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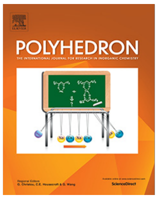

Complexes of $WOCl_4$ and $WSCl_4$ with neutral N- and O-donor ligands: Synthesis, spectroscopy and structures

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ABSTRACT

The complexes [$WOCl_4$(L)] and [$WSCl_4$(L)] (L = $OPPh_3$, $OPMe_3$, pyridine, 2,2′-bipyridyl), [{$WOCl_4$}$_2$(μ-L-L)] and [{$WSCl_4$}$_2$(μ-L-L)] (L-L = $Ph_2P(O)(CH_2)_nP(O)Ph_2$ (n = 1, 2)) have been prepared from $WOCl_4$ or $WSCl_4$ and the ligands in anhydrous CH_2Cl_2 solution, and characterised by microanalysis, IR and NMR (^{1}H, ^{31}P {^{1}H}) spectroscopy. X-Ray crystal structures are reported for [$WOCl_4(OPPh_3)$], [{$WOCl_4$}$_2$(μ-$Ph_2P(O)(CH_2)P(O)Ph_2$)] and [{$WSCl_4$}$_2$(μ-$Ph_2P(O)(CH_2)_2P(O)Ph_2$)]. All, except those of 2,2′-bipyridyl, are six-coordinate with the neutral donor *trans* to W═O or W═S. Spectroscopic data suggest that the [$WOCl_4$(2,2′-bipy)] and [$WSCl_4$(2,2′-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 [$WOCl_4(OPMe_3)$] in solution gave the cyclic trimer [W_3O_3(μ-O)$_3Cl_6(OPMe_3)_3$], the structure of which revealed a six-membered W_3O_3 ring core with very asymmetric oxido-bridges. The structure of the tungsten(V) complex [$WOCl_3$(2,2′-bipy)] is also reported.

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 $WOCl_4$ units linked into chains via asymmetric $W{=}O\cdots W$ bridges (W–O = 1.8, 2.2 Å) [2] whilst in $WSCl_4$ the square pyramidal core units are weakly chloride-bridged to form dimers [SCl_3W(μ-Cl)$_2WCl_3S$] [3]. A second polymorph of $WSCl_4$ is a tetramer [Cl_4SW(μ-Cl)SCl_2W(μ-Cl)$_2WCl_2$-S(μ-Cl)$WSCl_4$] in which the dimer core is linked by single chlorine bridges to two other $WSCl_4$ units [4]. Neutral ligand complexes of $WOCl_4$, were first reported some years ago, obtained by direct reaction of the ligand with $WOCl_4$, by abstraction of oxygen from O-donor ligands, and for some examples by hydrolysis of WCl_6 complexes [1,5,6]. Typical examples include [$WOCl_4$(RCN)] (R = Me, Et, Ph) [7,8], [$WOCl_4$(thf)] [7,9], [{$WOCl_4$}$_2$(1,4-dioxane)] [7,9], [$WOCl_4(OMe_2)$] [10], [$WOCl_4(Me_4urea)$] [11], [$WOCl_4${*o*-$C_6H_4(AsMe_2)_2$}] [12], [$WOCl_4(PR_3)$] (R_3 = Ph_3, Ph_2Et), [$WOCl_4(PR_3)_2$] (R_3 = Ph_3, Et_3) and [$WOCl_4(OPPh_3)_n$] (n = 1 or 2) [13]. Other workers have reported that phosphines abstract oxygen from $WOCl_4$ to form phosphine oxide complexes of W(IV) [14]. Detailed investigation of the reactions of WCl_6 with ethers, polyethers, ketones and amides have shown that while [$WOCl_4$(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 WCl_5 or $WOCl_3$ [10,11,15,16]. A few complexes of $WOBr_4$ have been described [1,5,6,7], along with the fluoro complexes, [WOF_4(L)] (L = MeCN, $OPPh_3$, thf, dmso, py, PMe_3) and [WOF_4(diphosphine)] (diphosphine = *o*-$C_6H_4(PMe_2)_2$ or $Me_2PCH_2CH_2PMe_2$) that were reported very recently [17,18].

Some corresponding tungsten(VI) sulfide tetrachloride complexes, including [$WSCl_4$(L)] (L = thf, py, RCN), [{$WSCl_4$}$_2$(μ-1,4-dioxane)] and [($WSCl_4$)$_2$(μ-$MeS(CH_2)_2SMe$)] have been prepared, but appear to be less stable than those of $WOCl_4$ [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 $WOCl_4$ and $WSCl_4$ with a series of neutral N- and O-donor ligands.

