

# Complexes of $\text{TaOCl}_3$ and $\text{TaSCl}_3$ with Neutral N- and O-donor ligands - synthesis, properties and comparison with the niobium analogues.

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## Abstract

The white complexes,  $[\text{TaOCl}_3(\text{OPPh}_3)_2]$ ,  $[\text{TaOCl}_3(\text{L-L})]$  ( $\text{L-L} = 1,10\text{-phenanthroline, 2,2'-bipyridyl, Ph}_2\text{P(O)CH}_2\text{P(O)Ph}_2, \text{Ph}_2\text{P(O)CH}_2\text{CH}_2\text{P(O)Ph}_2$  and  $o\text{-C}_6\text{H}_4(\text{P(O)Ph}_2)_2$ ), have been prepared from  $\text{TaCl}_5$ ,  $\text{O}(\text{SiMe}_3)_2$  and the ligands in anhydrous  $\text{CH}_2\text{Cl}_2$  solution. The corresponding yellow  $[\text{TaSCl}_3(\text{OPPh}_3)_2]$  and  $[\text{TaSCl}_3(\text{L-L})]$  were made similarly using  $\text{S}(\text{SiMe}_3)_2$ . The complexes have been characterised by microanalysis, IR and NMR ( $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ ) spectroscopy. X-ray crystal structures have been obtained for  $[\text{TaOCl}_3(1,10\text{-phen})]$ ,  $[\text{TaSCl}_3(1,10\text{-phen})]$ ,  $[\text{TaOCl}_3\{o\text{-C}_6\text{H}_4(\text{P(O)Ph}_2)_2\}]$ ,  $[\text{TaSCl}_3(\text{OPPh}_3)_2]$ ,  $[\text{TaSCl}_3\{\text{Ph}_2\text{P(O)CH}_2\text{CH}_2\text{P(O)Ph}_2\}]$  and  $[\text{TaSCl}_3(\text{MeCN})_2]$ , which all contain *mer*-chlorines and with the neutral ligands *trans* to O/Cl or S/Cl. The structure of the  $\text{Ta(V)}$  dimer  $[\text{Cl}_2\text{S}(1,10\text{-phen})\text{Ta}(\mu\text{-O})\text{Ta}(1,10\text{-phen})\text{S}\text{Cl}_2]$ , formed by trace hydrolysis, is also reported. Comparisons between the complexes of  $\text{TaOCl}_3$  and  $\text{TaSCl}_3$  and their niobium analogues are discussed.

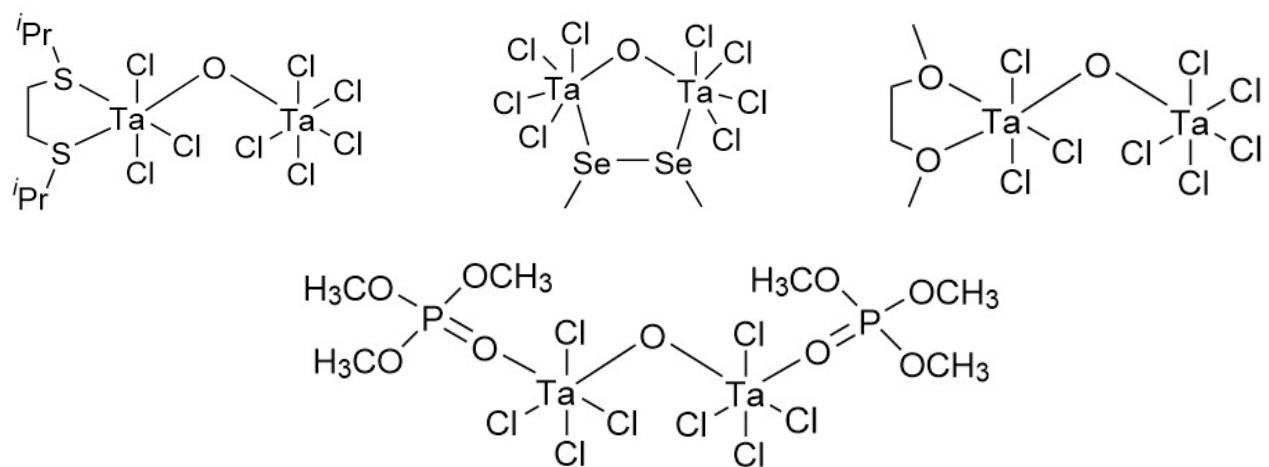
**Keywords:** tantalum oxide trichloride, tantalum sulfide trichloride, phosphine oxide, 2,2'-bipyridyl, 1,10-phenanthroline

## 1. Introduction

Niobium(V) oxide trichloride is formed by heating niobium in a  $\text{Cl}_2/\text{O}_2$  mixture, by heating  $\text{NbCl}_5$  with non-metal oxides, by Cl/O exchange from  $\text{NbCl}_5$  and siloxanes, and also forms in hydrolysis of  $\text{NbCl}_5$  [1]. Solid niobium oxide trichloride,  $\text{NbOCl}_3$  contains dimeric  $\text{Cl}_2\text{Nb}(\text{O})(\mu\text{-Cl})_2\text{Nb}(\text{O})\text{Cl}_2$  units linked into chains via unsymmetrical oxide bridges, giving six-coordinate niobium [2], and vaporises on heating to give  $\text{NbOCl}_3$  molecules as  $\text{C}_{3v}$  monomers [3]. In contrast,  $\text{TaOCl}_3$ , which is less stable [1], is made by reacting  $\text{TaCl}_5$  with  $\text{Cl}_2\text{O}$  in  $\text{CCl}_4$  [4] or by pyrolysis of  $[\text{TaCl}_5(\text{Et}_2\text{O})]$  [5,6]. Structural information is limited to an early powder X-ray pattern [7], which indicated similarity to the structure of  $\text{NbOCl}_3$ ; it decomposes on heating without vaporising [1]. Although most standard texts and reviews [1,8,9] discuss  $\text{NbOCl}_3$  and  $\text{TaOCl}_3$  coordination chemistry together, detailed study of the original work reveals that that of  $\text{TaOCl}_3$  is much less well developed, and the differences are often large. Thus,  $\text{NbOCl}_3$  forms complexes with most neutral N- and O-

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donor and some softer donor ligands; the majority are six-coordinate  $[\text{NbOCl}_3(\text{L})_2]$  ( $\text{L}$  for example =  $\text{PEt}_3$ ,  $\text{PPh}_3$ ,  $\text{OPR}_3$ ,  $\text{OSR}_2$ ,  $\frac{1}{2} \text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$ ,  $\frac{1}{2} \text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$ ,  $\frac{1}{2} 2,2'$ -bipy) [8,9,10], whilst seven coordination is present in  $[\text{NbOCl}_3(\text{PMe}_3)_3]$  and  $[(\text{NbOCl}_3)_2\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_3]$  [11,12]. Complexes of  $\text{TaOCl}_3$  reported in the older literature come from hydrolysis of  $\text{TaCl}_5$  complexes or by oxygen abstraction from ligands [8,9, 13,14]. Recent detailed studies by Marchetti *et. al.* [15,16,17,18] of the reactions of  $\text{TaCl}_5$  with various oxygen based ligands, including ethers, dialkoxyalkanes, aldehydes, ketones and esters, have produced a range of  $\text{TaOCl}_3$  complexes. However, crystallographically authenticated mononuclear examples are rare - often the structures found in crystals grown from the products are dinuclear with oxide bridges (Scheme 1). Examples of the latter include  $[\{\text{MeO}(\text{CH}_2)_2\text{OMe}\}\text{Cl}_3\text{Ta}(\mu\text{-O})\text{TaCl}_5]$  [15],  $[\text{LCl}_4\text{Ta}(\mu\text{-O})\text{TaCl}_4\text{L}]$  ( $\text{L}$  = trimethylphosphate) [18],  $[\text{Cl}_5\text{Ta}(\mu\text{-O})\text{TaCl}_3\{\text{iPrS}(\text{CH}_2)_2\text{S}^{\text{i}}\text{Pr}\}]$ ,  $[\text{Cl}_4\text{Ta}((\mu\text{-O})(\mu\text{-Me}_2\text{Se}_2)\text{TaCl}_4]$  [19].



**Scheme 1** Structures of tantalum oxide chloride complexes established by X-ray crystallography.

It is also notable that attempts to prepare neutral ligand adducts of  $\text{TaOF}_3$  have failed, whereas niobium analogues are well established [10].

