

## Complexes of $\text{WOCl}_4$ and $\text{WSCl}_4$ with neutral N- and O- donor ligands: synthesis, spectroscopy and structures.

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### Abstract

The complexes  $[\text{WOCl}_4(\text{L})]$  and  $[\text{WSCl}_4(\text{L})]$  ( $\text{L} = \text{OPPh}_3, \text{OPMe}_3, \text{pyridine}, 2,2'\text{-bipyridyl}$ ),  $[\{\text{WOCl}_4\}_2(\mu\text{-L-L})]$  and  $[\{\text{WSCl}_4\}_2(\mu\text{-L-L})]$  ( $\text{L-L} = \text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$  ( $n = 1, 2$ )) have been prepared from  $\text{WOCl}_4$  or  $\text{WSCl}_4$  and the ligands in anhydrous  $\text{CH}_2\text{Cl}_2$  solution, and characterised by microanalysis, IR and NMR ( $^1\text{H}, ^{31}\text{P}\{^1\text{H}\}$ ) spectroscopy. X-Ray crystal structures are reported for  $[\text{WOCl}_4(\text{OPPh}_3)]$ ,  $[\{\text{WOCl}_4\}_2(\mu\text{-Ph}_2\text{P}(\text{O})(\text{CH}_2)\text{P}(\text{O})\text{Ph}_2)]$  and  $[\{\text{WSCl}_4\}_2(\mu\text{-Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)]$ . All, except those of 2,2'-bipyridyl, are six-coordinate with the neutral donor *trans* to  $\text{W}=\text{O}$  or  $\text{W}=\text{S}$ . Spectroscopic data suggest that the  $[\text{WOCl}_4(2,2'\text{-bipy})]$  and  $[\text{WSCl}_4(2,2'\text{-bipy})]$  are seven-coordinate. Comparison of the structural and spectroscopic data for the two series of complexes indicate little difference in Lewis acidity between the two tungsten(VI) moieties. Decomposition of  $[\text{WOCl}_4(\text{OPMe}_3)]$  in solution gave the cyclic trimer  $[\text{W}_3\text{O}_3(\mu\text{-O})_3\text{Cl}_6(\text{OPMe}_3)_3]$ , the structure of which revealed a six-membered  $\text{W}_3\text{O}_3$  ring core with very asymmetric oxido-bridges. The structure of the tungsten(V) complex  $[\text{WOCl}_3(2,2'\text{-bipy})]$  is also reported.

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### 1. Introduction

The oxide and sulfide halides of the early d-block metals in their higher oxidation states are Lewis acidic and form complexes with a variety of neutral ligands [1]. In the solid state tungsten oxide tetrachloride contains square pyramidal  $\text{WOCl}_4$  units linked into chains via asymmetric  $\text{W}=\text{O}\cdots\text{W}$  bridges ( $\text{W}-\text{O} = 1.8, 2.2 \text{ \AA}$ ) [2] whilst in  $\text{WSCl}_4$  the square pyramidal

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core units are weakly chloride-bridged to form dimers  $[\text{SCl}_3\text{W}(\mu\text{-Cl})_2\text{WCl}_3\text{S}]$  [3]. A second polymorph of  $\text{WSCl}_4$  is a tetramer  $[\text{Cl}_4\text{SW}(\mu\text{-Cl})\text{SCl}_2\text{W}(\mu\text{-Cl})_2\text{WCl}_2\text{S}(\mu\text{-Cl})\text{WSCl}_4]$  in which the dimer core is linked by single chlorine bridges to two other  $\text{WSCl}_4$  units [4]. Neutral ligand complexes of  $\text{WOCl}_4$ , were first reported some years ago, obtained by direct reaction of the ligand with  $\text{WOCl}_4$ , by abstraction of oxygen from O-donor ligands, and for some examples by hydrolysis of  $\text{WCl}_6$  complexes [1,5,6]. Typical examples include  $[\text{WOCl}_4(\text{RCN})]$  ( $\text{R} = \text{Me}, \text{Et}, \text{Ph}$ ) [7,8],  $[\text{WOCl}_4(\text{thf})]$  [7,9],  $[\{\text{WOCl}_4\}_2(1,4\text{-dioxane})]$  [7,9],  $[\text{WOCl}_4(\text{OMe}_2)]$  [10],  $[\text{WOCl}_4(\text{Me}_4\text{urea})]$  [11],  $[\text{WOCl}_4\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}]$  [12],  $[\text{WOCl}_4(\text{PR}_3)]$  ( $\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Et}$ ),  $[\text{WOCl}_4(\text{PR}_3)_2]$  ( $\text{R}_3 = \text{Ph}_3, \text{Et}_3$ ) and  $[\text{WOCl}_4(\text{OPPh}_3)_n]$  ( $n = 1$  or  $2$ ) [13]. Other workers have reported that phosphines abstract oxygen from  $\text{WOCl}_4$  to form phosphine oxide complexes of  $\text{W}(\text{IV})$  [14]. Detailed investigation of the reactions of  $\text{WCl}_6$  with ethers, polyethers, ketones and amides have shown that while  $[\text{WOCl}_4(\text{ligand})]$  are formed in some cases, the chemistry depends upon the particular ligand and the reaction conditions, and other products include complexes of fragmented ligands and tungsten(V) complexes containing  $\text{WCl}_5$  or  $\text{WOCl}_3$  [10,11,15,16]. A few complexes of  $\text{WOBBr}_4$  have been described [1,5,6,7], along with the fluoro complexes,  $[\text{WOF}_4(\text{L})]$  ( $\text{L} = \text{MeCN}, \text{OPPh}_3, \text{thf}, \text{dmsO}, \text{py}, \text{PMe}_3$ ) and  $[\text{WOF}_4(\text{diphosphine})]$  (diphosphine =  $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$  or  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ) that were reported very recently [17,18].