2. Results and discussion

2.1. Phosphine oxide complexes.

The $WOCl_4$ and $WSCl_4$ precursors were made by minor modifications of the literature route from WCl_6 and $O(SiMe_3)_2$ or $S(SiMe_3)_2$, respectively, in CH_2Cl_2 [23]. The complexes were subse-

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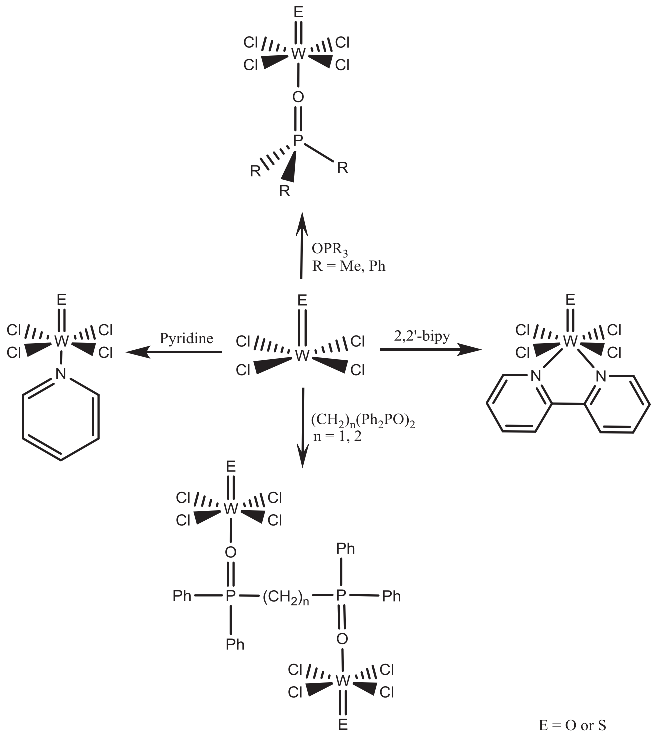
quently synthesised by reaction of the appropriate ligand with the $WECl_4$ (E = O or S) in anhydrous CH_2Cl_2 Attempts to prepare the complexes by "one pot" reactions, i.e. by adding the $O(SiMe_3)_2$ or $S(SiMe_3)_2$ to WCl_6 in CH_2Cl_2, followed by addition of the ligand, were less successful and often gave impure products or mixtures. The complexes are very readily hydrolysed with formation of the robust $[WO_2Cl_2(L)_n]$ (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 $[WO_2Cl_2(L)_n]$ complexes, as seen in other WOX_4/WO_2X_2 systems [1,17]. The reaction of $WOCl_4$ with one molar equivalent of $OPPh_3$ or $OPMe_3$ or 0.5 molar equivalents of $Ph_2P(O)(CH_2)_nP(O)Ph_2$ ($n = 1$, $dppmO_2$; $n = 2$, $dppeO_2$) in anhydrous CH_2Cl_2 solution gave orange or yellow complexes $[WOCl_4(OPR_3)]$ (R = Me, Ph) or $[\{WOCl_4\}_2(L\text{-}L)]$ (L-L = $dppmO_2$, $dppeO_2$) Scheme 1.

X-Ray crystal structures were determined for $[WOCl_4(OPPh_3)]$ and $[\{WOCl_4\}_2(dppmO_2)]$, with crystals grown from CH_2Cl_2 solution by slow evaporation. They show distorted octahedral tungsten centres (Figs. 1 and 2). Although they are not isomorphous, the structure of $[WOCl_4(OPPh_3)]$ is very similar to that of $[WOF_4(OPPh_3)]$ [17] with the $OPPh_3$ *trans* to W=O and the tungsten above the WCl_4 plane towards the oxido group, as usually found in complexes of this type. The d(W=O) are not significantly different, 1.6841(16) Å in the present complex and 1.682(5) Å in the fluoride, although the $W–O_P$ is shorter in the present complex. 2.1041(14) Å compared to 2.141(4) Å in the fluoride.

In the dimeric $[\{WOCl_4\}_2(dppmO_2)]$ (Fig. 2) the tungsten environments and the W=O and W–Cl bond lengths are similar to those in the $OPPh_3$ complex, while the $W–O_P$ 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 ν(W=O) in the range 957–985 cm^{-1}, broad ν(W–Cl) ~ 337 +/– 5 cm^{-1} and with the ν(P=O) reduced by >60 cm^{-1} from the values in the parent



Scheme 1. Synthesis of the complexes of $WECl_4$.

