H_4Me\text{-}2)_3]Cl_4 \cdot 1.5Et_2O$ (**1**) and the isolation of an unusual $Ta^{IV}$ dimer $[Ta\{OSi(C_6H_4Me\text{-}2)_3\}Me_3]_2$ on treatment of (**1**) with methylmagnesium chloride (4 equiv.). Compound (**1**) was formed as colourless cubic crystals when $TaCl_5$ was treated with the lithium silanolate as indicated in equation (1).

$$Li[OSi(C_6H_4Me\text{-}2)_3] + TaCl_5 \xrightarrow{Et_2O/\text{toluene}} \underset{(\mathbf{1})}{Ta[OSi(C_6H_4Me\text{-}2)_3]Cl_4 \cdot 1.5\ Et_2O} + LiCl \quad (1)$$

The structure of (**1**) was determined by *X*-ray crystallography, and is shown in Figure 1,† along with selected bond lengths and angles; the molecule is monomeric with octahedral geometry about the tantalum centre. The axial sites are occupied by the siloxy group and a co-ordinated disordered ether molecule, while the chlorides are in the equatorial plane. A second disordered ether molecule is included in each unit cell. The aryl groups attached to silicon adopt a propeller arrangement, the angles between the planes described by each ring being in the range 88—119°. An essentially linear arrangement of the Ta–O–Si atoms is seen, with short Ta–O and long Si–O distances implying some Ta–O multiple bonding.

On treatment with methylmagnesium chloride (4 equiv.) compound (**1**) gave a mixture of the tetramethyl derivative **A** and its decomposition product (**2**) as shown in equation (2). The tetramethyl derivative **A** was not isolated but resonances[2]‡ consistent with its formation were present in the $^1H$ n.m.r. spectrum of freshly prepared $C_6D_6$ solutions of the mixture from reaction (2). At room temperature the resonances due to **A** slowly decrease in intensity and eventually disappear while those of (**2**)‡ simultaneously increase in intensity relative to internal standard. Other, probably gaseous, products were not detected in these n.m.r. experiments. Pure (**2**) is deposited from pentane or toluene solutions of the mixture. Satisfactory elemental analyses for (**2**) were obtained and its mass spectrum shows a base peak at *m/z* 543 consistent with the monomeric species $[Ta\{OSi(C_6H_4\text{-}$

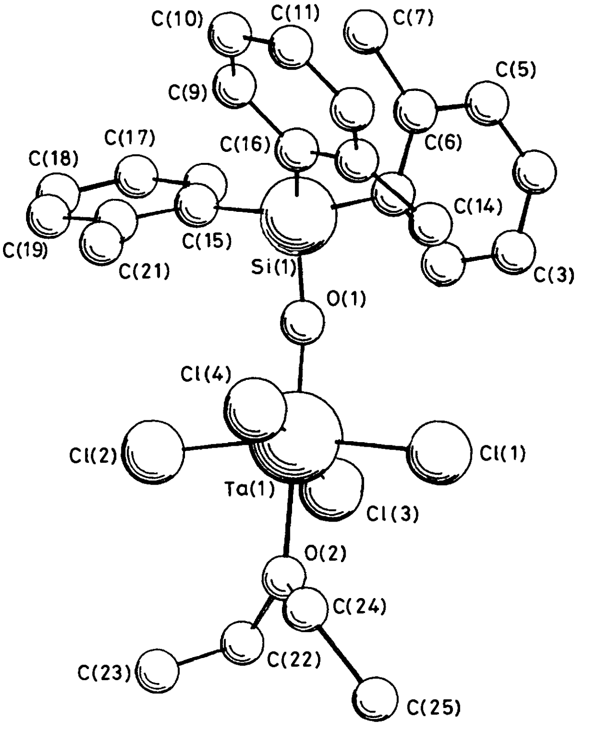

**Figure 1.** The crystal structure of [$(C_6H_4Me\text{-}2)_3SiOTaCl_4 \cdot 1.5Et_2O$] (**1**). Selected bond lengths (Å) and angles (°) are: Ta–Cl(1) 2.353(1), Ta–Cl(2) 2.328(1), Ta–Cl(3) 2.356(1), Ta–Cl(4) 2.351(1), Ta–O(1) 1.812(3), Ta–O(2) 2.263(3), Si–O(1) 1.706(3); Cl(1)–Ta–Cl(2) 168.64(5), Cl(3)–Ta–Cl(4) 170.41(5), Cl(1)–Ta–Cl(3) 88.48(5), Cl(1)–Ta–Cl(4) 90.84(5), Cl(2)–Ta–Cl(3) 88.42(5), Cl(2)–Ta–Cl(4) 90.40(5), O(1)–Ta–Cl av. 95.2(1), $O_2$–Ta–Cl av. 84.85(14), O(1)–Ta–O(2) 177.5(1), Ta–O(1)–Si 172.1(2).

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† *Crystal data* for (**1**): $C_{27}H_{36}Cl_4O_{2.5}SiTa$, $M = 751.43$, triclinic, space group $P\bar{1}$, $a = 10.287(4)$, $b = 12.609(6)$, $c = 13.057(4)$ Å, $\alpha = 78.34(3)$, $\beta = 71.16(3)$, $\gamma = 90.07(3)°$, $U = 1565$ cm$^3$, $Z = 2$, $D_c = 1.59$ g cm$^{-3}$; $\lambda$ (Mo–$K_\alpha$) = 0.71069 Å, $\mu = 38.76$ cm$^{-1}$. Data recorded using a CAD–4 diffractometer in $\omega/2\theta$ scan mode; 5858 unique reflections measured, 5006 observed with [$F > 3\sigma F_o$]. The structure was solved by routine Patterson and Fourier methods and refined by least squares, with anisotropic thermal parameters being assigned all ordered non-hydrogen atoms (except the included solvent molecule). Hydrogens were generated geometrically and were not refined. $R$ and $R_w$ values were 0.058 and 0.082 respectively. 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.

‡ $^1H$ n.m.r. for (**A**) ($C_6D_6$) $\delta$ 1.03 (s, TaMe, 12H), 2.41 (s, O–Me, 9H) and 6.9—7.6 (m, ArH).

For (**2**) ($C_6D_6$) $\delta$ 0.86 (s, TaMe, 9H), 2.52 (s, (O–Me, 9H), and 6.9—7.6 (m, ArH).

Me-2)$_3$}Me$_3$]$^+$. The molecular weight of (**2**) (by freezing point depression of benzene) was found to be 1004 indicative of the dimer (calc. 1087.82). An unbridged $D_{3h}$ structure with a single Ta–Ta bond between the two trigonal bipyramidal tantalum centres is consistent with the observation of a single sharp resonance in the $^1$H n.m.r. spectrum for the methyl groups attached to tantalum. A similar unbridged dimeric Ta$^{IV}$ structure has recently been proposed for the Ta$^{IV}$ hydride species [Ta(OSiBu$^t{}_3$)$_2$H$_2$]$_2$.[5]

$$\mathrm{Ta[OSi(C_6H_4Me\text{-}2)_3]Cl_4{\cdot}1.5Et_2O + 4MeMgCl} \xrightarrow{-78\,^\circ\mathrm{C}}$$

$$\mathrm{[Ta[OSi(C_6H_4Me\text{-}2)_3]Me_4] + 4MgCl_2}$$

$$\text{room temp.} \downarrow \mathbf{A}$$

$$\mathrm{[Ta\{OSi(C_6H_4Me\text{-}2)_3\}Me_3]_2} \qquad (2)$$

**(2)**

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