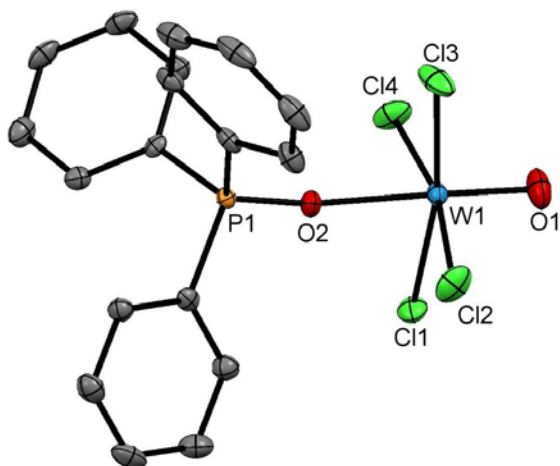
Some corresponding tungsten(VI) sulfide tetrachloride complexes, including  $[\text{WSCl}_4(\text{L})]$  ( $\text{L} = \text{thf}, \text{py}, \text{RCN}$ ),  $[\{\text{WSCl}_4\}_2(\mu\text{-}1,4\text{-dioxane})]$  and  $[(\text{WSCl}_4)_2(\mu\text{-MeS}(\text{CH}_2)_2\text{SMe})]$  have been prepared, but appear to be less stable than those of  $\text{WOCl}_4$  [1,5,19,20]. Possible applications of complexes of metal sulfide halides include their use as reagents for the chemical vapour deposition of the layered metal dichalcogenide thin film materials [21,22]. We report here a comparison of the complexes of  $\text{WOCl}_4$  and  $\text{WSCl}_4$  with a series of neutral N- and O-donor ligands.

## 2. Results and Discussion

### 2.1 Phosphine oxide complexes.

The  $\text{WOCl}_4$  and  $\text{WSCl}_4$  precursors were made by minor modifications of the literature route from  $\text{WCl}_6$  and  $\text{O}(\text{SiMe}_3)_2$  or  $\text{S}(\text{SiMe}_3)_2$ , respectively, in  $\text{CH}_2\text{Cl}_2$  [23]. The complexes were subsequently synthesised by reaction of the appropriate ligand with the  $\text{WECl}_4$  ( $\text{E} = \text{O}$  or  $\text{S}$ ) in anhydrous  $\text{CH}_2\text{Cl}_2$ . Attempts to prepare the complexes by “one pot” reactions, i.e. by adding the  $\text{O}(\text{SiMe}_3)_2$  or  $\text{S}(\text{SiMe}_3)_2$  to  $\text{WCl}_6$  in  $\text{CH}_2\text{Cl}_2$ , followed by addition of the ligand, were less

successful and often gave impure products or mixtures. The complexes are very readily hydrolysed with formation of the robust  $[\text{WO}_2\text{Cl}_2(\text{L})_n]$  (and other products) and use of anhydrous ligands and solvents with Schlenk and glove box techniques is essential to obtain pure complexes. In several cases, adventitious hydrolysis led to the isolation of  $[\text{WO}_2\text{Cl}_2(\text{L})_n]$  complexes, as seen in other  $\text{WOX}_4/\text{WO}_2\text{X}_2$  systems [1,17]. The reaction of  $\text{WOCl}_4$  with one molar equivalent of  $\text{OPPh}_3$  or  $\text{OPMe}_3$  or 0.5 molar equivalents of  $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$  ( $n = 1$ ,  $\text{dppmO}_2$ ;  $n = 2$ ,  $\text{dppeO}_2$ ) in anhydrous  $\text{CH}_2\text{Cl}_2$  solution gave orange or yellow complexes  $[\text{WOCl}_4(\text{OPR}_3)]$  ( $\text{R} = \text{Me}, \text{Ph}$ ) or  $[\{\text{WOCl}_4\}_2(\text{L-L})]$  ( $\text{L-L} = \text{dppmO}_2, \text{dppeO}_2$ ). X-Ray crystal structures were determined for  $[\text{WOCl}_4(\text{OPPh}_3)]$  and  $[\{\text{WOCl}_4\}_2(\text{dppmO}_2)]$ , with crystals grown from  $\text{CH}_2\text{Cl}_2$  solution by slow evaporation. They show distorted octahedral tungsten centres (Figures 1 and 2). Although they are not isomorphous, the structure of  $[\text{WOCl}_4(\text{OPPh}_3)]$  is very similar to that of  $[\text{WOF}_4(\text{OPPh}_3)]$  [17] with the  $\text{OPPh}_3$  *trans* to  $\text{W}=\text{O}$  and the tungsten above the  $\text{WCl}_4$  plane towards the oxido group, as usually found in complexes of this type. The  $d(\text{W}=\text{O})$  are not significantly different, 1.6841(16) Å in the present complex and 1.682(5) Å in the fluoride, although the  $\text{W}-\text{O}_\text{P}$  is shorter in the present complex, 2.1041(14) Å compared to 2.141(4) Å in the fluoride.

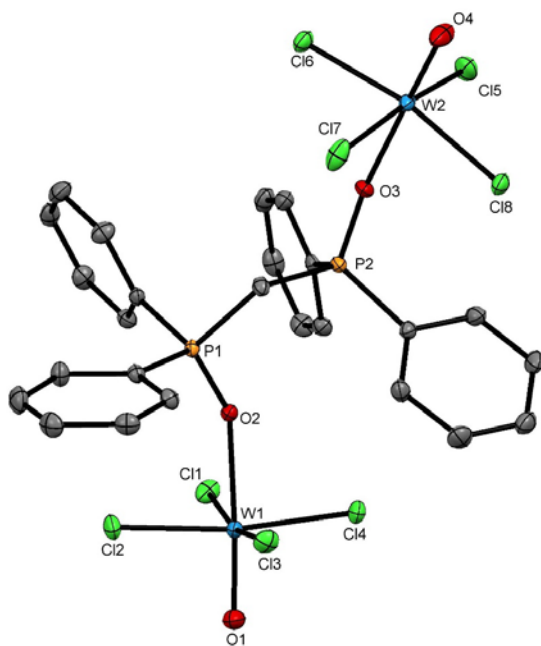


**Figure 1** The structure of  $[\text{WOCl}_4(\text{OPPh}_3)]$  showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) are:  $\text{W1}-\text{Cl1} = 2.3457(5)$ ,  $\text{W1}-\text{Cl2} = 2.3012(6)$ ,  $\text{W1}-\text{Cl3} = 2.2935(6)$ ,  $\text{W1}-\text{Cl4} = 2.3148(6)$ ,  $\text{W1}-\text{O1} = 1.6841(16)$ ,  $\text{W1}-\text{O2} = 2.1041(14)$ ,  $\text{Cl2}-\text{W1}-\text{Cl1} = 87.76(2)$ ,  $\text{Cl3}-\text{W1}-\text{Cl2} = 92.66(2)$ ,  $\text{Cl3}-\text{W1}-\text{Cl4} = 90.98(2)$ ,  $\text{Cl4}-\text{W1}-\text{Cl1} = 86.61(2)$ ,  $\text{O1}-\text{W1}-\text{Cl1} = 94.95(6)$ ,  $\text{O1}-\text{W1}-\text{Cl2} = 94.68(7)$ ,  $\text{O1}-\text{W1}-\text{Cl3} = 95.15(6)$ ,  $\text{O1}-\text{W1}-\text{Cl4} = 96.60(7)$ ,  $\text{O1}-\text{W1}-\text{O2} =$

178.33(8), O2–W1–Cl1 = 84.62(4), O2–W1–Cl2 = 83.69(4), O2–W1–Cl3 = 85.32(4), O2–W1–Cl4 = 85.00(4). The second molecule in the asymmetric unit is very similar.