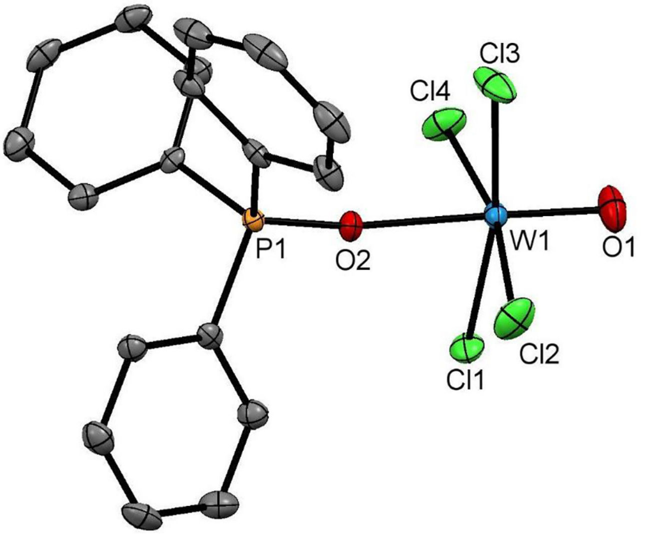


Fig. 1. The structure of $[WOCl_4(OPPh_3)]$ showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl1 = 2.3457(5), W1–Cl2 = 2.3012(6), W1–Cl3 = 2.2935(6), W1–Cl4 = 2.3148(6), W1–O1 = 1.6841(16), W1–O2 = 2.1041(14), Cl2–W1–Cl1 = 87.76(2), Cl3–W1–Cl2 = 92.66(2), Cl3–W1–Cl4 = 90.98(2), Cl4–W1–Cl1 = 86.61(2), O1–W1–Cl1 = 94.95(6), O1–W1–Cl2 = 94.68(7), O1–W1–Cl3 = 95.15(6), O1–W1–Cl4 = 96.60(7), O1–W1–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.

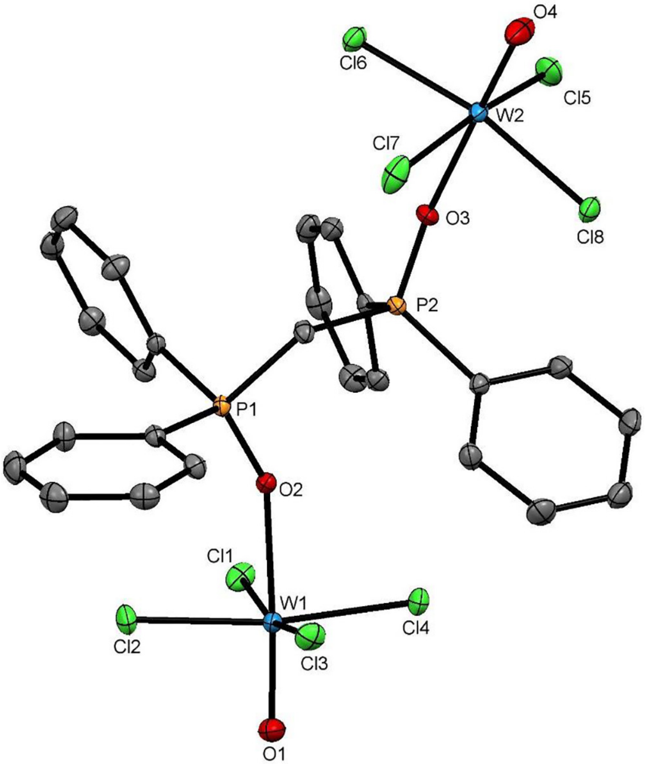


Fig. 2. The structure of $[\{WOCl_4\}_2(dppmO_2)]$ showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl1 = 2.3010(5), W1–Cl4 = 2.3092(5), W1–Cl3 = 2.3190(5), W1–Cl2 = 2.3142(5), W1–O2 = 2.1886(12), W1–O1 = 1.6861(14), W2–Cl6 = 2.3119(5), 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_P–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).

ligands. The IR spectrum of [WOCl$_4$(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}P{^{1}H} NMR spectra show substantial high frequency shifts for the phosphoryl group upon coordination and for the complexes of [WOCl$_4$(OPR$_3$)] are very similar to those observed for the corresponding [WOF$_4$(OPR$_3$)] [17]; (the [{WOF$_4$}$_2$(diphosphine dioxide)] complexes have not been reported). The report [13] that [WOCl$_4$(OPPh$_3$)] exhibits a ***low*** frequency coordination shift of −4 ppm is clearly in error.

