Pentagonal bipyramidal complexes of $WOCl_4$ and $WSCl_4$ with diphosphine and diarsine ligands.

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Abstract

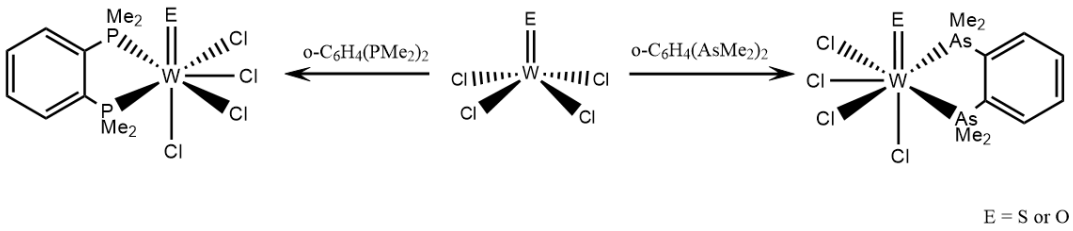
The seven-coordinate tungsten(VI) complexes, $[WOCl_4\{o\text{-}C_6H_4(EMe_2)_2\}]$ and $[WSCl_4\{o\text{-}C_6H_4(EMe_2)_2\}]$ (E = P, As), have been prepared by reaction of $WOCl_4$ or $WSCl_4$ with the ligands in anhydrous CH_2Cl_2 or toluene, and fully characterised by microanalysis, IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The X-ray crystal structures of $[WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ and $[WSCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ have been determined and revealed pentagonal bipyramidal geometries with axial O/Cl or S/Cl. Attempts to isolate similar complexes with *o*-$C_6H_4(PPh_2)_2$, PMe_3 or $AsEt_3$ were unsuccessful, due to facile reduction of the tungsten centre. Several reduction products have also been identified crystallographically, including the tungsten(V) species, $[WOCl_3\{o\text{-}C_6H_4(PMe_2)_2\}]$, $WOCl_3\{o\text{-}C_6H_4(PMe_2)(P(O)Me_2)\}]$ and $[WCl_4\{o\text{-}C_6H_4(PPh_2)_2\}_2][WCl_6]$.

1. Introduction

Tungsten(VI) oxide tetrachloride, $WOCl_4$, and tungsten(VI) sulfide tetrachloride, $WSCl_4$, are moderate Lewis acids [1-3] and form, in addition to the corresponding anions $[WOCl_5]^-$ and $[WSCl_5]^-$ [4,5], complexes with a range of hard, neutral N- and O-donor ligands. These include $[WOCl_4(RCN)]$ (R = Me, Et, Ph) [6,7], $[WOCl_4(thf)]$ [6,8], $[WOCl_4(Me_4urea)]$ [9], $[WOCl_4(OPPh_3)_n]$ (n = 1 or 2) [10], $[WSCl_4(L)]$ (L = thf, py, RCN) and $[\{WSCl_4\}_2(\mu\text{-}1,4\text{-dioxane})]$ [1,2,11]. The reactions of WCl_6 with ethers, polyethers or ketones produce $[WOCl_4(ligand)]$ complexes in some systems; the reactions involving oxygen abstraction from the ligand, but the chemistry depends upon the particular ligand and the reaction conditions, and other products include complexes of fragmented ligands and tungsten(V) species containing WCl_5 or $WOCl_3$. [12,13,14]. We recently reported a detailed (re)investigation of

W(VI) complexes of the types $[WOCl_4(L)]$ and $[WSCl_4(L)]$ (L = $OPPh_3$, $OPMe_3$, pyridine), $[\{WOCl_4\}_2(\mu\text{-L-L})]$ and $[\{WSCl_4\}_2(\mu\text{-L-L})]$ (L-L = $Ph_2P(O)(CH_2)_nP(O)Ph_2$, n = 1, 2), all of which were six-coordinate [15]. The 2,2'-bipyridyl complexes, $[WOCl_4(2,2'\text{-bipy})]$ and $[WSCl_4(2,2'\text{-bipy})]$ are probably seven-coordinate, but confirmation of this by X-ray crystallographic analysis failed despite many attempts to grow suitable crystals [15]. Complexes with neutral sulfur donor ligands have also been described [11,16], but examples with phosphorus or arsenic ligands are particularly rare [10,17,18], and the only structurally characterised example appears to be the seven-coordinate $[WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ [17]. We recently prepared two pentagonal bipyramidal complexes, $[WOF_4(\text{diphosphine})]$ (diphosphine = $Me_2PCH_2CH_2PMe_2$ or $o\text{-}C_6H_4(PMe_2)_2$) by reaction of $[WOF_4(MeCN)_2]$ with the ligands, but found that the analogous complex with $o\text{-}C_6H_4(AsMe_2)_2$ did not form [19].

Here we report the synthesis, spectroscopic and structural characterization of complexes of $WOCl_4$ and $WSCl_4$ with $o\text{-}C_6H_4(PMe_2)_2$ and $o\text{-}C_6H_4(AsMe_2)_2$, together with the identification of several reduction products.



Scheme 1: Synthesis of $[WECl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ and $[WECl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$, E = O or S.