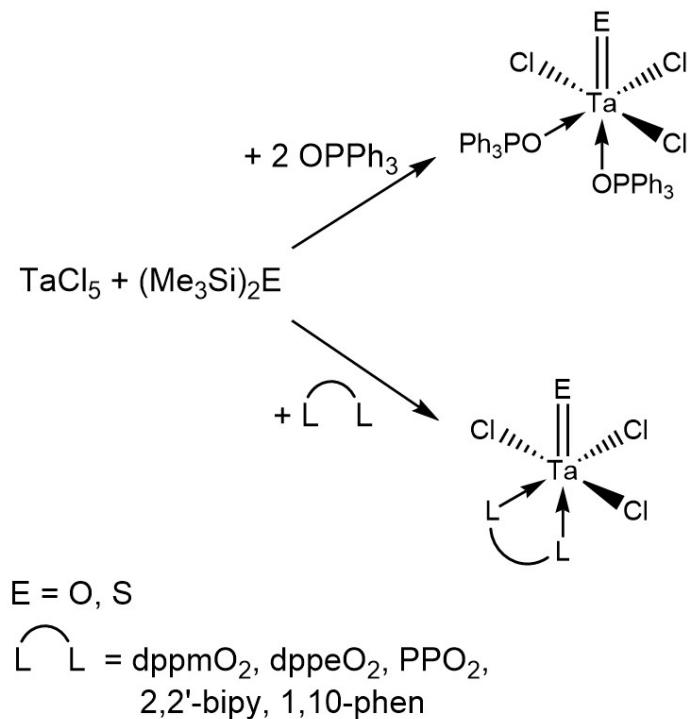
A comparison of the coordination chemistries of the sulfide trichlorides  $\text{NbSCl}_3$  and  $\text{TaSCl}_3$  reveals a similar pattern, with the niobium systems subjected to much more detailed study [8,9,20,21,22,23]. Both five- and six-coordinate complexes of  $\text{NbSCl}_3$  have been characterised and some thioether complexes, including  $[\text{NbSCl}_3(\text{S}^{\text{n}}\text{Bu}_2)_2]$  and  $[\text{NbSCl}_3(\text{n}^{\text{n}}\text{BuS}(\text{CH}_2)_2\text{S}^{\text{n}}\text{Bu})]$ , have been shown to function as single source low pressure chemical vapour deposition reagents for the production of thin films of  $\text{NbS}_2$  [23]. In contrast to the oxide trichloride chemistry, the sulfide trichloride chemistry is complicated by redox reactions involving the formation of species with  $(\text{S}_2)^{2-}$  groups [22,23]. The complexes of  $\text{TaSCl}_3$  are few [8,9] although  $[\text{TaSCl}_3\{\text{PhS}(\text{CH}_2)_2\text{SPh}\}]$  [24] and the anions  $[\text{TaSCl}_4(\kappa^1\text{-1,4-dioxan})]^-$  and  $[(\text{TaSCl}_4)_2(\mu\text{-1,4-dioxan})]^{2-}$  [25] have been structurally characterised.

Here we report the synthesis, spectroscopic and structural analyses of  $\text{TaOCl}_3$  and  $\text{TaSCl}_3$  with phosphine oxide and diimine ligands and compare these to their Nb analogues.

## 2. Results and Discussion

### 2.1. Complexes of $\text{TaOCl}_3$

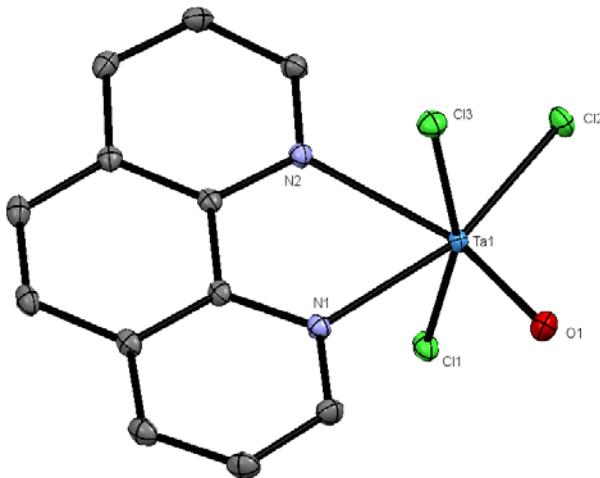
Direct reaction of (insoluble) polymeric  $\text{TaOCl}_3$  with neutral ligands is not a viable route to the desired complexes, and in this work the reaction of  $\text{TaCl}_5$  with  $\text{O}(\text{SiMe}_3)_2$  and the appropriate ligand in  $\text{MeCN}$  or  $\text{CH}_2\text{Cl}_2$  solution was used. After a variety of trial and error variations of the reaction conditions, the best routes were identified and are described in Section 3. Obtaining pure samples depends upon careful control of the reaction conditions, including the ratio of the reactants and maintaining rigorously anhydrous conditions. The complexes  $[\text{TaOCl}_3(\text{L-L})]$  ( $\text{L-L} = 2,2'\text{-bipy}, 1,10\text{-phen}, \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$  (dppmO<sub>2</sub>),  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$  (dppeO<sub>2</sub>),  $\text{o-C}_6\text{H}_4(\text{P}(\text{O})\text{Ph}_2)_2$  (PPO<sub>2</sub>)) and  $[\text{TaOCl}_3(\text{OPPh}_3)_2]$  were obtained as moisture sensitive white powders in moderate to good yields (40-70%) (Scheme 2).



**Scheme 2** Synthesis of the complexes.

The diimine complexes  $[\text{TaOCl}_3(1,10\text{-phen})]$  and  $[\text{TaOCl}_3(2,2'\text{-bipy})]$  are very poorly soluble in weak donor solvents like chlorocarbons and  $\text{MeCN}$ , a property common to complexes of these ligands with early d-block halides in high/medium oxidation states [12,26,27,28,29,30]. They are readily hydrolysed in solution with formation of protonated diimine, and generally seem less robust than the niobium analogues. Colourless crystals of  $[\text{TaOCl}_3(1,10\text{-phen})]$  were grown by slow evaporation of a  $\text{CH}_2\text{Cl}_2$  solution of the complex in the glove box. The structure (Figure 1) confirms the complex as a monomer with a terminal  $\text{Ta=O}$  and shows a six-coordinate tantalum centre with the diimine *trans* to  $\text{O}/\text{Cl}$ . In contrast to many complexes of this type [27

and below], the structure is free of O/Cl disorder. The tantalum coordination sphere is distorted by the short chelate bite of the rigid 1,10-phenanthroline, and the axial Cl-Ta-Cl unit is bent away from the Ta=O group ( $\text{Cl3-Ta1-Cl1} = 161.7^\circ$ ). The  $d(\text{Ta-Cl})_{\text{trans-N}}$  is shorter than the  $d(\text{Ta-Cl})_{\text{transCl}}$  and  $d(\text{Ta=O})$  is  $1.7268(13)$  Å. As indicated in the Introduction, although a range of complexes of  $\text{TaOCl}_3$  has been reported, a search of the CCDC (accessed January 2019) shows the  $[\text{TaOCl}_3(1,10\text{-phen})]$  is the first crystallographically authenticated example of a mononuclear complex of  $\text{TaOCl}_3$ .



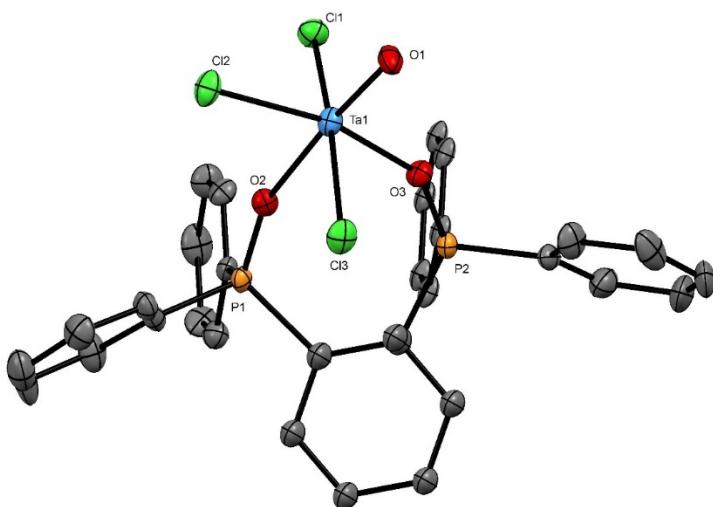
**Figure 1** The structure of  $[\text{TaOCl}_3(1,10\text{-phen})]$  showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are:  $\text{Ta1-Cl2} = 2.3449(4)$ ,  $\text{Ta1-Cl1} = 2.3729(4)$ ,  $\text{Ta1-Cl3} = 2.3807(4)$ ,  $\text{Ta1-O1} = 1.7268(13)$ ,  $\text{Ta1-N2} = 2.3849(14)$ ,  $\text{Ta1-N1} = 2.2374(15)$ ,  $\text{Cl2-Ta1-Cl1} = 92.315(15)$ ,  $\text{Cl2-Ta1-Cl3} = 94.463(15)$ ,  $\text{Cl2-Ta1-N2} = 91.15(4)$ ,  $\text{Cl1-Ta1-N2} = 82.35(4)$ ,  $\text{Cl3-Ta1-N2} = 80.51(4)$ ,  $\text{O1-Ta1-Cl2} = 106.40(4)$ ,  $\text{O1-Ta1-Cl1} = 97.14(5)$ ,  $\text{O1-Ta1-Cl3} = 97.24(5)$ ,  $\text{O1-Ta1-N1} = 91.60(6)$ ,  $\text{N1-Ta1-Cl1} = 83.32(4)$ ,  $\text{N1-Ta1-Cl3} = 84.98(4)$ ,  $\text{N1-Ta1-N2} = 70.88(5)$ .