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

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 [WSCl$_4$(py)] complexes [7,19] were made by reacting the constituents in a 1:1 molar ratio in dry CH$_2$Cl$_2$ 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$_2$Cl$_2$ 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 ^{1}H 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$_6$H$_4$(AsMe$_2$)$_2$}] [12] and in several complexes of WOF$_4$ [17,18,26]. The ν(W=O) of 970 cm^{-1} is lower than the values observed in the six-coordinate complexes, but similar to those in [WOCl$_4${o-C$_6$H$_4$(AsMe$_2$)$_2$}] (964 cm^{-1}) [12], [WOF$_4$(2,2′-bipy)] (968 cm^{-1}) or [WOF$_4$(py)$_2$] (973 cm^{-1}) [26], which supports the assignment of the higher coordination number, and the proposed geometry in which the oxido-group can occupy an axial position. The new complex [WSCl$_4$(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$_2$Cl$_2$ solution over several days resulted in crystals being obtained of the previously reported six-coordinate [WSCl$_3$(2,2′-bipy)] [19] (Fig. 4).

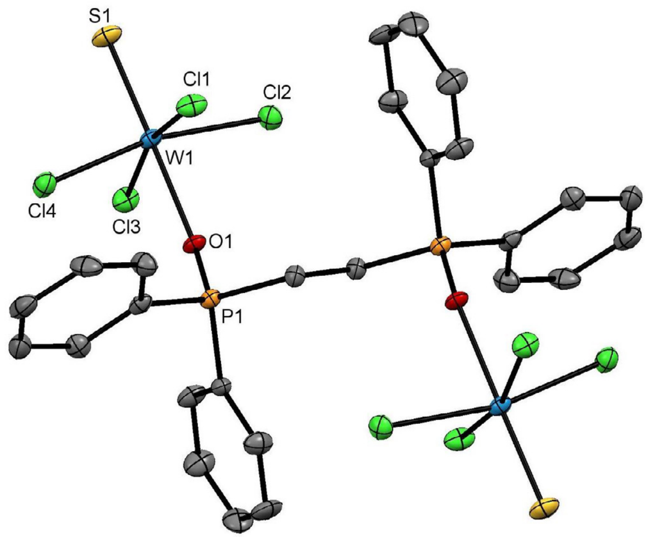


Fig. 3. The structure of [{WSCl$_4$}$_2$(dppeO$_2$)] showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl3 = 2.3126(8), W1–Cl4 = 2.3166(8), W1–Cl2 = 2.3484(8), W1–Cl1 = 2.3423(7), W1–S1 = 2.1059(9), W1–O1 = 2.159(2), Cl3–W1–Cl4 = 90.29(3), 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).

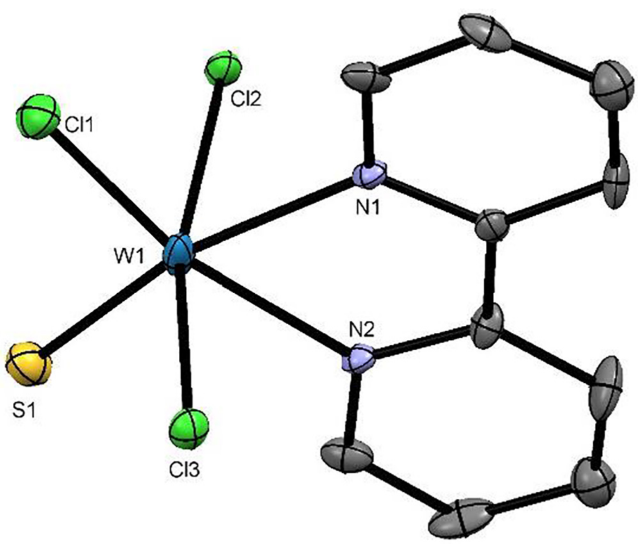


Fig. 4. The structure of [WSCl$_3$(bipy)] showing the atom numbering scheme. Two crystallographically independent molecules were present in the asymmetric unit, one is shown here for clarity. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl1 = 2.284(4), W1–Cl2 = 2.356(3),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

A complex [WOCl$_4$(1,10-phen)] has been claimed [25], but with no reported data. Our attempts using similar reaction conditions to those used for [WOCl$_4$(2,2′-bipy)] produced a mixture of products, one of which was identified by an X-ray structure determination as [WO$_2$Cl$_2$(1,10-phen)]·CH$_2$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 [WOF$_4$(1,10-phen)] from reaction of [WOF$_4$(MeCN)] with 1,10-phen failed, with [WO$_2$F$_2$(1,10-phen)] being identified as one major product [17].

As indicated above, decomposition (probably hydrolysis) of some of the WOCl$_4$ complexes to WO$_2$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 the [WOCl$_4$(OPR$_3$)] by slow evaporation from CH$_2$Cl$_2$ solutions. A few white crystals were isolated, which proved to be cyclic {W$_n$(μ-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 OPMe$_3$ system and the structure is shown in Fig. 5.