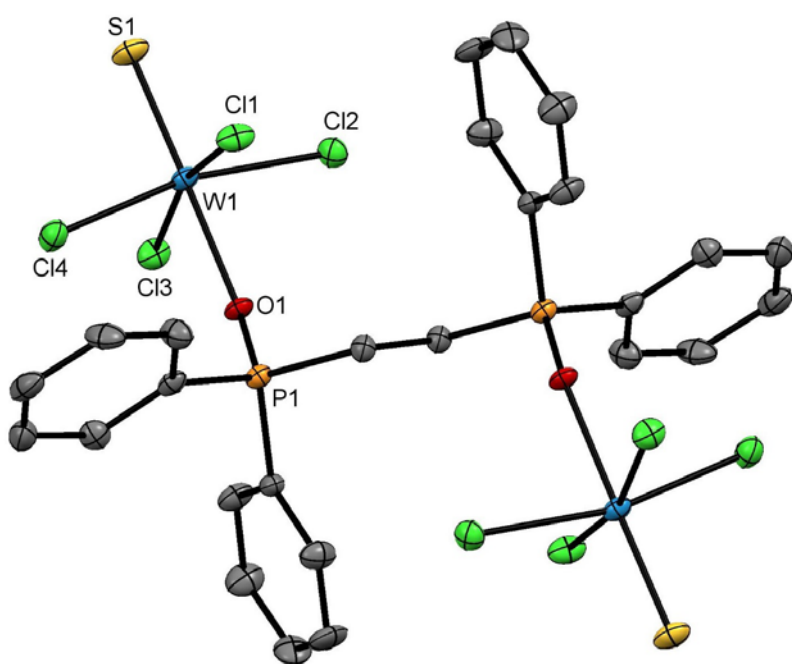
In the dimeric [ $\{\text{WOCl}_4\}_2(\text{dppmO}_2)$ ] (Figure 2) the tungsten environments and the W=O and W–Cl bond lengths are similar to those in the  $\text{OPPh}_3$  complex, while the W–O<sub>P</sub> are slightly longer, and also surprisingly disparate (W1–O2 = 2.1886(12), W2–O3 = 2.1224(13) Å).

The spectroscopic properties of the four complexes are unexceptional. The IR spectra exhibit a single strong  $\nu(\text{W}=\text{O})$  in the range 957–985  $\text{cm}^{-1}$ , broad  $\nu(\text{W}-\text{Cl}) \sim 337 \pm 5 \text{ cm}^{-1}$  and with the  $\nu(\text{P}=\text{O})$  reduced by  $> 60 \text{ cm}^{-1}$  from the values in the parent ligands. The IR spectrum of [ $\text{WOCl}_4(\text{OPPh}_3)$ ] has been reported twice, but with poor agreement [13,24]; our data are in agreement with the report of Behzadi *et al.* [24]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra show substantial high frequency shifts for the phosphoryl group upon coordination and for the complexes of [ $\text{WOCl}_4(\text{OPR}_3)$ ] are very similar to those observed for the corresponding [ $\text{WOF}_4(\text{OPR}_3)$ ] [17]; (the [ $\{\text{WOF}_4\}_2(\text{diphosphine dioxide})$ ] complexes have not been reported). The report [13] that [ $\text{WOCl}_4(\text{OPPh}_3)$ ] exhibits a *low* frequency coordination shift of  $-4 \text{ ppm}$  is clearly in error.



**Figure 2** The structure of  $[\{\text{WOCl}_4\}_2(\text{dppmO}_2)]$  showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl1 = 2.3010(5), W1–Cl4 = 2.3092(5), W1–Cl3 = 2.3190(5), W1–Cl2 = 2.3142(5), W1–O2 = 2.1886(12), W1–O1 = 1.6861(14), W2–Cl6 = 2.3119(5), W2–Cl8 = 2.3175(5), W2–Cl5 = 2.3143(5), W2–Cl7 = 2.3198(5), W2–O3 = 2.1224(13), W2–O4 = 1.6846(14), Cl–W–Cl(cis) 88.129(18)–90.672(19), O<sub>p</sub>–W–Cl = 83.60(4)–87.35(4), O–W–Cl = 93.36(5)–96.94(6), O1–W1–O2 = 176.96(6), O4–W2–O3 = 179.31(7).

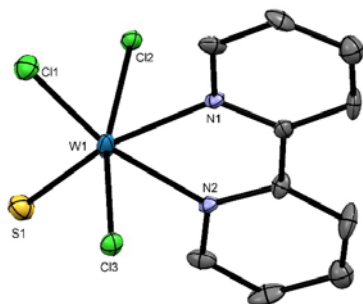
The reaction of  $\text{WScCl}_4$  with  $\text{OPPh}_3$ ,  $\text{OPMe}_3$ ,  $\text{dppmO}_2$  and  $\text{dppeO}_2$  in anhydrous  $\text{CH}_2\text{Cl}_2$  solution, produced brown powders,  $[\text{WScCl}_4(\text{OPR}_3)]$  (R = Me, Ph) and  $[\{\text{WOCl}_4\}_2(\text{L-L})]$  (L-L =  $\text{dppmO}_2$ ,  $\text{dppeO}_2$ ). The X-ray crystal structure of  $[\{\text{WScCl}_4\}_2(\text{dppeO}_2)]$  (Figure 3) shows a centrosymmetric dimer with the tungsten lying out of the  $\text{WCl}_4$  plane towards the sulfide group. The  $\text{W-O}_p = 2.159(2)$  Å, is similar to the average of the corresponding links in  $[\{\text{WOCl}_4\}_2(\text{dppmO}_2)]$  (2.155 (6) Å).