2. Experimental

Syntheses were performed by using standard Schlenk and glove-box techniques under a dry N_2 atmosphere. WCl_6 (Acros organics), $O(SiMe_3)_2$, $S(SiMe_3)_2$ and $o\text{-}C_6H_4(PPh_2)_2$ (Sigma-Aldrich) were used as received. Solvents were dried by distillation from CaH_2 (CH_2Cl_2, MeCN) or Na/benzophenone ketyl (toluene). $WOCl_4$ and $WSCl_4$ [15,20], $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)_2$ were made by literature routes [21,22].

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. $^{31}P\{^{1}H\}$ NMR spectra were obtained from CH_2Cl_2/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.

2.1 [$WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}$]

o-phenylenebis(dimethylarsine) (0.083 g, 0.29 mmol) in dichloromethane (2 mL) was slowly added to $WOCl_4$ (0.100 g, 0.29 mmol) in dichloromethane (4 mL). The solution was allowed to stir for 1 hour, concentrated *in vacuo* to 2 mL, and the resulting green precipitate was filtered off and dried *in vacuo*. Yield: 0.090 g, 49%. Required for $C_{10}H_{16}As_2Cl_4OW$ (627.73): C: 19.13, H: 2.57. Found: C: 19.02, H: 2.46%. IR spectrum (Nujol/ cm^{-1}): 955s W=O, 332s, 304s W-Cl. ^{1}H NMR (CD_2Cl_2): δ = 7.86 (m, [2H]), 7.74 (m, [2H]), 2.51 (s, [6H]), 2.42 (s, [6H]).

2.2 [$WSCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}$]

o-phenylenebis(dimethylarsine) (0.080 g, 0.28 mmol) in toluene (2 mL) was slowly added to a solution of $WSCl_4$ (0.100 g, 0.28 mmol) in toluene (4 mL). The solution was allowed to stir for 1 hour, concentrated *in vacuo* to 2 mL, after which the red/brown precipitate was filtered off and dried *in vacuo.* Yield: 0.130 g, 70%. Required for $C_{10}H_{16}As_2Cl_4SW$ (643.79): C: 18.66, H: 2.50. Found: C: 18.52, H: 2.47%. IR spectrum (Nujol/ cm^{-1}): 548s W=S, 333s, 307s W-Cl. ^{1}H NMR (CD_2Cl_2): δ = 7.71 (m, [4H]), 2.73 (s, [6H]), 2.39 (s, [6H]).

2.3 [$WOCl_4\{o\text{-}C_6H_4(PMe_2)_2\}$]

o-phenylenebis(dimethylphosphine) (0.087 g, 0.44 mmol) in dichloromethane (2 mL) was slowly added to a solution of $WOCl_4$ (0.15 g, 0.42 mmol) in dichloromethane (4 mL). The solution was allowed to stir for 1 hour, concentrated *in vacuo* to 2 mL, the green precipitate was filtered off and dried *in vacuo* Yield: 0.17 g, 74%. Required for $C_{10}H_{16}Cl_4OP_2W$ (539.8): C: 22.25, H: 2.99. Found: C: 22.28, H: 3.17%. IR spectrum (Nujol/ cm^{-1}): 954s W=O, 319s, 302s W-Cl.^{1}H NMR (CD_2Cl_2): δ = 7.95 – 7.51 (m, [4H]), 2.61 (t, [6H] $^{2}J+^{5}J_{HH}$ = 8Hz), 2.53 (m, [6H] $^{2}J+^{5}J_{HH}$ = 8Hz). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): +74.8 (s, $^{1}J_{WP}$ = 173 Hz).

2.4 [$WSCl_4\{o\text{-}C_6H_4(PMe_2)_2\}$]

o-phenylenebis(dimethylphosphine) (0.83 g, 0.42 mmol) in toluene (2 mL) was slowly added to a solution of $WSCl_4$ (0.15 g, 0.42 mmol) in toluene (4 mL). The solution was allowed to stir for 1 hour, concentrated *in vacuo* to 2 mL, the red/brown precipitate was filtered and dried *in vacuo.* Yield: 0.17 g,

71%. Required for $C_{10}H_{16}Cl_4P_2SW$ (555.9): C: 21.61, H: 2.90. Found: C: 21.72, H: 2.99%. IR spectrum (Nujol/ cm^{-1}): 561s W=S, 313s, 297s W-Cl. ^1H NMR (CD_2Cl_2): δ = 8.92 (br [2H]), 8.72 (br [2H] 2.62 (m, [6H]), 2. 54 (m, [6H]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): +74.8 (s, $^1J_{WP}$ = 168 Hz).

2.5 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 [23], and were mostly straightforward, although several of the structures showed significant residual electron peaks near to the tungsten, which are due to absorption correction problems. Several of the structures showed O/Cl or S/Cl of the axial ligands and these were modelled using split atom sites and the occupancies modeled as free and then fixed using EADP and refined.