The IR spectra of  $[\text{TaOCl}_3(1,10\text{-phen})]$  and  $[\text{TaOCl}_3(2,2'\text{-bipy})]$  show the single  $\nu(\text{Ta=O})$  at  $941$  and  $938$  cm<sup>-1</sup>, respectively, consistent with terminal Ta=O double bonds, and two  $\nu(\text{Ta-Cl})$  bands in the region  $315\text{--}350$  cm<sup>-1</sup> (theory: three bands,  $2\text{A}_1 + \text{E}$ , although often only two bands are resolved in practice [12,27]). The poor solubility made obtaining NMR spectra difficult, but the complexity of the  $^1\text{H}$  NMR spectra is consistent with inequivalent aromatic rings as found in the crystal structure; weaker resonances due to some protonated diimine formed by hydrolysis were also typically present.

Four phosphine oxide complexes were obtained, viz  $[\text{TaOCl}_3(\text{OPPh}_3)_2]$ ,  $[\text{TaOCl}_3(\text{dppmO}_2)]$ ,  $[\text{TaOCl}_3(\text{dppeO}_2)]$  and  $[\text{TaOCl}_3(\text{PPO}_2)]$ , all white, moisture sensitive powders. The IR spectra show  $\nu(\text{Ta=O})$  in the range  $919\text{--}935$  cm<sup>-1</sup>, two  $\nu(\text{Ta-Cl})$  stretches and two widely separated  $\nu(\text{P=O})$ , consistent with a six-coordinate tantalum centre with the phosphine oxide groups *trans* to O/Cl, again with terminal Ta=O groups. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra in  $\text{CH}_2\text{Cl}_2$  solution also show two  $\delta_{\text{P}}$  resonances, as required for this geometry. Several batches of crystals of  $[\text{TaOCl}_3(\text{OPPh}_3)_2]$  were grown by evaporation from a  $\text{CH}_2\text{Cl}_2$  solution and the X-ray crystal structure

solution confirmed the identity of the complex; the basic geometry and unit cell dimensions are similar to those in  $[\text{NbOCl}_3(\text{OPPh}_3)_2]$  and  $[\text{NbOF}_3(\text{OPPh}_3)_2]$  [12,31]. In the tantalum case the O/Cl *trans* to the phosphine oxides were disordered (as they are in the niobium complexes), and in view of the mediocre crystal quality and apparent disorder, the structure is not reported in detail here (see Supplementary Information).

Several sets of data were collected on crystals grown from  $[\text{TaOCl}_3\{o\text{-C}_6\text{H}_4(\text{P}(\text{O})\text{Ph}_2)_2\}]$ , all of which produced the same basic structure on refinement. The data showed a well-defined local environment about tantalum, but had disorder in two of the aromatic rings. The disorder problem is discussed in the Supplementary Information. Because of this disorder, the metrical data needs to be viewed with care, but it is certainly good enough to identify the structure as shown in Figure 2, which reveals the second example of a mononuclear  $\text{TaOCl}_3$  complex.



**Figure 2** The structure of  $[\text{TaOCl}_3\{o\text{-C}_6\text{H}_4(\text{P}(\text{O})\text{Ph}_2)_2\}]$  showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Due to serious disorder in two of the aromatic rings (not shown) the data should be viewed with care. Selected bond lengths (Å) and angles (°) are:  $\text{Ta1-Cl1} = 2.381(4)$ ,  $\text{Ta1-Cl2} = 2.353(3)$ ,  $\text{Ta1-Cl3} = 2.414(4)$ ,  $\text{Ta1-O1} = 1.760(10)$ ,  $\text{Ta1-O2} = 2.230(10)$ ,  $\text{Ta1-O3} = 2.047(9)$ ,  $\text{Cl(2)-Ta1-Cl1} = 93.14(13)$ ,  $\text{Cl2-Ta1-Cl3} = 91.68(13)$ ,  $\text{O1-Ta1-Cl1} = 97.3(4)$ ,  $\text{O1-Ta1-Cl2} = 98.1(4)$ ,  $\text{O1-Ta1-Cl3} = 96.0(4)$ ,  $\text{O1-Ta1-O3} = 96.7(4)$ ,  $\text{O2-Ta1-Cl1} = 81.5(3)$ ,  $\text{O2-Ta1-Cl2} = 87.7(3)$ ,  $\text{O2-Ta1-Cl3} = 84.5(3)$ ,  $\text{O3-Ta1-Cl1} = 87.8(3)$ ,  $\text{O3-Ta1-Cl3} = 84.0(3)$ ,  $\text{O3-Ta1-O2} = 77.5(4)$ .

The  $d(\text{Ta=O})$  and  $d(\text{Ta-Cl})$  are similar to those in  $[\text{TaOCl}_3(1,10\text{-phen})]$  and taken together with the disparate  $d(\text{Ta-O}_\text{P})$ , suggest the structure is free from Cl/O disorder.

## 2.2 Complexes of $\text{TaSCl}_3$

Previous syntheses of  $\text{TaSCl}_3$  complexes have used pre-isolated  $\text{TaSCl}_3$ , which was subsequently reacted with the ligands in an appropriate solvent [21,24]. In the present work,  $\text{TaSCl}_3$  was generated *in situ* by reaction of  $\text{TaCl}_5$  and  $\text{S}(\text{SiMe}_3)_2$  in  $\text{CH}_2\text{Cl}_2$ , followed by addition of the appropriate ligand. The complexes,  $[\text{TaSCl}_3(\text{L-L})]$  ( $\text{L-L} = 2,2'\text{-bipy}$ , 1,10-phen, dppmO<sub>2</sub>, dppeO<sub>2</sub> and PPO<sub>2</sub>) and  $[\text{TaSCl}_3(\text{OPPh}_3)_2]$  were obtained as yellow, moisture sensitive powders in 50 – 80% yield (Scheme 2). The reaction of  $\text{TaCl}_5$  and  $\text{S}(\text{SiMe}_3)_2$  in MeCN generated the

known yellow complex,  $[\text{Ta}(\text{SCl}_3(\text{MeCN})_2)]$  [21,24]. The spectroscopic data were in good agreement with the literature and are not discussed, but the X-ray structure was also determined and is shown in Figure 3.

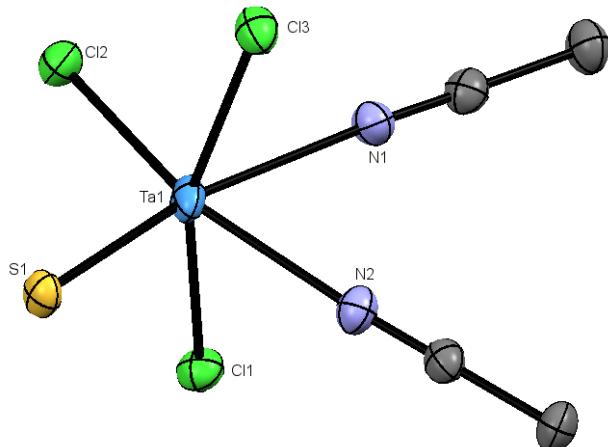


Figure 3 View of the structure of one of the two crystallographically independent molecules present in the asymmetric unit for  $[\text{Ta}(\text{SCl}_3(\text{MeCN})_2)]$  with atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Ta1-Cl1} = 2.3704(13)$ ,  $\text{Ta1-Cl3} = 2.3823(13)$ ,  $\text{Ta1-S1} = 2.2332(14)$ ,  $\text{Ta1-Cl2} = 2.2989(14)$ ,  $\text{Ta1-N2} = 2.280(5)$ ,  $\text{Ta1-N1} = 2.356(5)$ ,  $\text{Cl3-Ta1-N2} = 81.12(13)$ ,  $\text{S1-Ta1-Cl1} = 97.40(5)$ ,  $\text{S1-Ta1-Cl3} = 97.12(5)$ ,  $\text{S1-Ta1-Cl2} = 103.26(5)$ ,  $\text{S1-Ta1-N1} = 91.65(13)$ ,  $\text{Cl2-Ta1-Cl1} = 94.97(5)$ ,  $\text{Cl2-Ta1-Cl3} = 95.32(5)$ ,  $\text{Cl2-Ta1-N1} = 88.41(13)$ ,  $\text{N1-Ta1-Cl1} = 81.81(13)$ ,  $\text{N2-Ta1-Cl1} = 83.26(13)$ ,  $\text{N1-Ta1-Cl3} = 82.32(13)$ ,  $\text{N1-Ta1-N2} = 76.68(17)$ .