**Figure 3** The structure of  $[\{WScI_4\}_2(dppeO_2)]$  showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl3 = 2.3126(8), W1–Cl4 = 2.3166(8), W1–Cl2 = 2.3484(8), W1–Cl1 = 2.3423(7), W1–S1 = 2.1059(9), W1–O1 = 2.159(2), Cl3–W1–Cl4 = 90.29(3), Cl3–W1–Cl2 = 89.06(3), Cl4–W1–Cl1 = 89.47(3), Cl1–W1–Cl2 = 87.80(3), S1–W1–Cl3 = 97.99(3), S1–W1–Cl4 = 95.99(3), S1–W1–Cl2 = 97.18(3), S1–W1–Cl1 = 96.79(3), S1–W1–O1 = 179.02(6), O1–W1–Cl3 = 82.33(6), O1–W1–Cl4 = 83.08(6), O1–W1–Cl2 = 83.74(6), O1–W1–Cl1 = 82.91(6).

## 2.2 Complexes of N-heterocycles

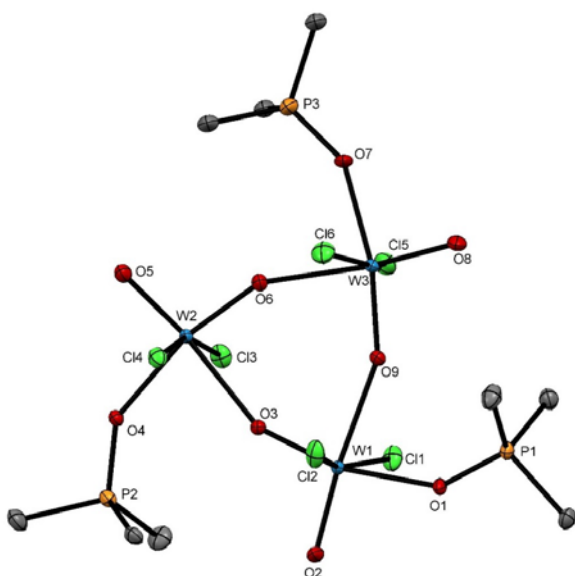
To compare the complexes of the O-donor phosphine oxides with those of N-donor ligands, the complexes with pyridine and 2,2'-bipyridyl were examined. The yellow  $[WOCl_4(py)]$  and brown  $[WScI_4(py)]$  complexes [7,19] were made by reacting the constituents in a 1:1 molar ratio in dry  $CH_2Cl_2$  solution. The products are diamagnetic and the spectroscopic properties are unexceptional. Under reflux or with longer reaction times, reduction to W(V) species occurs [19]. The reaction of  $WOCl_4$  with 2,2'-bipyridyl has been reported before [7,25], the green solid being variously formulated as  $[WOCl_4(2,2'-bipy)]$  or the paramagnetic W(V) complex,  $[WOCl_3(2,2'-bipy)]$ . By conducting the reaction in  $CH_2Cl_2$  solution at room temperature and with a relatively short reaction time, we obtained a green complex  $[WOCl_4(2,2'-bipy)]$ , which was diamagnetic and with the  $^1H$  NMR spectrum showing equivalent pyridyl rings. Repeated attempts to obtain crystals for an X-ray study have been unsuccessful, but it is highly likely that the complex  $[WOCl_4(2,2'-bipy)]$ , contains seven-coordinate tungsten, probably pentagonal bipyramidal with axial O/Cl. Similar seven-coordination is established in  $[WOCl_4\{o-C_6H_4(AsMe_2)_2\}]$  [12] and in several complexes of  $WOF_4$  [17,18,26]. The  $\nu(W=O)$  of  $970\text{ cm}^{-1}$  is lower than the values observed in the six-coordinate complexes, but similar to those in  $[WOCl_4\{o-C_6H_4(AsMe_2)_2\}]$  ( $964\text{ cm}^{-1}$ ) [12],  $[WOF_4(2,2'-bipy)]$  ( $968\text{ cm}^{-1}$ ) or  $[WOF_4(py)_2]$  ( $973\text{ cm}^{-1}$ ) [26], which supports the assignment of the higher coordination number. The new complex  $[WScI_4(2,2'-bipy)]$  was obtained as a red solid, and is spectroscopically very similar. Attempts to grow crystals of the seven-coordinate W(VI) complex from  $CH_2Cl_2$  solution over several days resulted in crystals being obtained of the previously reported six-coordinate  $[WScI_3(2,2'-bipy)]$  [19] (Figure 4).



**Figure 4** The structure of  $[\text{WCl}_3(\text{bipy})]$  showing the atom numbering scheme. Two crystallographically independent molecules were present in the asymmetric unit, one is shown here for clarity. H atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are:  $\text{W1-Cl1} = 2.284(4)$ ,  $\text{W1-Cl2} = 2.356(3)$ ,  $\text{W1-Cl3} = 2.363(3)$ ,  $\text{W1-S1} = 2.206(4)$ ,  $\text{W1-N1} = 2.268(11)$ ,  $\text{W1-N2} = 2.215(11)$ ,  $\text{Cl2-W1-Cl3} = 166.21(11)$ ,  $\text{S1-W1-Cl2} = 96.40(13)$ ,  $\text{S1-W1-N1} = 166.1(3)$ ,  $\text{S1-W1-N2} = 93.3(3)$ ,  $\text{S1-W1-Cl3} = 95.79(13)$ ,  $\text{N1-W1-Cl2} = 83.5(3)$ ,  $\text{N1-W1-Cl3} = 83.1(3)$ ,  $\text{N2-W1-Cl2} = 86.2(3)$ ,  $\text{N2-W1-Cl3} = 86.7(3)$ ,  $\text{N2-W1-N1} = 72.8(4)$ ,  $\text{N2-W1-Cl1} = 91.45(12)$ .

A complex  $[\text{WOCl}_4(1,10\text{-phen})]$  has been claimed [25], but with no reported data. Our attempts using similar reaction conditions to those used for  $[\text{WOCl}_4(2,2'\text{-bipy})]$  produced a mixture of products, one of which was identified by an X-ray structure determination as  $[\text{WO}_2\text{Cl}_2(1,10\text{-phen})] \cdot \text{CH}_2\text{Cl}_2$  by comparison of the unit cell parameters with the literature [27]. It is possible that the more rigid 1,10-phenanthroline is poorly matched to the seven-coordinate tungsten centre. It is notable that attempts to isolate  $[\text{WOF}_4(1,10\text{-phen})]$  from reaction of  $[\text{WOF}_4(\text{MeCN})]$  with 1,10-phen failed, with  $[\text{WO}_2\text{F}_2(1,10\text{-phen})]$  being identified as one major product [17].