Table 1 Crystallographic data[a]

Compound	$[WSCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$	$[WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$	$[WOCl_3\{o\text{-}C_6H_4(PMe_2)_2\}]$
Formula	$C_{10}H_{16}Cl_4P_2SW$	$C_{10}H_{16}As_2Cl_4OW$	$C_{10}H_{16}Cl_3OP_2W$
M	555.88	627.72	504.37
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group (no)	Pbca (61)	Pbca (61)	$P2_12_12_1$ (19)
a /Å	13.1473(4)	15.6918(3)	16.4487(3)
b /Å	15.8140(5)	13.7435(2)	13.9540(2)
c /Å	16.1052(6)	15.9443(3)	14.4660(2)
α /°	90	90	90
β /°	90	90	90
γ /°	90	90	90
U /Å^3	3348.46(19)	3438.55(10)	3320.31(9)
Z	8	8	8
μ(Mo-K_α) /mm^{-1}	7.834	11.146	7.617
F(000)	2112	2336	1912
Total number reflns	27246	70940	37813
R_{int}	0.056	0.074	0.069

Unique reflns	5218	5431	9786
No. of params, restraints	165, 18	194, 132	325, 20
GOF	1.091	1.275	1.050
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.058, 0.107	0.051, 0.079	0.066, 0.151
R_1, wR_2 (all data)[b]	0.084, 0.114	0.060, 0.082	0.081, 0.161

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

Table 1 cont.

Compound	$[WOCl_3\{o\text{-}C_6H_4(PMe_2)(P(O)Me_2)\}]\cdot 0.5CH_2Cl_2$	$[WCl_4\{o\text{-}C_6H_4(PPh_2)_2\}_2][WCl_6]\cdot 2.5C_7H_8$
Formula	$C_{10.50}H_{17}Cl_4O_2P_2W$	$C_{77.50}H_{68}Cl_{10}P_4W_2$
M	562.83	1845.40
Crystal system	orthorhombic	Monoclinic
Space group (no)	Pbcn (60)	$P2_1/c$ (14)
a /Å	15.5425(2)	12.68450(10)
b /Å	17.6076(2)	22.6209(2)
c /Å	13.1080(2)	26.0710(2)
α /°	90	90
β /°	90	100.0200(10)
γ /°	90	90
U /Å^3	3587.22(8)	7366.57(11)
Z	8	4
μ(Mo-K_α) /mm^{-1}	7.210	3.614
F(000)	2144	3644
Total number reflns	38057	203082
R_{int}	0.057	0.027
Unique reflns	5453	23949
No. of params, restraints	181, 0	877, 122
GOF	1.110	1.027
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.057, 0.115	0.020, 0.037
R_1, wR_2 (all data)[b]	0.0622, 0.1175	0.0250, 0.0381

3. Results and Discussion

3.1 [$WOCl_4${o-$C_6H_4(EMe_2)_2$}] and [$WSCl_4${o-$C_6H_4(EMe_2)_2$}] (E = P, As).

The reaction of $WOCl_4$ with o-$C_6H_4(EMe_2)_2$ in a 1:1 molar ratio in anhydrous CH_2Cl_2 produced good yields of green [$WOCl_4${o-$C_6H_4(EMe_2)_2$}]. The corresponding reactions using $WSCl_4$ afforded red-brown [$WSCl_4${o-$C_6H_4(EMe_2)_2$}]. The solid complexes are stable for many weeks in the glove box, but have more limited solution stability, especially those of the thiochloride, and are readily hydrolysed in air or by wet solvents. Small amounts of crystals of tungsten(V) reduction products were produced during some attempts to grow crystals of the tungsten(VI) complexes, and several of these were identified by determining the structures present (Section 3.2). Attempts to isolate the analogous complex of $WOCl_4$ with o-$C_6H_4(PPh_2)_2$ were unsuccessful, with only reduction products found. The formation of [$WOCl_4${o-$C_6H_4(AsMe_2)_2$}] (and the thiochloride analogue) contrasts with the failure of WOF_4 to form a complex with the diarsine [19], and probably indicates that $WOCl_4$ is a softer Lewis acid than WOF_4. In general, the phosphine complexes with high valent metal-fluoro species in both the d- and p-blocks are significantly more stable than their arsine analogues [24], although we note that both types of ligand form complexes with WF_6 [25,26]. Attempts to synthesise complexes of $WOCl_4$ or $WSCl_4$ with PMe_3 or $AsEt_3$ under a variety of conditions gave highly impure samples or mixtures including reduction products, hence these were no pursued further. An unstable [$WOF_4(PMe_3)$] has been characterised [19].