The X-ray structure of  $[\text{Ta}(\text{SCl}_3(1,10\text{-phen})]$  is shown in Figure 4 and is similar to that of  $[\text{Ta}(\text{OCl}_3(1,10\text{-phen})]$  discussed above, although in the thiochloride complex the S/Cl in plane are disordered. As discussed elsewhere [20,22,23], disorder is a particular problem in thiochloride complexes since the similar scattering power of S and Cl makes it very difficult/impossible to establish that some degree of disorder is *not* present. If disorder is absent (or only slight), one would expect  $d(\text{Ta-Cl})$  and  $d(\text{Ta-S})$  to differ by  $\sim 0.15 \text{ \AA}$  and the  $d(\text{Ta-N})$  should also differ due to the different *trans* influence of S and Cl [22,24].

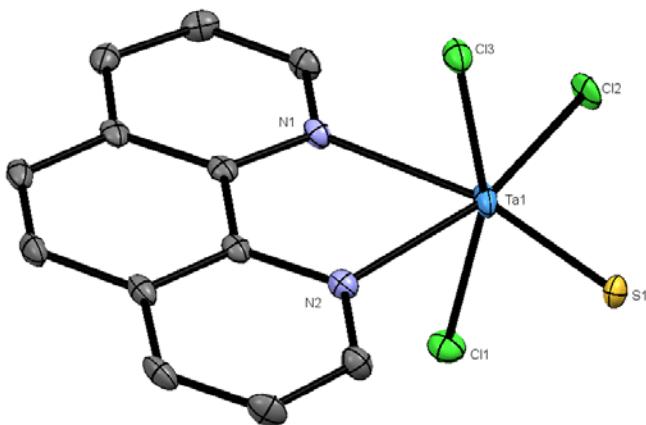
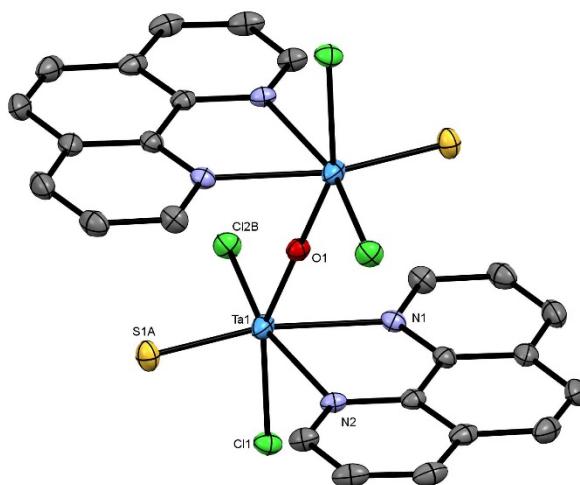


Figure 4 The structure of  $[\text{Ta}(\text{SCl}_3(1,10\text{-phen})]$  showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Note that S1/Cl2 are disordered. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are:  $\text{Ta1-S1} = 2.2347(7)$ ,  $\text{Ta1-Cl2} = 2.2548(7)$ ,  $\text{Ta1-N1} = 2.294(2)$ ,  $\text{Ta1-N2} = 2.309(2)$ ,  $\text{Ta1-Cl1} = 2.3692(7)$ ,  $\text{Ta1-Cl3} = 2.3733(7)$ ,  $\text{Cl2-Ta1-N1} = 93.40(6)$ ,  $\text{S1-Ta1-N2} = 91.23(6)$ ,  $\text{N1-Ta1-N2} = 71.64(8)$ ,  $\text{S1-Ta1-Cl1} = 96.69(3)$ ,  $\text{Cl2-}$

$\text{Ta1-Cl1} = 97.10(3)$ ,  $\text{N1-Ta1-Cl1} = 82.14(6)$ ,  $\text{N2-Ta1-Cl1} = 82.58(6)$ ,  $\text{S1-Ta1-Cl3} = 95.22(3)$ ,  $\text{Cl2-Ta1-Cl3} = 94.90(3)$ ,  $\text{N1-Ta1-Cl3} = 81.97(6)$ ,  $\text{N2-Ta1-Cl3} = 81.88(6)$ ,  $\text{S1-Ta1-Cl2} = 103.71(3)$ .

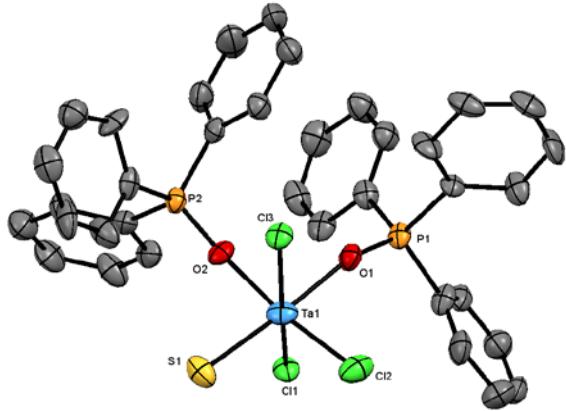
The spectroscopic properties of  $[\text{TaSCl}_3(1,10\text{-phen})]$  and  $[\text{TaSCl}_3(2,2'\text{-bipy})]$  are similar, with  $\nu(\text{Ta=S})$  in the range  $500\text{--}505\text{ cm}^{-1}$  and  $\nu(\text{Ta-Cl})$   $315\text{--}345\text{ cm}^{-1}$ . As in the case of the oxido-chloride analogues, the  $^1\text{H}$  NMR spectra show inequivalent rings, consistent with the structures proposed, and often show evidence of some hydrolysis in solution. From one attempt to grow crystals of the 1,10-phen complex a few colourless crystals were obtained, which proved, on structure solution, to contain a hydrolysis product, the oxido-bridged  $\text{Ta(V)}$  dimer,  $[\text{Cl}_2\text{S}(1,10\text{-phen})\text{Ta}(\mu\text{-O})\text{Ta}(1,10\text{-phen})\text{SCl}_2]$  (Figure 5). The complex contains a linear  $\text{Ta-O-Ta}$  bridge, with the tantalum geometry distorted from regular octahedral by the short chelate bite of the diimine ( $\text{N-Ta-N} = 71.7^\circ$ ). The in plane  $\text{Cl/S}$  ( $\text{Cl2B}$ ,  $\text{S1A}$ ) are disordered.



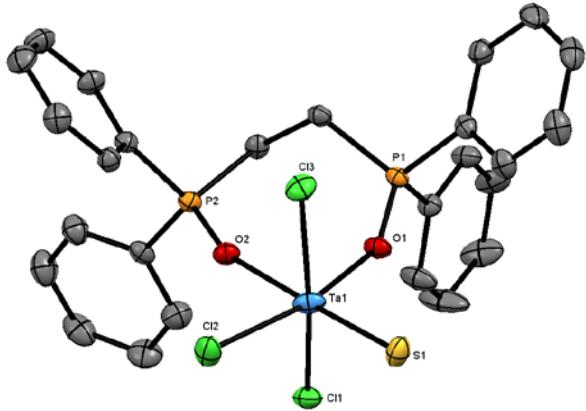
**Figure 5** The structure of  $[\text{Cl}_2\text{S}(1,10\text{-phen})\text{Ta}(\mu\text{-O})\text{Ta}(1,10\text{-phen})\text{SCl}_2]\cdot2\text{CH}_2\text{Cl}_2$  showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Note that  $\text{Cl2B}$  and  $\text{S1A}$  are disordered. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are:  $\text{Ta1-Cl1} = 2.4275(7)$ ,  $\text{Ta1-O1} = 1.88314(12)$ ,  $\text{Ta1-N1} = 2.318(2)$ ,  $\text{Ta1-N2} = 2.313(2)$ ,  $\text{Ta1-S1A} = 2.29(2)$ ,  $\text{Ta1-Cl2B} = 2.23(3)$ ,  $\text{O1-Ta1-N1} = 79.81(5)$ ,  $\text{O1-Ta1-N2} = 79.35(5)$ ,  $\text{O1-Ta1-S1A} = 99.3(10)$ ,  $\text{O1-Ta1-Cl2B} = 96.7(9)$ ,  $\text{N1-Ta1-Cl1} = 81.62(6)$ ,  $\text{N2-Ta1-Cl1} = 83.83(6)$ ,  $\text{N2-Ta1-N1} = 71.65(8)$ ,  $\text{S1A-Ta1-Cl1} = 95.7(10)$ ,  $\text{S1A-Ta1-N2} = 93.7(10)$ ,  $\text{Cl2B-Ta1-Cl1} = 95.3(9)$ ,  $\text{Cl2B-Ta1-N1} = 91.6(6)$ ,  $\text{Ta1-O1-Ta1'} = 180.0$ .