As indicated above, decomposition (probably hydrolysis) of some of the  $\text{WOCl}_4$  complexes to  $\text{WO}_2\text{Cl}_2$  species was noted, whereas under more forcing condition (higher temperatures, excess ligand or extended reaction time) reduction to tungsten(V) species sometimes occurs [1,7,19,28]. During attempts to grow crystals from of the  $[\text{WOCl}_4(\text{OPR}_3)]$  by slow evaporation from  $\text{CH}_2\text{Cl}_2$  solutions, a few white crystals were isolated, which proved to be cyclic  $\{\text{W}_n(\mu\text{-O})_n\}$  species. Several batches of white crystals were obtained, most with the crystal quality too poor to merit report, but a few good crystals were obtained on one occasion from the  $\text{OPMe}_3$  system and the structure is shown in Figure 5.



**Figure 5** The structure of  $[\text{W}_3\text{O}_3(\mu\text{-O})_3\text{Cl}_6(\text{OPMe}_3)_3] \cdot 2\text{CH}_2\text{Cl}_2$  showing the atom numbering scheme. The Me groups on P3 show disorder over two sites, only one is shown. H atoms and the lattice  $\text{CH}_2\text{Cl}_2$  molecules are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are:  $\text{W1}-\text{Cl2} = 2.3491(8)$ ,  $\text{W1}-\text{Cl1} = 2.3397(8)$ ,  $\text{W1}-\text{O9} = 2.2211(18)$ ,  $\text{W1}-\text{O1} = 2.0817(18)$ ,  $\text{W1}-\text{O3} = 1.7651(18)$ ,  $\text{W1}-\text{O2} = 1.710(2)$ ,  $\text{W2}-\text{Cl4} = 2.3528(7)$ ,  $\text{W2}-\text{Cl3} = 2.3522(8)$ ,  $\text{W2}-\text{O4} = 2.0715(18)$ ,  $\text{W2}-\text{O6} = 1.7669(19)$ ,  $\text{W2}-\text{O3} = 2.2301(18)$ ,  $\text{W2}-\text{O5} = 1.7167(19)$ ,  $\text{W3}-\text{Cl5} = 2.3522(8)$ ,  $\text{W3}-\text{Cl6} = 2.3549(8)$ ,  $\text{W3}-\text{O9} = 1.7539(18)$ ,  $\text{W3}-\text{O6} = 2.2239(18)$ ,  $\text{W3}-\text{O7} = 2.0681(19)$ ,  $\text{W3}-\text{O8} = 1.715(2)$ ,  $\text{W}-\text{O}_b-\text{W} = 152.97(11)$ ,  $154.90(11)$ ,  $154.52(11)$ ,  $\text{O}_b-\text{W}-\text{O}_b = 86.07(8)$ ,  $85.01(8)$ ,  $86.07(8)$ .

The crystals contain W(VI) with a distorted octahedral coordination environment composed of  $\text{WO}_2\text{Cl}_2(\text{OPMe}_3)$  units linked via very asymmetric oxido-bridges into a six-membered ring. Thus, the  $\text{W}=\text{O}$  group *trans* to the phosphine oxide with  $\text{W}=\text{O} \sim 1.8 \text{ \AA}$  forms a weak bridge to a second tungsten ( $\sim 2.35 \text{ \AA}$ ), distances which may be compared with the terminal  $\text{W}=\text{O}$  of  $\sim 1.7 \text{ \AA}$ . The remaining bond lengths and angles about the tungsten centre are not significantly different to those in the other phosphine oxide complexes. Attempts to prepare a bulk sample of the complex directly by varying the conditions in the  $\text{WOCl}_4$ ,  $\text{O}(\text{SiMe}_3)_2$ ,  $\text{OPMe}_3$  reaction were unsuccessful.



### 3. Conclusions

The synthesis of a series of phosphine oxide and pyridyl ligand complexes of  $\text{WOCl}_4$  and  $\text{WScCl}_4$  has been described. Under the mild synthesis conditions used, reduction to lower oxidation states of tungsten is not significant, although all complexes are hydrolytically unstable, and must be manipulated and stored under strictly anhydrous conditions. Except for the 2,2'-bipy complexes, where the small ring chelate produces seven-coordination, the other complexes are six-coordinate. Comparison of the data from various spectroscopic probes, viz the IR  $\nu(\text{P}=\text{O})$  data, the coordination shift observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the phosphine oxide species, and the  $d(\text{W}-\text{O}_\text{p})$  bond lengths in the structures, show only small differences between the corresponding complexes of  $\text{WOCl}_4$  and  $\text{WScCl}_4$ . The data suggest that  $\text{WScCl}_4$  may be a marginally less strong Lewis acid than  $\text{WOCl}_4$ , but the differences in the various parameters are small. Future work will examine the corresponding complexes of these two hard W(VI) Lewis acids with much softer sulfur or phosphorus donor ligands, to establish if the trends are replicated.

### 4. Experimental

Syntheses were performed by using standard Schlenk and glove-box techniques under a dry  $\text{N}_2$  atmosphere.  $\text{WCl}_6$  (Acros organics),  $\text{O}(\text{SiMe}_3)_2$  and  $\text{S}(\text{SiMe}_3)_2$  (Sigma-Aldrich) were used as received. Solvents were dried by distillation from  $\text{CaH}_2$  ( $\text{CH}_2\text{Cl}_2$ , MeCN) or Na/benzophenone ketyl (toluene, n-hexane). Ligands (2,2'-bipy, 1,10-phen,  $\text{OPPh}_3$ ) were obtained from Sigma-Aldrich and dried by heating *in vacuo* before use. Pyridine was dried over sodium and freshly distilled. The diphosphine dioxides,  $\text{dppmO}_2$  and  $\text{dppeO}_2$ , were made by dry air oxidation of the corresponding diphosphines in  $\text{CH}_2\text{Cl}_2$  solution, catalysed by  $\text{SnI}_4$  [29] and were checked for purity by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. They were also dried by heating *in vacuo*.