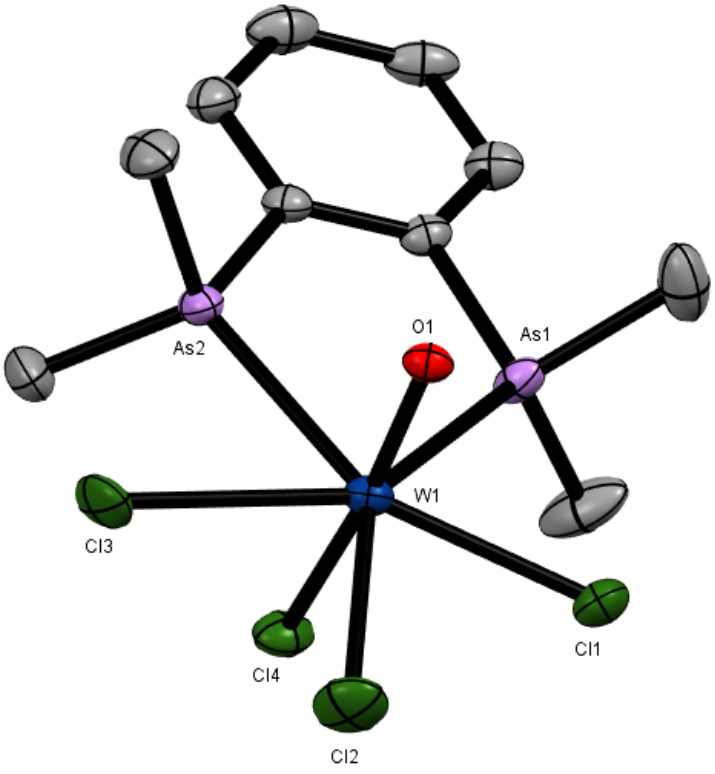


Fig. 1. The structure of [$WOCl_4${o-$C_6H_4(AsMe_2)_2$}] showing the atom numbering scheme. H atoms are omitted for clarity. Note that the axial O/Cl exhibited disorder, which was modelled with split atom sites and refined to occupancies of 0.23 : 0.77. Only the major form is shown. Selected bond lengths (Å) and angles (°) are: W1–As1 = 2.6798(6), W1– As2 = 2.7082(6), W1–O1 = 1.706(11), W1–Cl1 = 2.424(4), W1–Cl2 = 2.382(17), W1– Cl4 = 2.445(3), W1–Cl3 = 2.458(3), As1–W1–As2 = 72.327(17), O1–W1–As1 = 88.3(4), O1–W1–As2 = 88.8(3), O1–W1–Cl1= 93.6(4), O1–W1–Cl2 = 107.5(6), O1–W1–Cl4 = 164.3(4), O1–W1–Cl3 = 101(2), Cl1–W1–As1 = 67.77(6), Cl1–W1–Cl4 = 90.3(2), Cl2–W1–Cl1 = 76.8(4), Cl2–W1–Cl4 = 88.2(4), Cl2–W1–Cl3 = 77.2(10), Cl4–W1–As1 = 79.18(11), Cl4–W1–As2 = 78.49(11), Cl4–W1–Cl3 = 82(2), Cl3–W1–As2 = 63.8(11).

The structure of [$WOCl_4${o-$C_6H_4(AsMe_2)_2$}] is essentially the same as that reported [17], but the improvements in diffractometer hardware and computing since the original publication has allowed a much more precise structure to be obtained. The original report did not identify any axial disorder, and the reported W=O (1.89 Å) and W–Cl_{ax} (2.26 Å) differ significantly from those reported here (W=O = 1.706(11), W1–Cl4 = 2.445(3) Å, respectively), but the agreement in the W-As and the in-plane W-Cl distances is good between the studies. As usual in structures of this general type, the axial unit is bent away from linearity towards the neutral ligand (O1–W1–Cl4 = 164.3(4)°). Although not isomorphous, the structure is very similar to that of [WOF_4{o-$C_6H_4(PMe_2)_2$}] [19].