The crystals contain W(VI) with a distorted octahedral coordination environment composed of WO$_2$Cl$_2$(OPMe$_3$) units linked

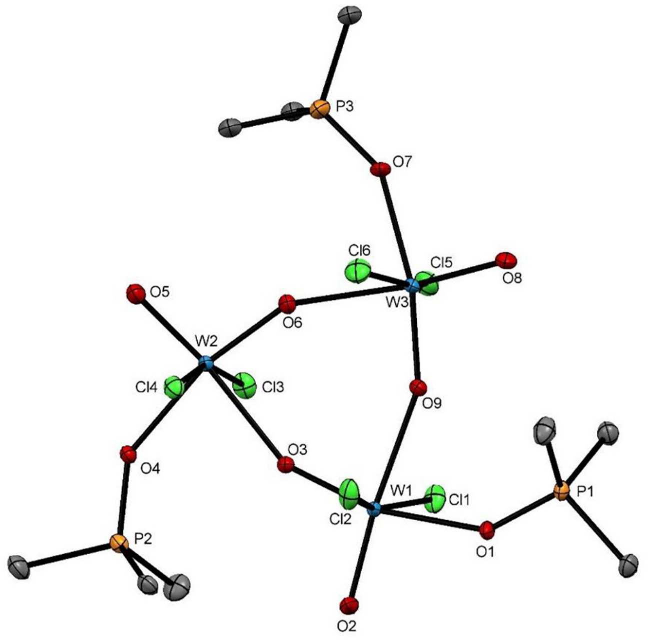


Fig. 5. The structure of $[W_3O_3(\mu\text{-}O)_3Cl_6(OPMe_3)_3]\cdot 2CH_2Cl_2$ showing the atom numbering scheme The Me groups on P3 show disorder over two sites, only one is shown. H atoms and the lattice CH_2Cl_2 molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl2 = 2.3491(8), W1–Cl1 = 2.3397(8), W1–O9 = 2.2211(18), W1–O1 = 2.0817(18), W1–O3 = 1.7651(18), W1–O2 = 1.710(2), W2–Cl4 = 2.3528(7), W2–Cl3 = 2.3522(8), W2–O4 = 2.0715(18), W2–O6 = 1.7669(19), W2–O3 = 2.2301(18), W2– O5 = 1.7167(19), W3–Cl5 = 2.3522(8), W3–Cl6 = 2.3549(8), W3–O9 = 1.7539(18), W3–O6 = 2.2239(18), W3–O7 = 2.0681(19), W3–O8 = 1.715(2), $W\text{–}O_b\text{–}W$ = 152.97(11), 154.90(11), 154.52(11), $O_b\text{–}W\text{–}O_b$ = 86.07(8), 85.01(8), 86.07(8).

via very asymmetric oxido-bridges into a six-membered ring. Thus, the W═O group *trans* to the phosphine oxide with W═O ~ 1.8 Å forms a weak bridge to a second tungsten (~2.22 Å), distances which may be compared with the terminal W═O of ~1.7 Å. 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 $WOCl_4$, $O(SiMe_3)_2$, $OPMe_3$ reaction were unsuccessful.

3. Conclusions

The synthesis of a series of phosphine oxide and pyridyl ligand complexes of $WOCl_4$ and $WSCl_4$ 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 ν(P═O) data, the coordination shifts observed in the $^{31}P\{^1H\}$ NMR spectra of the phosphine oxide species, and the $d(W\text{–}O_p)$ bond lengths in the structures, show only small differences between the corresponding complexes of $WOCl_4$ and $WSCl_4$. The data suggest that $WSCl_4$ may be a marginally less strong Lewis acid than $WOCl_4$, 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 N_2 atmosphere. WCl_6 (Acros organics), $O(SiMe_3)_2$ and $S(SiMe_3)_2$ (Sigma–Aldrich) were used as received. Solvents were dried by distillation from CaH_2 (CH_2Cl_2, MeCN) or Na/benzophenone ketyl (toluene, *n*-hexane). Ligands (2,2′-bipy, 1,10-phen, $OPPh_3$) were obtained from Sigma–Aldrich and dried by heating *in vacuo* before use. Pyridine was dried over sodium and freshly distilled. The diphosphine dioxides, $dppmO_2$ and $dppeO_2$, were made by dry air oxidation of the corresponding diphosphines in CH_2Cl_2 solution, catalysed by SnI_4 [29] and were checked for purity by $^{31}P\{^1H\}$ NMR spectroscopy. They were also dried by heating *in vacuo*.