Four phosphine oxide complexes,  $[\text{TaSCl}_3(\text{OPPh}_3)_2]$ ,  $[\text{TaSCl}_3(\text{dppmO}_2)]$ ,  $[\text{TaSCl}_3(\text{dppeO}_2)]$  and  $[\text{TaSCl}_3(\text{PPO}_2)]$ , were obtained as yellow powders from reaction of  $\text{TaCl}_5$ ,  $\text{S}(\text{SiMe}_3)_2$  and the phosphine oxide in anhydrous  $\text{CH}_2\text{Cl}_2$ . The IR spectra show a strong  $\nu(\text{Ta=S})$  vibration at  $\sim 500\text{ cm}^{-1}$ ,  $\nu(\text{Ta-Cl})$  in the range  $290\text{--}330\text{ cm}^{-1}$ , and two well separated  $\nu(\text{P=O})$  vibrations indicative of six-coordinate tantalum with *mer*-chlorides and the  $\text{P=O}$  groups *trans* S/Cl. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra also show two phosphorus resonances of equal intensity due to  $\text{PO}_{\text{transCl}}$  and  $\text{PO}_{\text{transS}}$ . X-ray crystal structures were obtained for two examples,  $[\text{TaSCl}_3(\text{OPPh}_3)_2]$  and  $[\text{TaSCl}_3(\text{dppeO}_2)]$ , shown in Figures 6 and 7. The  $[\text{TaSCl}_3(\text{OPPh}_3)_2]$  shows S/Cl disorder *trans* to the phosphine oxide groups, but the  $[\text{TaSCl}_3(\text{dppeO}_2)]$  appears largely free from such disorder (with the caveat about the difficulty of eliminating the presence of some disorder discussed above). In particular, the  $d(\text{Ta=S}) = 2.206(1)$

Å and  $d(\text{Ta}-\text{Cl}_{\text{transPO}}) = 2.318(1)$  Å are much as expected, whilst the  $d(\text{Ta}-\text{O}_\text{P})$  are 2.061(3) Å and 2.184(3) Å, reflecting the expected *trans* influence S > Cl [23].



**Figure 6** The structure of  $[\text{TaSCl}_3(\text{OPPh}_3)_2]$  showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Note that Cl2 and S1 are disordered. Selected bond lengths (Å) and angles (°) are:  $\text{Ta1}-\text{O}2 = 2.089(6)$ ,  $\text{Ta1}-\text{O}1 = 2.108(7)$ ,  $\text{Ta1}-\text{Cl}2 = 2.271(3)$ ,  $\text{Ta1}-\text{S}1 = 2.275(3)$ ,  $\text{Ta1}-\text{Cl}1 = 2.386(2)$ ,  $\text{Ta1}-\text{Cl}3 = 2.388(2)$ ,  $\text{O}2-\text{Ta1}-\text{O}1 = 83.09(13)$ ,  $\text{O}1-\text{Ta1}-\text{Cl}2 = 90.84(19)$ ,  $\text{O}2-\text{Ta1}-\text{S}1 = 91.3(2)$ ,  $\text{Cl}2-\text{Ta1}-\text{S}1 = 95.01(6)$ ,  $\text{O}2-\text{Ta1}-\text{Cl}1 = 85.67(17)$ ,  $\text{O}1-\text{Ta1}-\text{Cl}1 = 84.00(17)$ ,  $\text{Cl}2-\text{Ta1}-\text{Cl}1 = 97.04(9)$ ,  $\text{S}1-\text{Ta1}-\text{Cl}1 = 92.01(8)$ ,  $\text{O}2-\text{Ta1}-\text{Cl}3 = 83.93(16)$ ,  $\text{O}1-\text{Ta1}-\text{Cl}3 = 85.76(17)$ ,  $\text{Cl}2-\text{Ta1}-\text{Cl}3 = 92.34(9)$ ,  $\text{S}1-\text{Ta1}-\text{Cl}3 = 97.25(9)$ .



**Figure 7** The structure of  $[\text{TaSCl}_3(\text{dppeO}_2)]$  showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are:  $\text{Ta1}-\text{O}1 = 2.061(3)$ ,  $\text{Ta1}-\text{O}2 = 2.184(3)$ ,  $\text{Ta1}-\text{S}1 = 2.2025(11)$ ,  $\text{Ta1}-\text{Cl}2 = 2.3175(11)$ ,  $\text{Ta1}-\text{Cl}1 = 2.3826(10)$ ,  $\text{Ta1}-\text{Cl}3 = 2.3849(11)$ ,  $\text{O}1-\text{Ta1}-\text{O}2 = 80.09(11)$ ,  $\text{O}1-\text{Ta1}-\text{S}1 = 96.55(9)$ ,  $\text{O}2-\text{Ta1}-\text{Cl}2 = 84.67(8)$ ,  $\text{S}1-\text{Ta1}-\text{Cl}2 = 98.70(4)$ ,  $\text{O}1-\text{Ta1}-\text{Cl}1 = 84.93(8)$ ,  $\text{O}2-\text{Ta1}-\text{Cl}1 = 82.10(8)$ ,  $\text{S}1-\text{Ta1}-\text{Cl}1 = 96.37(4)$ ,  $\text{Cl}2-\text{Ta1}-\text{Cl}1 = 93.37(4)$ ,  $\text{O}1-\text{Ta1}-\text{Cl}3 = 85.83(8)$ ,  $\text{O}2-\text{Ta1}-\text{Cl}3 = 84.10(8)$ ,  $\text{S}1-\text{Ta1}-\text{Cl}3 = 97.00(4)$ ,  $\text{Cl}2-\text{Ta1}-\text{Cl}3 = 92.28(4)$ .

### 3. Experimental

Syntheses were performed by using standard Schlenk and glove-box techniques under a dry  $\text{N}_2$  atmosphere.  $\text{TaCl}_5$ ,  $\text{O}(\text{SiMe}_3)_2$  and  $\text{S}(\text{SiMe}_3)_2$  were obtained from Sigma-Aldrich and used as received. Solvents were dried

by distillation from  $\text{CaH}_2$  ( $\text{CH}_2\text{Cl}_2$ , MeCN) or Na/benzophenone ketyl (n-hexane). Ligands (2,2'-bipy, 1,10-phen,  $\text{Ph}_3\text{PO}$ ) were obtained from Sigma-Aldrich and dried by heating *in vacuo*. The diphosphine dioxides  $\text{dppmO}_2$ ,  $\text{dppeO}_2$  and  $\text{PPO}_2$  were made by dry air oxidation of the corresponding diphosphines in anhydrous  $\text{CH}_2\text{Cl}_2$  solution, catalysed by  $\text{SnI}_4$  [32] and were checked for purity by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy prior to use.

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer in the range 4000–200  $\text{cm}^{-1}$ , with samples prepared as Nujol mulls between two CsI plates.  $^1\text{H}$  NMR spectra were recorded using a Bruker AV 400 spectrometer and referenced to the residual protio-resonance of the solvent.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were obtained from  $\text{CD}_2\text{Cl}_2$  solutions using a Bruker AV 400 spectrometer and referenced external 85%  $\text{H}_3\text{PO}_4$ . Microanalyses on new compounds were undertaken by London Metropolitan University.

### X-ray experimental:

Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum ( $\lambda = 0.71073$ ) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K ( $\text{N}_2$  cryostream). Crystallographic parameters are in the (Table 1). Structure solution and refinement were performed using SHELL(S/L)97, SHELL-2014/7 [33], H atoms were added and refined with a riding model. In  $[\text{TaOCl}_3(\text{PPO}_2)]$  discordant thermal displacement parameters were interpreted as disorder in two of the rings and refined as such using geometrical and thermal parameter restraints and constraints (see SI).