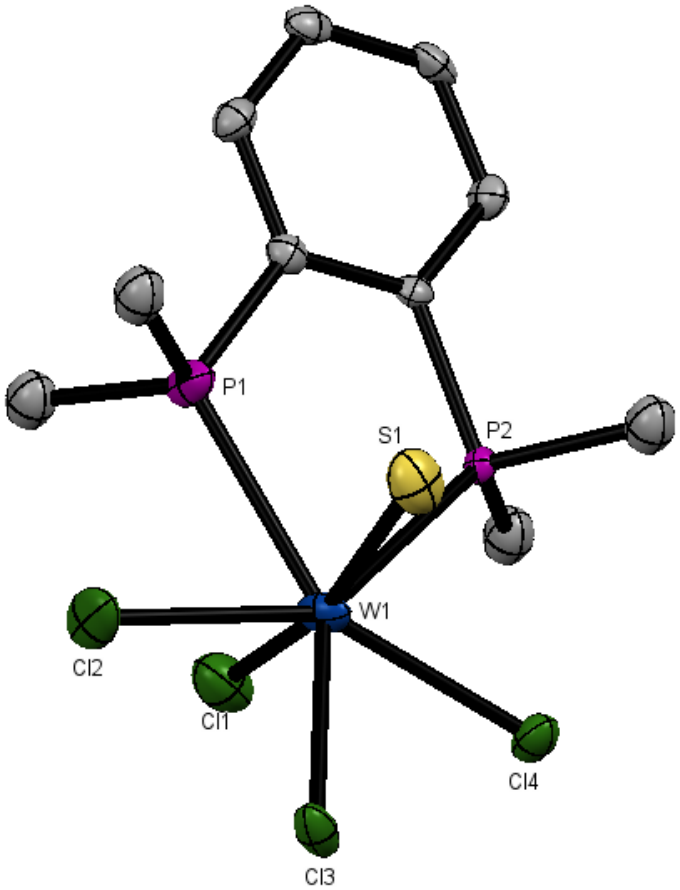


Fig.2. The structure of [$WSCl_4${o-$C_6H_4(PMe_2)_2$}] showing the atom numbering scheme. H atoms are omitted for clarity. Note that the axial S/Cl exhibited disorder, which was modelled as split sites and refined to occupancies of 0.29 : 0.71. Only the major form is shown. Selected bond lengths (Å) and angles (°) are: W1– P2 = 2.591(3), W1– P1 = 2.580(3), W1– Cl3 = 2.403(3), W1–Cl4 = 2.453(3), W1–Cl2 = 2.420(3), W1–Cl1 = 2.295(9), W1–S1 = 2.216(9), S1–W1–Cl1 = 162.3(4), Cl3–W1—Cl4 = 75.10(10), Cl3–W1–Cl2 = 75.51(10), Cl4–W1–P2 = 67.47(8), P1–W1–P2 = 73.59(8), Cl2–W1–P1 = 68.75(9), S1–W1–P2 = 84.4(4), S1–W1–Cl3 = 98.1(5), S1–W1–Cl4 = 98.9(5), S1–W1–P1 = 80.7(4), S1–W1–Cl2 = 94.4(4), Cl1–W1–P2 = 83.3(4), Cl1–W1–Cl3 = 99.5(5), Cl1–W1–Cl4 = 88.0(5), Cl1–W1–P1 = 83.6(4), Cl1–W1–Cl2 = 87.6(4) .

The d(W=S) in the seven-coordinate diphosphine complex is ~0.1Å longer than in the six-coordinate [{$WSCl_4$}$_2$($dppeO_2$)] (dppeO2 = $Ph_2P(O)CH_2CH_2P(O)Ph_2$) (2.106(1)Å [15] which is probably mainly due to the higher coordination number.

The IR spectrum of [$WOCl_4${o-$C_6H_4(EMe_2)_2$}] exhibits a strong υ(W=O) at ~954 cm^{-1} which is at a similar frequency to those reported in the seven-coordinate [WOF_4{o-$C_6H_4(PMe_2)_2$}] (961 cm^{-1}) [19], [WOF_4(2,2'-bipy)] (968 cm^{-1}) [27] or [$WOF_4(py)_2$] (973 cm^{-1}) [28], whereas the six-coordinate complexes, [WOX_4(L)] (X = F or Cl; L = py, R_3PO, dmso, etc.) typically exhibit υ(W=O) at > 980 cm^{-1} [15,29]. The υ(W=S) in [$WSCl_4${o-$C_6H_4(EMe_2)_2$}] are observed in the range 545-560 cm^{-1}, while the υ(W-Cl) appear as two broad overlapping bands ~295-335 cm^{-1}; four bands are predicted by symmetry, but are not clearly resolved.

The ^{1}H NMR spectra show two CH_3 resonances with equal intensity due to the methyl groups *syn* and *anti* to the W=O/S, whilst the $^{31}P\{^1H\}$ NMR spectra show a single resonance at δ ~ +75, a very large coordination shift of ~ +130 ppm (Fig. 3). For comparison, the $^{31}P\{^1H\}$ NMR chemical shifts of [WOF_4{o-$C_6H_4(PMe_2)_2$}] and $[WF_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]^{2+}$ (which are multiplets due to P-F couplings) are δ + 75.5 and +122.5 [19,25].

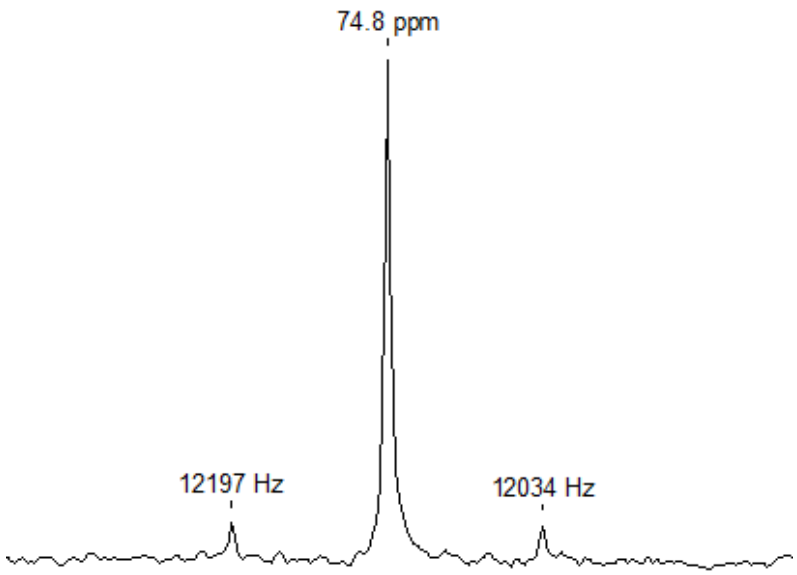


Fig 3: $^{31}P\{^{1}H\}$ NMR spectrum of $[WSCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ in CD_2Cl_2.