Infrared spectra were recorded on a Perkin–Elmer Spectrum 100 spectrometer in the range 4000–200 cm^{-1}, with samples prepared as Nujol mulls between CsI plates. ^1H NMR spectra were recorded using a Bruker AV 400 spectrometer and referenced to the residual protio-resonance of the solvent. $^{31}P\{^1H\}$ NMR spectra were obtained from CD_2Cl_2 solutions using a Bruker AV 400 spectrometer and referenced external 85% H_3PO_4. Microanalyses on new compounds were undertaken by London Metropolitan University or Medac.

4.1. [$WOCl_4$]

Following the literature method [23], a solution of $(Me_3Si)_2O$ (0.82 g, 5.04 mmol) in dichloromethane (5 mL) was added to a stirred solution of 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 × 1 mL), and dried *in vacuo*. IR spectrum (Nujol, cm^{-1}): 889sh W═O, 875s W═O, 381s, br W–Cl, 326s W–Cl.

4.2. [$WSCl_4$]

WCl_6 (2.5 g, 6.3 mmol) in toluene (5 mL) was chilled to 0 °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, cm^{-1}): 556 m W═S, 372s W–Cl.

4.3. [$WOCl_4(OPPh_3)$]

A solution of $OPPh_3$ (0.105 g, 0.44 mmol) in dichloromethane (5 mL) was added slowly to a suspension of $WOCl_4$ (0.150 g, 0.44 mmol) in dichloromethane (5 mL). The clear orange solution was then stirred for 1 h, concentrated to ~5 mL *in vacuo*, filtered, and the resulting orange solid washed with hexane (2 × 1 mL), and dried *in vacuo*. Yield: 0.130 g, 48%. Required for $C_{18}H_{15}Cl_4O_2PW$ (619.9): C, 34.85; H, 2.44. Found: C, 35.01; H, 2.44%. IR spectrum (Nujol, cm^{-1}): 1135 s P═O, 981 s W═O, 338s W–Cl. ^1H NMR ($CDCl_3$): δ = 7.88 (m, [6H]), 7.70 (m, [3H]), 7.58 (m, [6H]). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = +46.6 (s).

4.4. [$WOCl_4(OPMe_3)$]

$OPMe_3$ (0.059 g, 0.44 mmol) in dichloromethane (5 mL) was slowly added to a suspension of $WOCl_4$ (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 × 1 mL), and dried *in vacuo*. Yield: 0.140 g, 73%. Required for $C_3H_9Cl_4O_2PW$ (433.7): C, 8.31;

H, 2.09. Found: C, 8.55; H, 2.02%. IR spectrum (Nujol, cm^{-1}): 1089s, br P=O, 957s W=O, 337s W–Cl. ^1H NMR ($CDCl_3$): δ = 1.88 (d, $^2J_{HP}$ = 13 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = +64.2 (s).

4.5. $[(WOCl_4)_2(dppmO_2)]$

Powdered $dppmO_2$ (0.120 g, 0.29 mmol) in dichloromethane (5 mL) was added slowly to an orange suspension of $WOCl_4$ (0.200 g, 0.58 mmol) in dichloromethane (5 mL). The clear orange/brown solution formed was stirred for 1 h, then concentrated to ~5 mL, filtered and the orange powder washed with hexane (2 × 1 mL) and dried *in vacuo*. Yield: 0.264 g, 83%. Required for $C_{25}H_{22}Cl_8O_4P_2W_2$ (1099.7): C, 27.30; H, 2.02. Found: C, 27.42; H, 2.14%. IR spectrum (Nujol, cm^{-1}): 1076m, br P=O, 981s W=O, 338s, br W–Cl. ^1H NMR ($CDCl_3$): δ = 7.81(m, [8H]), 7.61 (m, [4H]), 7.43 (m, [8H]), 4.62 (t, [2H], $^2J_{H\text{-}P}$ = 15.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = +44.6 (s).

4.6. $[(WOCl_4)_2(dppeO_2)]$

Was made similarly to $[(WOCl_4)_2(dppmO_2)]$ as a yellow powder. Yield 31%. Required for $C_{26}H_{24}Cl_8O_4P_2W_2$ (113.7): C, 28.04; H, 2.17. Found: C, 27.96; H, 2.12%. IR spectrum (Nujol, cm^{-1}): 1091s P=O, 985s W=O, 337s W–Cl. ^1H NMR ($CDCl_3$): δ = 7.86 (m, [8H]), 7.70 (m, [4H]), 7.59 (m, [8H]), 3.15 (br, s, [4H]). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = +53.2 (s).

4.7. $[WSCl_4(OPPh_3)]$

$OPPh_3$ (0.078 g, 0.28 mmol) in dichloromethane (2 mL) was slowly added to a red solution of $WSCl_4$ (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 × 1 mL) and dried *in vacuo*. Yield: 0.120 g, 69%. Required for $C_{18}H_{15}Cl_4OPSW$ (636.0): C, 33.99; H, 2.38. Found: C, 34.14; H, 2.45%. IR spectrum (Nujol, cm^{-1}): 1137 m P=O, 329s W–Cl, 310sh W–Cl. ^1H NMR (CD_2Cl_2) δ = 7.81 (m, [6H]), 7.68 (t, [3H]), 7.55 (m, [6H]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = +45.9 (s).