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer in the range  $4000\text{--}200\text{ cm}^{-1}$ , with samples prepared as Nujol mulls between 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 or Medac.

#### 3.1 [ $\text{WOCl}_4$ ]

Following the literature method [23], a solution of  $(\text{Me}_3\text{Si})_2\text{O}$  (0.82 g, 5.04 mmol) in dichloromethane (5 mL) was added to a stirred solution of  $\text{WCl}_6$  (2.0 g, 5.04 mmol) in dichloromethane (5 mL). The orange solution was stirred for 1 h and the orange precipitate was filtered off and washed with cold hexane (2 x 1 mL), and dried *in vacuo*. IR spectrum (Nujol,  $\text{cm}^{-1}$ ): 889s W=O, 875s W=O, 381s,br W-Cl, 326s W-Cl.

### 3.2 [ $\text{WSCl}_4$ ]

$\text{WCl}_6$  (2.5 g, 6.3 mmol) in toluene (5 mL) was chilled to  $0^\circ\text{C}$  and hexamethyldisilathane (1.35 g, 6.3 mmol) in toluene (5 mL) was added dropwise over 15 min. The red/brown solution formed was stirred for 30 min. and taken to dryness *in vacuo*, resulting in a brown powder. The brown powder was sublimed *in vacuo* yielding a red powder on the cold finger. Yield: 0.950 g, 42%. IR spectrum (Nujol,  $\text{cm}^{-1}$ ): 556m W=S, 372s W-Cl.

### 3.3 [ $\text{WOCl}_4(\text{OPPh}_3)$ ]

A solution of  $\text{OPPh}_3$  (0.105 g, 0.44 mmol) in dichloromethane (5 mL) was added slowly to a suspension of  $\text{WOCl}_4$  (0.150 g, 0.44 mmol) in dichloromethane (5 mL). The clear orange solution was then stirred for 1 h, concentrated to  $\sim 5$  mL *in vacuo*, filtered, and the resulting orange solid washed with hexane (2 x 1 mL), and dried *in vacuo*. Yield: 0.130 g, 48%. Required for  $\text{C}_{18}\text{H}_{15}\text{Cl}_4\text{O}_2\text{PW}$  (619.9): C, 34.85; H, 2.44. Found: C, 35.01; H, 2.44%. IR spectrum (Nujol,  $\text{cm}^{-1}$ ): 1135s P=O, 981s W=O, 338s W-Cl.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 7.88$  (m, [6H]), 7.70 (m, [3H]), 7.58 (m, [6H]).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = +46.6$  (s).

### 3.4 [ $\text{WOCl}_4(\text{OPMe}_3)$ ]

$\text{OPMe}_3$  (0.059 g, 0.44 mmol) in dichloromethane (5 mL) was slowly added to a suspension of  $\text{WOCl}_4$  (0.150 g, 0.44 mmol) in dichloromethane (5 mL). The yellow solution was then stirred for 1 h, concentrated to half the volume, filtered and the resulting yellow solid washed with hexane (2 x 1 mL), and dried *in vacuo*. Yield: 0.140 g, 73%. Required for  $\text{C}_3\text{H}_9\text{Cl}_4\text{O}_2\text{PW}$  (433.7): C, 8.31; H, 2.09. Found: C, 8.55; H, 2.02%. IR spectrum (Nujol,  $\text{cm}^{-1}$ ): 1089s,br P=O, 957s W=O, 337s W-Cl.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.88$  (d,  $^2J_{\text{HP}} = 13$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = +64.2$  (s).

### 3.5 [ $(\text{WOCl}_4)_2(\text{dppmO}_2)$ ]

Powdered  $\text{dppmO}_2$  (0.120 g, 0.29 mmol) in dichloromethane (5 mL) was added slowly to an orange suspension of  $\text{WOCl}_4$  (0.200 g, 0.58 mmol) in dichloromethane (5 mL). The clear orange/brown solution formed was stirred for 1 h, then concentrated to  $\sim 5$  mL, filtered and the

orange powder washed with hexane (2 x 1 mL) and dried *in vacuo*. Yield: 0.264 g, 83%. Required for C<sub>25</sub>H<sub>22</sub>Cl<sub>8</sub>O<sub>4</sub>P<sub>2</sub>W<sub>2</sub> (1099.7): C, 27.30; H, 2.02. Found: C, 27.42; H, 2.14%. IR spectrum (Nujol, cm<sup>-1</sup>): 1076m,br P=O, 981s W=O, 338s,br W-Cl. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.81(m, [8H]), 7.61 (m, [4H]), 7.43 (m, [8H]), 4.62 (t, [2H]), <sup>2</sup>J<sub>H-P</sub> = 15.5 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = +44.6 (s).

### 3.6 [(WOCl<sub>4</sub>)<sub>2</sub>(dppeO<sub>2</sub>)]

Was made similarly to [(WOCl<sub>4</sub>)<sub>2</sub>(dppmO<sub>2</sub>)] as a yellow powder. Yield 31%. Required for C<sub>26</sub>H<sub>24</sub>Cl<sub>8</sub>O<sub>4</sub>P<sub>2</sub>W<sub>2</sub> (113.7): C, 28.04; H, 2.17. Found: C, 27.96; H, 2.12%. IR spectrum (Nujol, cm<sup>-1</sup>): 1091s P=O, 985s W=O, 337s W-Cl. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.86 (m, [8H]), 7.70 (m, [4H]), 7.59 (m, [8H]), 3.15 (br,s, [4H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ = +53.2 (s).

### 3.7 [WScL<sub>4</sub>(OPPh<sub>3</sub>)]

OPPh<sub>3</sub> (0.078 g, 0.28 mmol) in dichloromethane (2 mL) was slowly added to a red solution of WScL<sub>4</sub> (0.100 g, 0.28 mmol) in dichloromethane (5 mL). The solution was then stirred for 1 h., concentrated *in vacuo* to ~ 4 mL. The brown precipitate was filtered off, washed with hexane (2 x 1 mL) and dried *in vacuo*. Yield: 0.120 g, 69 %. Required for C<sub>18</sub>H<sub>15</sub>Cl<sub>4</sub>OPSW (636.0): C, 33.99; H, 2.38. Found: C, 34.14; H, 2.45%. IR spectrum (Nujol, cm<sup>-1</sup>): 1137m P=O, 329s W-Cl, 310sh W-Cl. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ = 7.81 (m, [6H]), 7.68 (t, [3H]), 7.55 (m, [6H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = +45.9 (s).