3.2 Tungsten(V) complexes

As noted above, the $[WOCl_4\{o\text{-}C_6H_4(EMe_2)_2\}]$ and $[WSCl_4\{o\text{-}C_6H_4(EMe_2)_2\}]$ complexes have limited stability in solution and over the several days necessary for some crystal growing attempts, small amounts of crystals with a different colour and habit were often observed. Typically, the quantity of crystals of a particular type were too small for microanalytical or detailed spectroscopic study. However, in several cases they were identified by X-ray crystallography: some were poor quality structures which do not merit mention, but in others, good quality data resulted and given the scarcity of tungsten(V) pnictine structures [30,31,32], these results are reported here. Generally, the bond lengths and angles are unexceptional, and the interest lies in the identification of some of these reduction products.

From a solution of $[WOCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ in CH_2Cl_2, a green crystal was identified as the W(V) complex, $[WOCl_3\{o\text{-}C_6H_4(PMe_2)_2\}]$. The complex has been reported before [33], made from $[WOCl_3(thf)_2]$ and the diphosphine, although its structure was not determined. The structure (Fig. 4) shows an octahedral tungsten centre with the diphosphine *trans* to Cl and with axial O/Cl. The latter showed disorder which was modelled and refined to an occupancy of 0.17 : 0.83.

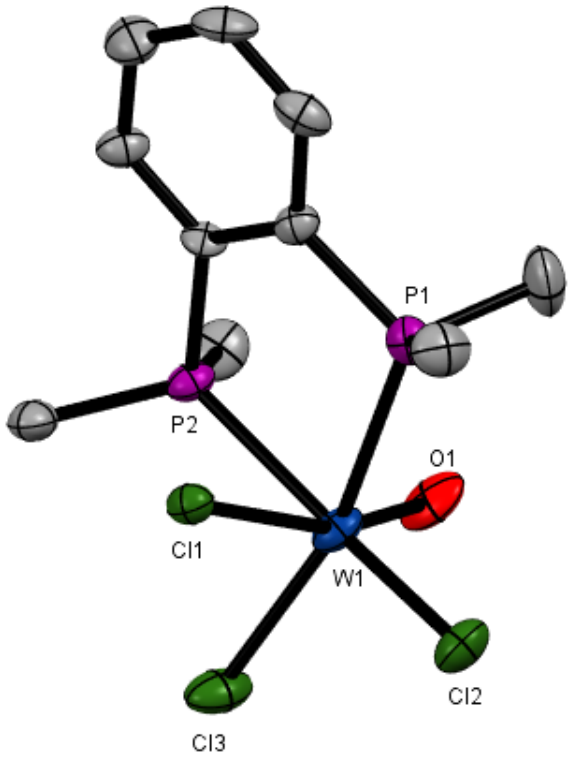


Fig. 4. The structure of [$WOCl_3${o-$C_6H_4(PMe_2)_2$}] showing the atom numbering scheme. H atoms are omitted for clarity. Note that the axial O/Cl were disordered and only the major form is shown. Selected bond lengths (Å) and angles (°) are: W1–O1 = 1.717(11), W1–Cl1 = 2.510(3), W1–Cl2 = 2.378(3), W1–Cl3 = 2.369(4), W1–P1 = 2.513(4), W1–P2 = 2.509(4), O1–W1–Cl1 = 162.9(4), O1–W1–P1 = 89.8(4), O1–W1–Cl2 = 101.8(4), O1–W1–P2 = 89.3(4), O1–W1–Cl3 = 103.1(4), Cl1–W1–P1 = 76.99(11), Cl2–W1–Cl1 = 89.20(12), Cl2–W1–P1= 89.98(13), P2–W1–Cl1 = 77.95(11), P2–W1–P1 80.30(11), Cl3–W1–Cl1 = 88.44(13), Cl3–W1–Cl2 = 96.59(14), Cl3–W1–P2 = 90.21(13).

A deep blue crystal obtained from a different batch of [$WOCl_4${o-$C_6H_4(PMe_2)_2$}] in CH_2Cl_2 was found to contain [$WOCl_3${*o*-$C_6H_4(PMe_2)(P(O)Me_2)$}]. The diphosphine monoxide does not appear to have been identified before, although two complexes of the corresponding diphosphine dioxide o-$C_6H_4(P(O)Me_2)_2$ have been characterized [34,35]. The origin of the oxygen is probably adventitious atmospheric dioxygen rather than the W=O group, although we note that $WOCl_4$ and $WSCl_4$ react with excess PPh_3 over several days to form the yellow W(IV) complex [$WCl_4(PPh_3)_2$] [36] by removal of the O/S from the tungsten centre. The structure of the [$WOCl_3${*o*-$C_6H_4(PMe_2)(P(O)Me_2)$}] shows an octahedral species with *mer*-chlorines and with the phosphoryl oxygen *trans* to W=O (Fig. 5).