4.8. $[WSCl_4(OPMe_3)]$

A brown powder, made in an analogous way to $[WSCl_4(OPPh_3)]$. Yield: 43%. Required for $C_3H_9Cl_4OPSW$ (449.8): C, 8.01; H, 2.00. Found: C, 8.14; H, 2.14%. IR spectrum (Nujol, cm^{-1}): 1075s, br P=O, 522m W=S, 322 s, br W–Cl. ^1H NMR (CD_2Cl_2): δ = 1.81 (d, $^2J_{PH}$ = 13 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = +63.8 (s).

4.9. $[(WSCl_4)_2(dppmO_2)]$

Dried $dppmO_2$ (0.086 g, 0.21 mmol) in dichloromethane (5 mL) was added slowly to a red suspension of $WSCl_4$ (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 × 1 mL), and them dried *in vacuo*. Yield: 0.115 g, 48%. Required for $C_{25}H_{22}Cl_8O_2P_2S_2W_2$ (1131.8): C, 26.53; H, 1.96. Found: C, 26.52; H, 2.06%. IR spectrum (Nujol, cm^{-1}): 1074m P=O, 530m W=S, 338sh W–Cl, 327s W–Cl. ^1H NMR (CD_2Cl_2): δ = 7.76 (br, [8H]), 7.56 (br, [4H]), 7.43 (br, [8H]), 3.82 (br, [2H]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = +45.4 (s).

4.10. $[(WSCl_4)_2(dppeO_2)]$

Dried $dppeO_2$ (0.090 g, 0.21 mmol) in dichloromethane (5 mL) was slowly added to a red suspension of $WSCl_4$ (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 × 1 mL) and dried *in vacuo*. Yield: 0.190 g, 79%. Required for $C_{26}H_{24}Cl_8O_2P_2S_2W_2$ (1145.85): C, 27.25; H, 2.11. Found: C, 27.00; H, 2.02%. IR spectrum (Nujol, cm^{-1}): 1077s P=O, 536s W=S, 330s W–Cl. ^1H NMR (CD_2Cl_2): δ = 7.93 (br, [8H]), 7.66 (br, [4H]), 7.59 (br, [8H]), 2.78 (m, [4H]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = +49.2 (s).

4.11. $[WOCl_4(C_5H_5N)]$

Pyridine (0.050 g, 0.58 mmol) in toluene (2 mL) was added to a red suspension of $WOCl_4$ (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 $C_5H_5Cl_4NOW$ (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^{-1}): 987m W=O, 338s W–Cl. ^1H NMR (CD_2Cl_2): δ = 9.37 (dd, [2H], J_{HH} = 6.6, 1.5 Hz), 8.06 (tt, [H], J_{HH} = 7.7, 1.5 Hz), 7.65 (td, [2H], J_{HH} = 6.6, 1.2 Hz).

4.12. $[WSCl_4(C_5H_5N)]$

Pyridine (0.050 g, 0.58 mmol) in toluene (2 mL) was added to a red solution of $WSCl_4$ (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 $C_5H_5Cl_4NSW$ (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^{-1}): 533s W=S, 334s, br W–Cl. ^1H NMR (CD_2Cl_2): δ = 8.78 (br, [2H]), 8.56 (br, [H]), 8.11 (br, [2H]).

4.13. $[WOCl_4(2,2'\text{-bipy})]$

2,2′-Bipy (0.068 g, 0.44 mmol) in dichloromethane (5 mL) was added slowly to an orange suspension of $WOCl_4$ (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 ~10 mL *in vacuo*. The green solid was isolated by filtration, washed with hexane (2 × 1 mL) and dried *in vacuo*. Yield: 0.067 g, 30%. Required for $C_{10}H_8Cl_4N_2OW$ (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^{-1}): 970s W=O, 329s, br W–Cl. ^1H NMR ($CDCl_3$): δ = 8.99 (d, [2H], J_{HH} = 8.1 Hz), 8.85 (d, [2H], J_{HH} = 4.4 Hz), 8.22 (t, [2H], J_{HH} = 7.8 Hz), 7.66 (t, [2H], J_{HH} = 4.0 Hz).