### 3.1 $[\text{TaOCl}_3(1,10\text{-phen})]$

$\text{TaCl}_5$  (0.300 g, 0.837 mmol) was dissolved in acetonitrile (10 mL) at 70 °C. To the clear solution was added  $\text{O}(\text{SiMe}_3)_2$  (0.136 g, 0.837 mmol), in acetonitrile, dropwise and the clear solution was stirred for 1 hour. A solution of 1,10-phen (0.151 g, 0.837 mmol) in acetonitrile (5 mL) was added dropwise and the resulting clear solution was allowed to cool to room temperature, whilst stirring for 1 hour. The reaction solution slowly precipitated a white solid, which was filtered off and dried *in vacuo*. Yield: 0.236 g, 58%. Anal: Required for  $\text{C}_{12}\text{H}_8\text{Cl}_3\text{N}_2\text{OTa}$  (483.37): C, 29.79; H, 1.67; N, 5.79. Found: C, 29.77; H, 1.75; N, 5.71 %.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.12$  (m, [2H]), 8.20 (m, [2H]), 8.73 (m, [H]), 8.82 (m, [H]) 9.57 (d, [H]) 9.93 (d, [H]). IR spectrum (Nujol)/ $\text{cm}^{-1}$ : 322 s, 350 s (Ta-Cl), 941 s (Ta=O). Colourless crystals were obtained by slow evaporation from a dichloromethane solution of the product.

### 3.2 $[\text{TaOCl}_3(2,2'\text{-bipy})]$

$\text{TaCl}_5$  (0.300 g, 0.837 mmol) was dissolved in dichloromethane (10 mL) at 70 °C. To the clear solution was added  $\text{O}(\text{SiMe}_3)_2$  (0.136 g, 0.837 mmol) in dichloromethane (5mL), dropwise and the solution was stirred for 30 min. A solution of 2,2'-bipy (0.151 g, 0.837 mmol) in dichloromethane (5 mL) was added dropwise and the resulting clear solution was allowed to cool to room temperature, whilst stirring for 1 hour. The reaction mixture was then filtered to remove particulates, leaving a colourless solution. The solvent was removed *in*

*vacuo*, yielding a white powder, which was washed with hexane (2 mL), and dried *in vacuo*. Yield: 0.197 g, 51%. Anal: Required for  $C_{10}H_8Cl_3N_2OTa$  (459.37): C, 26.12; H, 1.76; N, 6.10. Found: C, 26.11; H, 1.84; N, 6.03 %.  $^1H$  NMR ( $CD_2Cl_2$ , 298 K):  $\delta$  = 7.75 (m, [H]), 7.85 (m, [H]), 8.21 (m, [2H]), 8.35 (m, [2H]), 8.92 (m, [H]), 8.97 (m, [H]). IR (Nujol/cm $^{-1}$ ): 319 (s), 350 m (Ta-Cl), 938 s (Ta=O).

### 3.3 $[TaOCl_3(OPPh_3)_2] \cdot 2CH_2Cl_2$

$TaCl_5$  (0.300 g, 0.837 mmol) was dissolved in dichloromethane (10 mL) at 70 °C. To the solution was added  $O(SiMe_3)_2$  (0.136 g, 0.837 mmol) in dichloromethane (5 mL), and the solution was stirred for 30 min. A solution of  $OPPh_3$  (0.466 g, 1.68 mmol) in dichloromethane (5 mL) was added dropwise and the reaction mixture was allowed to cool to room temperature. The solution was filtered, the filtrate concentrated, and a white precipitate was formed with the addition of hexane (2 mL); this was then filtered off and dried *in vacuo*. Yield: 0.368 g, 43 %. Anal: Required for  $C_{38}H_{34}Cl_7O_3P_2Ta$  (1029.32): C, 44.32; H, 3.33. Found: C, 44.51; H, 3.21 %.  $^1H$  NMR ( $CD_2Cl_2$ , 298 K):  $\delta$  = 7.34-7.94(m).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ , 298 K):  $\delta$  = 53.4 (s, [P]), 42.5 (s, [P]). IR (Nujol/cm $^{-1}$ ): 302 s, 325 s (Ta-Cl), 930 s (Ta=O), 1076 s (P=O), 1160 s (P=O). Crystals were grown from  $CH_2Cl_2$  by slow evaporation in the glove box.

### 3.4 $[TaOCl_3(dppmO_2)]$

$TaCl_5$  (0.100 g, 0.279 mmol) was dissolved in dichloromethane (10 mL) at 70 °C. To the clear solution was added  $O(SiMe_3)_2$  (0.045 g, 0.279 mmol) in dichloromethane and the solution was stirred for 30 min. A solution of  $dppmO_2$  (0.116 g, 0.279 mmol) in dichloromethane (5 mL) was added dropwise and the reaction mixture was allowed to cool to room temperature. The solution was filtered and the filtrate concentrated *in vacuo*. A white precipitate was formed with the addition of n-hexane (2 mL). This was then filtered off and dried *in vacuo*. Yield: 0.080 g, 40 %. Anal: Required for  $C_{25}H_{22}Cl_3O_3P_2Ta$  (719.41): C, 41.70; H, 3.08. Found: C, 41.85; H, 3.19 %.  $^1H$  NMR ( $CD_2Cl_2$ , 298 K):  $\delta$  = 3.87 (t, [2H],  $PCH_2P$ ), 7.37 (m, [8H], Ph), 7.55 (m, [4H], Ph), 7.66 (m, [8H], Ph).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$  298 K):  $\delta$  = 38.3 (s, [P]), 49.9 (s, [P]). IR (Nujol/cm $^{-1}$ ): 312 s, 334 m (Ta-Cl), 919 s (Ta=O), 1095 m (P=O), 1154 s (P=O).

### 3.5 $[TaOCl_3(dppeO_2)]$

$TaCl_5$  (0.150 g, 0.419 mmol) was dissolved in acetonitrile (10 mL) at 70 °C. To the clear solution was added  $O(SiMe_3)_2$  (0.068 g, 0.419 mmol) in acetonitrile (5 mL), and the solution was stirred for 30 min.. A solution of  $dppeO_2$  (0.180 g, 0.419 mmol) in acetonitrile (5 mL) was added dropwise and the reaction mixture was allowed to cool to room temperature. This was filtered and concentrated *in vacuo*, yielding a white precipitate, which was filtered off and dried *in vacuo*. Yield: 0.237 g, 77 %. Anal: Required for  $C_{26}H_{24}Cl_3O_3P_2Ta$  (733.43): C, 42.54; H, 3.30. Found: C, 42.31; H, 3.16 %.  $^1H$  NMR ( $CD_2Cl_2$ , 298 K):  $\delta$  = 2.78 (m, [2H]  $CH_2CH_2$ ), 2.83 (m, [2H],  $CH_2CH_2$ ), 7.46-7.65 (m, [12H]), 7.91 (m, [8H]).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$  298 K):  $\delta$  = 47.3 (s, [P]), 59.0 (s, [P]). IR (Nujol/cm $^{-1}$ ): 297 s, 337 s (Ta-Cl), 934, (Ta=O), 1075 s (P=O), 1173 s (P=O).

### 3.6 [TaOCl<sub>3</sub>(PPO<sub>2</sub>)]

TaCl<sub>5</sub> (0.150 g, 0.419 mmol) was dissolved in acetonitrile (10 mL) at 70 °C. To the solution was added dropwise O(SiMe<sub>3</sub>)<sub>2</sub> (0.068 g, 0.419 mmol) in acetonitrile (5mL) and the clear solution was stirred for 30 min. A solution of PPO<sub>2</sub> (0.200 g, 0.419 mmol) in acetonitrile (5 mL) was added dropwise and the reaction mixture was allowed to cool to room temperature. The solution was filtered and the filtrate concentrated, yielding a white precipitate. This was filtered off and dried *in vacuo*. Yield: 0.212 g, 65 %. Anal: Required for C<sub>30</sub>H<sub>24</sub>Cl<sub>3</sub>O<sub>3</sub>P<sub>2</sub>Ta (781.43): C, 46.07; H, 3.10. Found: C, 46.19; H, 3.27 %. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 42.4 (s, [P]), 52.5 (s, [P]). IR (Nujol/ cm<sup>-1</sup>): 306 br s, 324 sh (Ta-Cl), 935 s (Ta=O), 1068 s (P=O), 1162 s (P=O). Crystals were grown from CH<sub>2</sub>Cl<sub>2</sub> by slow evaporation.