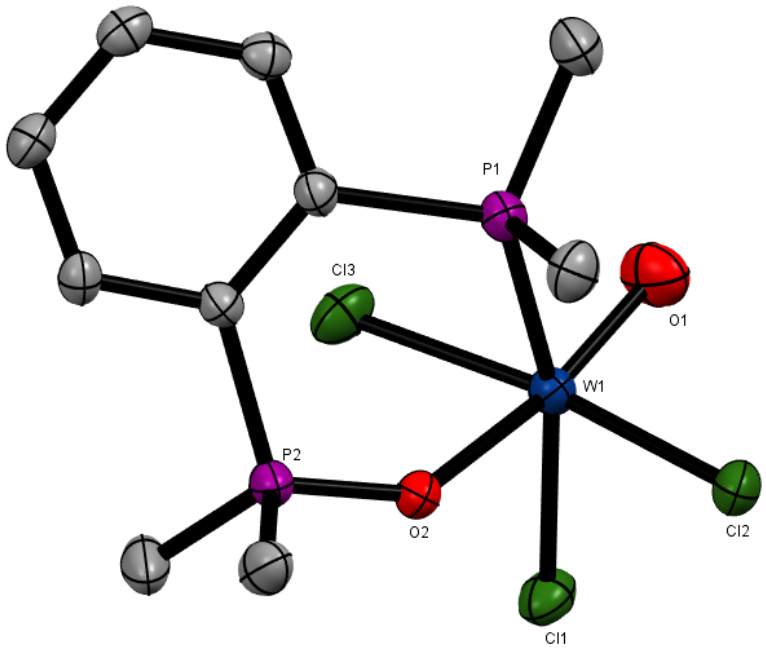


Fig. 5. The structure of $[WOCl_3\{o\text{-}C_6H_4(PMe_2)(P(O)Me_2)\}]\cdot 0.5CH_2Cl_2$ showing the atom numbering scheme. H atoms and solvate molecule are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl2 = 2.3666(18), W1– Cl3 = 2.3717(18), W1–Cl1 = 2.3780(17), W1–P1 = 2.5616(18), W1–O2 = 2.146(5), W1–O1 = 1.701(5), P2– O2 = 1.523(5), Cl2–W1–Cl1= 89.66(6), Cl2–W1–P1 = 89.46(6), Cl3–W1–Cl1= 89.66(6), Cl3–W1–P1 = 88.20(6), O2–W1–Cl2 = 84.82(13) , O2–W1–Cl3 = 85.71(13), O2–W1–Cl1 = 88.55(13), O2–W1–P1 = 73.04(13), O1–W1–Cl2 = 95.1(2), O1–W1–Cl3 = 94.2(2), O1–W1–Cl1 = 106.1(2), O1–W1–P1 = 92.3(2).

As described in Section 3.1, attempts to obtain a W(VI) complex with $o\text{-}C_6H_4(PPh_2)_2$ failed, but from the reaction of $WOCl_4$ and $o\text{-}C_6H_4(PPh_2)_2$ in toluene, some green crystals, identified as $[WCl_4\{o\text{-}C_6H_4(PPh_2)_2\}_2][WCl_6]\cdot 2.5C_7H_8$ were isolated. The structure, shown in Fig. 6, reveals a dodecahedral cation and an octahedral $[WCl_6]^-$ anion.