4.14. $[WSCl_4(2,2'\text{-bipy})]$

2,2′-Bipy (0.065 g, 0.42 mmol) in dichloromethane (5 mL) was added slowly to a red suspension of $WSCl_4$ (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 × 1 mL), and dried *in vacuo*, yielding a red/pink powder. Yield: 0.165 g, 76%. Required for $C_{10}H_8Cl_4N_2SW$ (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^{-1}): 521s W=S, 316s W–Cl. ^1H NMR (CD_2Cl_2): δ = 8.97 (d, [2H], J_{HH} = 8.3 Hz), 8.89 (d, [2H], J_{HH} = 5.1 Hz), 8.27 (t, [2H], J_{HH} = 7.6 Hz), 7.73 (t, [2H], J_{HH} = 7.6 Hz).

4.15. 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 (λ = 0.71073) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K (N_2 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 $OPMe_3$ group is noted in the structure of $[W_3O_3(\mu\text{-}O)_3Cl_6($-

Table 1
Crystallographic data.[a]

Compound	$[WOCl_4(OPPh_3)]$	$[(WOCl_4)_2(dppmO_2)]$	$[(WSCl_4)_2dppeO_2]$
Formula	$C_{36}H_{30}Cl_8O_4P_2W_2$	$C_{25}H_{22}Cl_8O_4P_2W_2$	$C_{13}H_{12}Cl_4OPSW$
M	1239.84	1099.66	572.91
Crystal system	triclinic	triclinic	triclinic
Space group (no)	*P* −1 (2)	*P* −1 (2)	*P* −1 (2)
a (Å)	9.36630(10)	10.3428(2)	9.1134(5)
b (Å)	15.4398(2)	11.0799(2)	9.3623(3)
c (Å)	16.0484(2)	15.3764(2)	11.7376(4)
α (°)	109.4180(10)	81.7770(10)	97.087(3)
β (°)	97.1570(10)	70.3800(10)	106.333(4)
γ (°)	105.4190(10)	80.1300(10)	112.441(4)
U $(Å)^3$	2051.31(5)	1628.27(5)	857.70(7)
Z	2	2	2
μ (Mo Kα) / mm^{-1}	6.241	7.846	7.565
F(0 0 0)	1184	1036	542
Total number reflns	53 470	44 544	23 334
R_{int}	0.024	0.028	0.055
Unique reflections	8081	9901	5298
No. of parameterss, restraints	190, 0	469, 0	370, 0
Goodness-of-fit (GOF) on F^2	1.035	1.081	1.083
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.014, 0.033	0.017, 0.036	0.026, 0.063
R_1, wR_2 (all data)[b]	0.016, 0.033	0.022, 0.036	0.031, 0.064

Compound	$[W_3O_3(\mu\text{-}O)_3Cl_6(OPMe_3)_3]\cdot 2CH_2Cl_2$	$[WSCl_3(2,2'\text{-}bipy)]$
Formula	$C_{11}H_{31}Cl_{10}O_9P_3W_3$	$C_{10}H_8Cl_3N_2SW$
M	1306.32	478.44
Crystal system	monoclinic	triclinic
Space group (no.)	$P2_1/c$ (14)	*P*1 (1)
a (Å)	19.1399(5)	6.6843(2)
b (Å)	11.2360(2)	8.1998(2)
c (Å)	18.2845(5)	12.3744(4)
α (°)	90	74.743(2)
β (°)	116.616(3)	89.939(2)
γ (°)	90	89.988(2)
U $(Å)^3$	3515.49(17)	654.34(3)
Z	4	2
μ (Mo Kα)/mm^{-1}	10.724	9.575
F(0 0 0)	2424	446
Total number reflections	37 791	19 122
R_{int}	0.030	0.028
Unique reflections	6842	5139
No. of parameters, restraints	336, 0	278, 3
Goodness-of-fit (GOF) on F^2	1.028	1.131
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.016, 0.030	0.039, 0.070
R_1, wR_2 (all data)[b]	0.020, 0.030	0.030, 0.071

[a] Common data: wavelength (Mo K_α) = 0.71073 Å; θ(max) = 27.5°.
[b] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma wFo^4]^{1/2}$.

$OPMe_3)_3]\cdot 2CH_2Cl_2$, this was modelled satisfactorily using split C atom site occupancies. H atoms were added and refined with a riding model.

Conflicts of interest

The authors have no conflicts to declare.

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Appendix A. Supplementary data

CCDC 1882209: $[WOCl_4(OPPh_3)]$, 1882210: $[\{WOCl_4\}_2(\text{-}dppmO_2)]$, 882211: $[\{WSCl_4\}_2(dppeO_2)]$, 1882212: $[W_3O_3(\mu\text{-}O)_3\text{-}Cl_6(OPMe_3)_3]\cdot 2CH_2Cl_2$, 1883854: $[WSCl_3(bipy)]$ contains the supplementary crystallographic data. 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; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2019.01.044.

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