### 3.8 [WScL<sub>4</sub>(OPMe<sub>3</sub>)]

A brown powder, made in an analogous way to [WScL<sub>4</sub>(OPPh<sub>3</sub>)]. Yield: 43%. Required for C<sub>3</sub>H<sub>9</sub>Cl<sub>4</sub>OPSW (449.8): C, 8.01; H, 2.00. Found: C, 8.14; H, 2.14%. IR spectrum (Nujol, cm<sup>-1</sup>): 1075s,br P=O, 522m W=S, 322s,br W-Cl. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.81 (d, <sup>2</sup>J<sub>PH</sub> = 13 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = +63.8 (s).

### 3.9 [(WScL<sub>4</sub>)<sub>2</sub>(dppmO<sub>2</sub>)]

Dried dppmO<sub>2</sub> (0.086 g, 0.21 mmol) in dichloromethane (5 mL) was added slowly to a red suspension of WScL<sub>4</sub> (0.150 g, 0.42 mmol) in dichloromethane (5 mL). The resulting brown solution was then stirred for 1 h, concentrated *in vacuo* and the brown solid filtered off and rinsed with hexane (2 x 1 mL), and them dried *in vacuo*. Yield: 0.115 g, 48%. Required for C<sub>25</sub>H<sub>22</sub>Cl<sub>8</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>W<sub>2</sub> (1131.8): C, 26.53; H, 1.96. Found: C, 26.52; H, 2.06%. IR spectrum (Nujol, cm<sup>-1</sup>): 1074m P=O, 530m W=S, 338sh W-Cl, 327s W-Cl. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.76

(br, [8H]), 7.56 (br, [4H]), 7.43 (br, [8H]), 3.82 (br, [2H]).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = +45.4$  (s).

### 3.10 [ $\text{WSCl}_4(\text{dppeO}_2)$ ]

Dried dppeO<sub>2</sub> (0.090 g, 0.21 mmol) in dichloromethane (5 mL) was slowly added to a red suspension of WSCl<sub>4</sub> (0.150 g, 0.42 mmol) in dichloromethane (5 mL), when a brown solution was formed. After 1 h, the solution was concentrated *in vacuo*, the brown solid filtered off, washed with hexane (2 x 1 mL) and dried *in vacuo*. Yield: 0.190 g, 79%. Required for C<sub>26</sub>H<sub>24</sub>Cl<sub>8</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>W<sub>2</sub> (1145.85): C, 27.25; H, 2.11. Found: C, 27.00; H, 2.02%. IR spectrum (Nujol, cm<sup>-1</sup>): 1077s P=O, 536s W=S, 330s W-Cl.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 7.93$  (br, [8H]), 7.66 (br, [4H]), 7.59 (br, [8H]), 2.78 (m, [4H]).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta = +49.2$  (s).

### 3.11 [ $\text{WOCl}_4(\text{C}_5\text{H}_5\text{N})$ ]

Pyridine (0.050 g, 0.58 mmol) in toluene (2 mL) was added to a red suspension of WOCl<sub>4</sub> (0.200 g, 0.58 mmol). The red solution formed was stirred for 1 h and then taken to dryness *in vacuo* to obtain a yellow powder. Yield: 0.120 g, 49%. Required for C<sub>5</sub>H<sub>5</sub>Cl<sub>4</sub>NOW (420.75): C, 14.27; H, 2.20; N, 3.33. Found: C, 14.23; H, 2.15; N, 3.31%. IR spectrum (Nujol, cm<sup>-1</sup>): 987m W=O, 338s W-Cl.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 9.37$  (dd, [2H],  $J_{\text{HH}} = 6.6, 1.5$  Hz), 8.06 (tt, [H],  $J_{\text{HH}} = 7.7, 1.5$  Hz), 7.65 (td, [2H],  $J_{\text{HH}} = 6.6, 1.2$  Hz).

### 3.12 [ $\text{WSCl}_4(\text{C}_5\text{H}_5\text{N})$ ]

Pyridine (0.050 g, 0.58 mmol) in toluene (2 mL) was added to a red solution of WSCl<sub>4</sub> (0.200 g, 0.58 mmol). The brown solution formed was stirred for 1 h, and then taken to dryness *in vacuo* to yield a brown/grey powder. Yield: 0.160 g, 87%. Required for C<sub>5</sub>H<sub>5</sub>Cl<sub>4</sub>NSW (436.8): C, 13.75; H, 1.15; N, 3.21. Found: C: 14.06, H: 1.20, N: 3.29%. IR spectrum (Nujol, cm<sup>-1</sup>): 533s W=S, 334s,br W-Cl.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.78$  (br, [2H]), 8.56 (br, [H]), 8.11 (br, [2H]).

### 3.13 [ $\text{WOCl}_4(2,2'\text{-bipy})$ ]

2,2'-bipy (0.068 g, 0.44 mmol) in dichloromethane (5 mL) was added slowly to an orange suspension of WOCl<sub>4</sub> (150 mg, 0.44 mmol) in dichloromethane (5 mL). The green solution formed was stirred for 1 h at room temperature and then concentrated to ~ 10mL *in vacuo*. The green solid was isolated by filtration, washed with hexane (2 x 1 mL) and dried *in vacuo*. Yield: 0.067 g, 30%. Required for C<sub>10</sub>H<sub>8</sub>Cl<sub>4</sub>N<sub>2</sub>OW (499.85): C, 24.11; H, 1.62; N, 5.63. Found: C, 24.33; H, 1.73; N, 5.84%. IR spectrum (Nujol, cm<sup>-1</sup>): 970s W=O, 329s,br W-Cl.  $^1\text{H}$  NMR

(CDCl<sub>3</sub>):  $\delta$  = 8.99 (d, [2H], J<sub>HH</sub> = 8.1 Hz), 8.85 (d, [2H], J<sub>HH</sub> = 4.4 Hz), 8.22 (t, [2H], J<sub>HH</sub> = 7.8 Hz), 7.66 (t, [2H], J<sub>HH</sub> = 4.0 Hz).