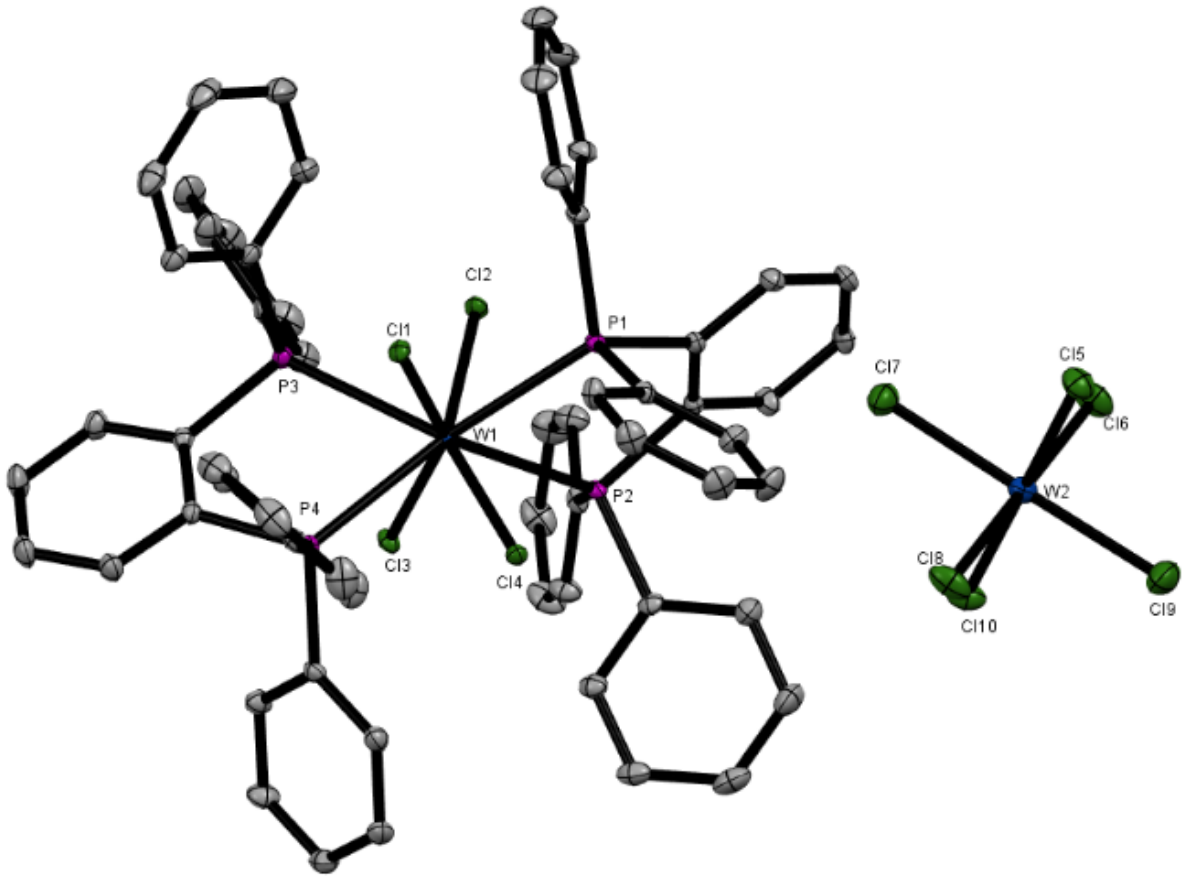


Fig. 6. The structure of $[WCl_4\{o\text{-}C_6H_4(PPh_2)_2\}_2][WCl_6]\cdot$showing the atom numbering scheme. The toluene solvate is omitted for clarity. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl1 = 2.3879(3), W1–Cl3 = 2.4157(3), W1–Cl4 = 2.3931(3), W–Cl2 = 2.4091(3), W1–P2 = 2.6599(4), W1–P1 = 2.6606(4), W1–P4 = 2.6593(3), W1–P3 = 2.6423(4), Cl1–W1–Cl4 = 88.105(11), Cl1–W1–Cl2 = 101.020(11), Cl1–W1–P1 = 70.385(11), Cl1–W1–P4 = 76.393(11), Cl1–W1–P3 = 77.363(11), Cl3–W1–P2 = 72.662(11), Cl3–W1–P4 = 73.330(11), Cl3–W1–P3 = 76.413(11), Cl4–W1–Cl3 = 99.354(12), Cl4–W1–P2 = 78.786(11) , Cl4–W1–P1 = 78.461(11), Cl4–W1–P4 = 70.511(11), Cl2–W1–Cl3 = 92.565(11), Cl2–W1–P2 = 73.900(11), Cl2–W1–P1 = 73.480(11), Cl2–W1–P3 = 70.081(11), P2–W1–P1 = 73.117(11), P3–W1–P4 = 74.510(11).

Yellow-brown crystals obtained from decomposition of $[WSCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ in CH_2Cl_2 solution were found to contain the dodecahedral $[WCl_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]^+$ cation with the anion a disordered mixture of $[WOCl_4]^-$ and $[WSCl_4]^-$. The square pyramidal tungsten(V) anions have been structurally characterised previously [37,38]. The orange diarsine analogue, $[WCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}_2][WOCl_4]$, was obtained similarly. However, in both cases the crystal quality was poor and the structures are not described, although the identity of the cations is not in doubt (see Appendix A).

In early studies, a series of purportedly seven-coordinate $[MCl_5(L\text{-}L)]$ (L-L = bidentate phosphine or arsine ligand), with M = Nb, Ta, W and Mo, were reported. Subsequent crystallographic studies revealed

that these complexes contained similar dodecahedral $[MCl_4(L\text{-}L)_2]^+$ cations and octahedral anions, often $[MCl_6]^-$, but sometimes $[MCl_5(OR)]^-$, $[MOCl_4]^-$ or $[I_3]^-$ were found [18,39,40,41 and refs therein].

4. Conclusions

Four examples of rare, seven-coordinate (pentagonal bipyramidal) tungsten(VI) complexes have been isolated and fully characterised spectroscopically and in two cases by X-ray crystallography. The only close analogues are the $[WOF_4(\text{diphosphine})]$ (diphosphine = $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(PMe_2)_2$) [19]. The $[WOCl_4(\text{bipy})]$ and $[WSCl_4(\text{bipy})]$ may also be analogues, although their structures have not been established crystallographically [15]. Similar complexes with o-$C_6H_4(PPh_2)_2$ or monodentate PMe_3 or $AsEt_3$ could not be isolated, with the tungsten instead being reduced to W(V) species, several of which were identified by determining their structures.

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Conflict of Interest

The authors have no conflicts to declare.

Appendix A

Contains the supplementary crystallographic data for this paper. CCDC numbers are: 1968989: $[WOCl_3\{o\text{-}C_6H_4(PMe_2)_2\}]$, 1968990: $[WSCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$, 1968991: $[WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$, 1968992: $[WOCl_3\{o\text{-}C_6H_4(PMe_2)(P(O)Me_2)\}]\cdot 0.5CH_2Cl_2$, 1968993: $[WCl_4\{o\text{-}C_6H_4(PPh_2)_2\}_2][WCl_6]\cdot 2.5\ C_7H_8$. 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://..... Appendix A also contains the IR and NMR data for new complexes.

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