### 3.7 [TaSCl<sub>3</sub>(1,10-phen)]

TaCl<sub>5</sub> (0.300 g, 0.837 mmol) was dissolved in dichloromethane (20 mL) at 50 °C and the solution cooled to room temperature. To the clear solution was added S(SiMe<sub>3</sub>)<sub>2</sub> (0.149 g, 0.837 mmol) in dichloromethane (5mL). The solution immediately turned bright yellow and then a precipitate formed and the solution turned light brown. The reaction mixture was stirred for 1 h. A solution of 1,10-phen (0.151 g, 0.837 mmol) in dichloromethane (5 mL) was added dropwise to the solution and the reaction mixture was stirred for a further 2 h. No visible change was observed. The mixture was filtered giving a light brown solution that was concentrated *in vacuo* yielding a light brown solid. This was collected by filtration and dried *in vacuo*. Yield: 0.251 g, 60%. Yellow crystals were obtained by layering a dichloromethane solution of the product with n-hexane. Anal: Required for C<sub>12</sub>H<sub>8</sub>Cl<sub>3</sub>N<sub>2</sub>STa (499.35): C, 28.84; H, 1.61; N, 5.61. Found: C, 28.76; H, 1.59; N, 5.51 %. δ = 8.02 (m, [H]), 8.12 (m, [H]), 8.17 (m, [2H]), 8.70 (m, [H]), 8.83 (m, [H]), 9.51 (m, [H]), 10.41 (m, [H]). IR spectrum (Nujol)/cm<sup>-1</sup>: 317 br, s (Ta-Cl), 502 s (Ta=S).

### 3.8 [TaSCl<sub>3</sub>(2,2'-bipy)]

TaCl<sub>5</sub> (0.300 g, 0.837 mmol) was dissolved in dichloromethane (10 mL) at 50 °C and the solution cooled to room temperature. To the clear solution was added S(SiMe<sub>3</sub>)<sub>2</sub> (0.149 mg, 0.837 mmol) in dichloromethane (5 mL). The solution immediately turned bright yellow and then a precipitate formed and the solution turned light brown. A solution of 2,2'-bipy (0.130 g, 0.837 mmol) in dichloromethane (5 mL) was added dropwise whilst stirring for 1 h. The reaction mixture was then filtered, leaving a clear yellow solution. This was concentrated to 5 mL and a yellow precipitate was formed through the addition of n-hexane (3 mL), which was filtered off and dried *in vacuo*. Yield: 0.267 g, 67 %. Anal: Required for C<sub>10</sub>H<sub>8</sub>Cl<sub>3</sub>N<sub>2</sub>STa (475.35): C, 25.24; H, 1.70; N, 5.89. Found: C, 25.43; H, 1.85; N, 5.86 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 7.77 (m, [H]), 7.78 (m, [H]), 8.30-8.34 (m, [2H]), 8.77 (m, [H]), 8.79 (m, [H]), 8.92 (m, [H]), 8.93 (m, [H]). IR (Nujol/cm<sup>-1</sup>): 322 s, 345 s (Ta-Cl), 504 s (Ta=S).

### 3.9 [TaSCl<sub>3</sub>(OPPh<sub>3</sub>)<sub>2</sub>] · 0.5CH<sub>2</sub>Cl<sub>2</sub>

TaCl<sub>5</sub> (0.300 g, 0.837 mmol) was dissolved in dichloromethane (10 mL) at 50 °C and the solution cooled to room temperature. To the clear solution was added S(SiMe<sub>3</sub>)<sub>2</sub> (0.149 g, 0.837 mmol) in dichloromethane (3mL), when the solution immediately turned bright yellow and then a precipitate formed. A solution of OPPh<sub>3</sub> (0.466 g, 1.68 mmol) in dichloromethane (5 mL) was added and the precipitate redissolved. The solution was stirred for 1 h., then filtered, giving a dark orange solution. This was concentrated and a small amount of orange precipitate formed which was removed by filtration. The yellow filtrate was concentrated *in vacuo* to give a yellow powder. Yield: 0.415 g, 54% Anal: Required for C<sub>36</sub>H<sub>30</sub>Cl<sub>3</sub>O<sub>2</sub>P<sub>2</sub>STa·0.5CH<sub>2</sub>Cl<sub>2</sub> (918.41): C, 49.35; H, 3.45. Found: C, 47.72; H, 3.40 %. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 43.9 (s, [P]), 54.4 (s, [P]). IR (Nujol/ cm<sup>-1</sup>): 294 s, 320 s (Ta-Cl), 495 (m, Ta=S), 1064 s (P=O), 1152 s (P=O).

### 3.10 [TaS<sub>2</sub>Cl<sub>3</sub>(dppmO<sub>2</sub>)]

TaCl<sub>5</sub> (0.100 g, 0.279 mmol) was dissolved in dichloromethane (10 mL) at 50 °C and then cooled to room temperature. To the clear solution was added S(SiMe<sub>3</sub>)<sub>2</sub> (0.050 g, 0.279 mmol) in dichloromethane (3 mL). The solution immediately turned bright yellow and then a precipitate formed and the solution turned light brown. A solution of dppmO<sub>2</sub> (0.116 g, 0.279 mmol) in dichloromethane (5 mL) was added dropwise. After 30 min., the reaction mixture was filtered and yellow crystals formed from the resulting yellow filtrate. The solution was concentrated *in vacuo* and then the crystals were collected by filtration and dried *in vacuo*. Yield: 0.125 g, 61 %. Anal: Required for C<sub>25</sub>H<sub>22</sub>Cl<sub>3</sub>O<sub>2</sub>P<sub>2</sub>STa (735.39): C, 40.79; H, 3.02. Found: C, 40.93; H, 3.16%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 3.89 (m, [2H], PCH<sub>2</sub>), 7.40 (m, [8H], Ph), 7.64-7.74 (m, [12H], Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 38.1 (s, [P]), 48.7 (s, [P]). IR (Nujol/cm<sup>-1</sup>): 293 s, 322 s (Ta-Cl), 503 m (Ta=S), 1093 s (P=O), 1145 (P=O).

### 3.11 [TaS<sub>2</sub>Cl<sub>3</sub>(dppeO<sub>2</sub>)]

TaCl<sub>5</sub> (0.150 g, 0.419 mmol) was dissolved in dichloromethane (10 mL) at 50 °C and then cooled to room temperature. To the clear solution was added S(SiMe<sub>3</sub>)<sub>2</sub> (0.075 g, 0.419 mmol) in dichloromethane. A solution of dppeO<sub>2</sub> (0.180 g, 0.419 mmol) in dichloromethane (5 mL) was then added dropwise. After 1 h., the reaction mixture was filtered giving a bright yellow solution. The solution was concentrated *in vacuo* and a yellow precipitate was formed through the addition of hexane (2 mL). This was filtered off and dried *in vacuo*. Yield: 0.240 g, 76 %. Anal: Required for C<sub>26</sub>H<sub>24</sub>Cl<sub>3</sub>O<sub>2</sub>P<sub>2</sub>STa (749.40): C, 41.63; H, 3.23. Found: C, 41.44; H, 3.33 %. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 2.81 (m, [2H], CH<sub>2</sub>CH<sub>2</sub>), 2.95 (m, [2H], CH<sub>2</sub>CH<sub>2</sub>), 7.48-7.73 (m, [12H]), 7.90 (m, [8H], Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub> 298 K): δ = 46.71 (s, [P]), 57.15 (s, [P]). IR (Nujol/cm<sup>-1</sup>): 300 (s), 323 s (Ta-Cl), 497 s (Ta=S), 1057 s br (P=O), 1168 (P=O).

### 3.12 [TaS<sub>2</sub>Cl<sub>3</sub>(PPO<sub>2</sub>)]

TaCl<sub>5</sub> (0.150 g, 0.419 mmol) was dissolved in dichloromethane (10 mL) at 50 °C and then cooled to room temperature. To the solution was added S(SiMe<sub>3</sub>)<sub>2</sub> (0.075 g, 0.419 mmol) in dichloromethane (3mL) forming

a brown precipitate. A solution of  $\text{PPO}_2$  (0.200 g, 0.419 mmol) in dichloromethane (5 mL) was added dropwise and the precipitate immediately dissolved. After 10 min. a straw coloured precipitate formed. The reaction was stirred for 1 h., then filtered, giving a dark yellow solution. This was concentrated and a yellow precipitate formed, which was filtered off and dried *in vacuo*. Yield: 0.220 g, 66 %. Anal: Required for  $\text{C}_{30}\text{H}_{24}\text{Cl}_3\text{O}_2\text{P}_2\text{STA}$  (797.40): C, 45.15; H, 3.03. Found: C, 44.91; H, 3.06 %.  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  = 42.4 (s, [P]), 52.4 (s, [P]). IR (Nujol/ $\text{cm}^{-1}$ ): 304 s, 322 s (Ta-Cl), 494 s (Ta=S), 1066 s (P=O), 1156 s (P=O).