### 3.14 [WScCl<sub>4</sub>(2,2'-bipy)]

2,2'-bipy (0.065 g, 0.42 mmol) in dichloromethane (5 mL) was added slowly to a red suspension of WScCl<sub>4</sub> (0.150 g, 0.42 mmol) in dichloromethane (5 mL). The purple/red solution was stirred for 1 h, concentrated to ~5 mL and the red-pink powder filtered off, washed with hexane (2 x 1 mL), and dried *in vacuo*, yielding a red/pink powder. Yield: 0.165 g, 76%. Required for C<sub>10</sub>H<sub>8</sub>Cl<sub>4</sub>N<sub>2</sub>SW (513.9): C, 23.37; H, 1.57; N, 5.45. Found: C, 23.36; H, 1.59; N, 5.50%. IR spectrum (Nujol, cm<sup>-1</sup>): 521s W=S, 316s W-Cl. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.97 (d, [2H], J<sub>HH</sub> = 8.3 Hz), 8.89 (d, [2H], J<sub>HH</sub> = 5.1 Hz), 8.27 (t, [2H], J<sub>HH</sub> = 7.6 Hz), 7.73 (t, [2H], J<sub>HH</sub> = 7.6 Hz).

### 3.15 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 (N<sub>2</sub> cryostream). Crystallographic parameters are in Table 1. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2014/7 [30] and were mostly straightforward, some minor disorder within one PMe<sub>3</sub> group is noted in the structure of [W<sub>3</sub>O<sub>3</sub>( $\mu$ -O)<sub>3</sub>Cl<sub>6</sub>(OPMe<sub>3</sub>)<sub>3</sub>]·2CH<sub>2</sub>Cl<sub>2</sub>, this was modelled satisfactorily using split C atom site occupancies. H atoms were added and refined with a riding model.

### Conflicts

The authors have no conflicts to declare.

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### Appendix A. Supplementary data

Contain the supplementary crystallographic data for this paper. CCDC numbers are 1882209: [WOCl<sub>4</sub>(OPPh<sub>3</sub>)], 1882210: [{WOCl<sub>4</sub>}<sub>2</sub>(dppmO<sub>2</sub>)], 882211: [{WScCl<sub>4</sub>}<sub>2</sub>(dppeO<sub>2</sub>)], 1882212: [W<sub>3</sub>O<sub>3</sub>( $\mu$ -O)<sub>3</sub>Cl<sub>6</sub>(OPMe<sub>3</sub>)<sub>3</sub>]·2CH<sub>2</sub>Cl<sub>2</sub>, 1883854: [WScCl<sub>3</sub>(bipy)]. 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; Other supplementary materials include IR and NMR spectra for the complexes. Supplementary data associated with this article can be found in the online version, at <http://.....>

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

Compound	[WOCl <sub>4</sub> (OPPh <sub>3</sub> )]	[(WOCl <sub>4</sub> ) <sub>2</sub> (dppmO <sub>2</sub> )]	[(WScCl <sub>4</sub> ) <sub>2</sub> dppeO <sub>2</sub> ]
Formula	C <sub>36</sub> H <sub>30</sub> Cl <sub>8</sub> O <sub>4</sub> P <sub>2</sub> W <sub>2</sub>	C <sub>25</sub> H <sub>22</sub> Cl <sub>8</sub> O <sub>4</sub> P <sub>2</sub> W <sub>2</sub>	C <sub>13</sub> H <sub>12</sub> Cl <sub>4</sub> OPSW
<i>M</i>	1239.84	1099.66	572.91
Crystal system	triclinic	triclinic	triclinic
Space group (no)	P -1 (2)	P -1 (2)	P -1 (2)
<i>a</i> /Å	9.36630(10)	10.3428(2)	9.1134(5)
<i>b</i> /Å	15.4398(2)	11.0799(2)	9.3623(3)
<i>c</i> /Å	16.0484(2)	15.3764(2)	11.7376(4)
$\alpha$ /°	109.4180(10)	81.7770(10)	97.087(3)
$\beta$ /°	97.1570(10)	70.3800(10)	106.333(4)
$\gamma$ /°	105.4190(10)	80.1300(10)	112.441(4)
<i>U</i> /Å <sup>3</sup>	2051.31(5)	1628.27(5)	857.70(7)
<i>Z</i>	2	2	2
$\mu$ (Mo-K $\alpha$ ) /mm <sup>-1</sup>	6.241	7.846	7.565
<i>F</i> (000)	1184	1036	542
Total number reflns	53470	44544	23334
<i>R</i> <sub>int</sub>	0.024	0.028	0.055
Unique reflns	8081	9901	5298
No. of params, restraints	469, 0	370, 0	190, 0
GOF	1.035	1.081	1.083
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.014, 0.033	0.017, 0.036	0.026, 0.063
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> (all data) <sup>b</sup>	0.016, 0.033	0.022, 0.036	0.031, 0.064

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



**Table 1** Continued

Compound	[W <sub>3</sub> O <sub>3</sub> (μ-O) <sub>3</sub> Cl <sub>6</sub> (OPMe <sub>3</sub> ) <sub>3</sub> ]. 2CH <sub>2</sub> Cl <sub>2</sub>	[WScI <sub>3</sub> (2,2'-bipy)]
Formula	C <sub>11</sub> H <sub>31</sub> Cl <sub>10</sub> O <sub>9</sub> P <sub>3</sub> W <sub>3</sub>	C <sub>10</sub> H <sub>8</sub> Cl <sub>3</sub> N <sub>2</sub> SW
<i>M</i>	1306.32	478.44
Crystal system	monoclinic	triclinic
Space group (no.)	P2 <sub>1</sub> /c (14)	P1 (1)
<i>a</i> /Å	19.1399(5)	6.6843(2)
<i>b</i> /Å	11.2360(2)	8.1998(2)
<i>c</i> /Å	18.2845(5)	12.3744(4)
$\alpha$ /°	90	74.743(2)
$\beta$ /°	116.616(3)	89.939(2)
$\gamma$ /°	90	89.988(2)
<i>U</i> /Å <sup>3</sup>	3515.49(17)	654.34(3)
<i>Z</i>	4	2
$\mu$ (Mo-K $\alpha$ ) /mm <sup>-1</sup>	10.724	9.575
<i>F</i> (000)	2424	446
Total number reflns	37791	19122
<i>R</i> <sub>int</sub>	0.030	0.028
Unique reflns	6842	5139
No. of params, restraints	336, 0	278, 3
GOF	1.028	1.131
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.016, 0.030	0.039, 0.070
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> (all data) <sup>b</sup>	0.020, 0.030	0.030, 0.071

**Commented [RG1]:** P1 is VERY rare as space group – are you really sure??