### 3.13 $[\text{TaSCl}_3(\text{MeCN})_2]$

$\text{TaCl}_5$  (0.30 g, 0.837 mmol) was stirred in acetonitrile (5 mL) and then  $\text{S}(\text{Me}_3\text{Si})_2$  (0.149 g, 0.837 mmol) dissolved in acetonitrile added the mixture and stirred for 16 h., when it turned from yellow to orange to a very dark brown. The solution was concentrated, and hexane (1 mL) was added, forming some yellow crystals suitable for X-ray structure determination. The complex has been reported previously [24] and the spectroscopic data are in excellent agreement.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  = 2.02(s). IR (Nujol/ $\text{cm}^{-1}$ ): 349(sh), 329 (Ta-Cl), 515 (Ta=S), 2283, 2314 (C≡N). Lit. [24].  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  = 2.02(s). IR (Nujol/ $\text{cm}^{-1}$ ): 320 br, s (Ta-Cl), 510 (Ta=S),

## 4. Conclusion

Two series of complexes derived from  $\text{TaOCl}_3$  and  $\text{TaSCl}_3$  with neutral N- and O-donor ligands have been synthesised from  $\text{TaCl}_5$  and  $\text{O}(\text{SiMe}_3)_2$  or  $\text{S}(\text{SiMe}_3)_2$ , respectively and characterised spectroscopically and in seven cases by X-ray crystallography. The X-ray structures have confirmed rare octahedral monomer structures derived from  $\text{TaECl}_3$ . The tantalum complexes appear significantly less robust than their niobium analogues [10], being both more difficult to obtain in a pure form and more readily hydrolysed in solution, with loss of the neutral ligand. Although the thiochloride complexes appear less stable than the oxochloride analogues, suggesting  $\text{TaSCl}_3$  is the weaker Lewis acid, comparison of the spectroscopic data on the phosphine oxide complexes, specifically  $\nu(\text{P=O})$  and  $\delta(^{31}\text{P})$ , reveals only small and irregular differences between comparable complexes.

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## Appendix A. Supplementary data

CCDC 1897444 [ $[\text{TaSCl}_3(1,10\text{-phen})]$ ], CCDC 1897445 [ $[\text{TaOCl}_3(1,10\text{-phen})]$ ], CCDC 1897446, [ $[\text{Ta}_2\text{Cl}_6(1,10\text{-phen})_2\text{O}]$ ], CCDC 1897447 [ $[\text{TaSCl}_3(\text{dppeO}_2)]$ ], CCDC 1897448 [ $[\text{TaSCl}_3(\text{MeCN})_2]$ ], CCDC 1897449 [ $[\text{TaOCl}_3(\text{PPO}_2)]$ ], CCDC 1897450 [ $[\text{TaSCl}_3(\text{OPPh}_3)_2]$ ] contain the supplementary crystallographic data for this paper. These data

can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK. The disorder issue in  $[\text{TaOCl}_3(\text{PPO}_2)]$  is discussed further. Other supplementary materials include IR and NMR spectra for the complexes.

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Table 1 Crystallographic data<sup>a</sup>

Compound	[TaS <sub>2</sub> Cl <sub>3</sub> (1,10-phen)]	[TaS <sub>2</sub> Cl <sub>3</sub> (dppeO <sub>2</sub> )]	[TaS <sub>2</sub> Cl <sub>3</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ]
Formula	C <sub>12</sub> H <sub>8</sub> Cl <sub>3</sub> N <sub>2</sub> STa	C <sub>26</sub> H <sub>24</sub> Cl <sub>3</sub> O <sub>2</sub> P <sub>2</sub> STa	C <sub>36</sub> H <sub>30</sub> Cl <sub>3</sub> O <sub>2</sub> P <sub>2</sub> STa
<i>M</i>	499.56	749.75	875.90
Crystal system	monoclinic	monoclinic	monoclinic
Space group (no.)	P2 <sub>1</sub> /c (14)	P2 <sub>1</sub> /c (14)	P2 <sub>1</sub> /n (14)
<i>a</i> /Å	7.3598(2)	15.7268(3)	13.7854(3)
<i>b</i> /Å	19.3732(4)	9.63510(10)	13.0247(5)
<i>c</i> /Å	10.4977(2)	18.0202(3)	19.3056(6)
$\alpha$ /°	90	90	90
$\beta$ /°	107.787(2)	97.254(2)	95.087(2)
$\gamma$ /°	90	90	90
<i>U</i> /Å <sup>3</sup>	1425.24(6)	2708.73(7)	3452.68(19)
<i>Z</i>	4	4	4
$\mu$ (Mo-K $\alpha$ ) /mm <sup>-1</sup>	8.405	4.573	3.601
<i>F</i> (000)	936	1464	1728
Total number reflns	15172	30650	68989
<i>R</i> <sub>int</sub>	0.022	0.023	0.055
Unique reflns	2796	5325	9623
No. of params, restraints	172, 1	316, 1	408, 22
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.015, 0.032	0.030, 0.063	0.044, 0.109
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.017, 0.033	0.035, 0.065	0.097, 0.138

Compound	[TaOCl <sub>3</sub> (1,10-phen)]	[TaOCl <sub>3</sub> (PPO <sub>2</sub> )]	[Ta <sub>2</sub> O(1,10-phen) <sub>2</sub> Cl <sub>4</sub> S <sub>2</sub> ]·2CH <sub>2</sub> Cl <sub>2</sub>
Formula	C <sub>12</sub> H <sub>8</sub> Cl <sub>3</sub> N <sub>2</sub> OTa	C <sub>30</sub> H <sub>24</sub> Cl <sub>3</sub> O <sub>3</sub> P <sub>2</sub> Ta	C <sub>26</sub> H <sub>20</sub> Cl <sub>8</sub> N <sub>4</sub> OS <sub>2</sub> Ta <sub>2</sub>
<i>M</i>	483.50	781.73	1114.08
Crystal system	Monoclinic	orthorhombic	triclinic
Space group (no.)	P2 <sub>1</sub> /c (14)	C222 <sub>1</sub> (20)	P-1 (2)
<i>a</i> /Å	7.75820(12)	10.86425(9)	8.6177(3)
<i>b</i> /Å	17.6961(2)	17.33118(17)	10.3709(3)
<i>c</i> /Å	10.24375(14)	30.4143(2)	11.3478(4)
$\alpha/^\circ$	90	90	101.753(3)
$\beta/^\circ$	106.3180(15)	90	109.543(3)
$\gamma/^\circ$	90	90	111.146(3)
<i>U</i> /Å <sup>3</sup>	1349.71(3)	5726.71(9)	828.48(5)
<i>Z</i>	4	8	1
$\mu$ (Mo-K <sub>α</sub> ) /mm <sup>-1</sup>	8.727	4.262	7.400
<i>F</i> (000)	904	356	526
Total number reflns	34031	15834	17672
<i>R</i> <sub>int</sub>	0.020	0.042	0.044
Unique reflns	3487	9605	4199
No. of params, restraints	172, 0	238, 0	202, 0
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.012, 0.028	0.064, 0.181	0.020, 0.049
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.013, 0.029	0.065, 0.181	0.023, 0.050

Compound	[TaSCl <sub>3</sub> (MeCN) <sub>2</sub> ]
Formula	C <sub>8</sub> H <sub>12</sub> Cl <sub>6</sub> N <sub>4</sub> S <sub>2</sub> Ta <sub>2</sub>
<i>M</i>	401.47
Crystal system	Triclinic
Space group (no.)	P-1 (2)
<i>a</i> /Å	6.0617(3)
<i>b</i> /Å	7.1013(3)
<i>c</i> /Å	12.7630(9)
$\alpha$ /°	80.152(5)
$\beta$ /°	85.422(5)
$\gamma$ /°	80.847(4)
<i>U</i> /Å <sup>3</sup>	533.63(5)
<i>Z</i>	2
$\mu$ (Mo-K <sub>α</sub> ) /mm <sup>-1</sup>	11.189
<i>F</i> (000)	368
Total number reflns	11003
<i>R</i> <sub>int</sub>	0.037
Unique reflns	2756
No. of params, restraints	102, 0
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.030, 0.082
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> (all data)	0.034, 0.084

<sup>a</sup> common data: wavelength (Mo-K<sub>α</sub>) = 0.71073 Å;  $\theta(\max)$  = 27.5°; <sup>b</sup>  $R_1 = \sum |F_O| - |F_C| | / \sum |F_O|$ ;  $wR_2 = [\sum w(F_O^2 - F_C^2)^2 / \sum wF_O^4]^{1/2}$