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Synthesis and Characterisation of W^{VI} Complexes of Phosphane Oxide Ligands, $[WO_2X_2(OPR_3)_2]$ (X = F, Cl or Br; R = Me or Ph), and of the $[MoO_2F_2(OPR_3)_2]$

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Phosphane oxide complexes of dioxidotungsten^{VI}, $[WO_2X_2(OPR_3)_2]$ (X = Cl or Br, M = Ph or Me) have been prepared under anhydrous conditions from the reaction of WX_6 with $(Me_3Si)_2O$ in CH_2Cl_2, followed by addition of OPR_3. Some diphosphane dioxide analogues have been made similarly, viz, $[WO_2X_2(L–L)]$ {L–L = $Ph_2P(O)(CH_2)_nP(O)Ph_2$ (*n* = 1 or 2), *o*-$C_6H_4[P(O)Ph_2]_2$}. The complexes have been characterised by elemental analysis, IR and NMR (^1H and $^{31}P\{^1H\}$) spectroscopy, and the structures of $[WO_2Br_2(OPPh_3)_2]$ and $[WO_2Cl_2(OPMe_3)_2]$ determined, revealing distorted six-coordinate tungsten centres with *cis*-WO_2 and *trans*-WX_2 units. The difluorido-dioxido complexes $[MO_2F_2(OPR_3)_2]$ (M = Mo or W) and $[WO_2F_2(L'–L')]$ (L′–L′ = 2,2′-bipyridyl, 1,10-phenanthroline) have been prepared by fluorination of the corresponding chlorido complexes with Me_3SnF in CH_2Cl_2. These are characterised similarly and by $^{19}F\{^1H\}$ NMR spectroscopy. Attempts to make $[MO_2I_2(OPR_3)_2]$ were unsuccessful. No adduct formation occurs between CrO_2Cl_2 and $OPPh_3$ under rigorously anhydrous conditions. Crystal structures of $[Me_3SnCl(OPPh_3)]$ and two forms of $[WO_2Cl_2(1,10\text{-phen})]$ are also reported and discussed.

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Introduction

The coordination chemistries of Mo^{VI} and W^{VI} continue to attract much research effort, their importance including such diverse areas as metalloenzymes,[1] oxido-transfer reagents, catalyst precursors and epoxidation catalysts.[2–4] Complexes of the MoO_2X_2 (X = Cl or Br) with a wide range of O- and N-donor ligands are known and can be obtained by direct reaction of MoO_2X_2 [5,6] or MoO_3/aqueous HX[7] with the ligands, or more rarely by halogenation of $[Mo(CO)_4(\text{ligand})]$.[8] The WO_2X_2 (X = Cl or Br) are insoluble and relatively unreactive and their chemistry has been less thoroughly explored. Some complexes were initially obtained by reaction of WO_2X_2 with excess molten ligand,[9] but more recently routes based upon the reaction of $WOCl_4$ with a disiloxane to produce WO_2Cl_2 in situ, followed by reaction with the ligand have been developed.[10] Little is known about WO_2F_2[11] and the only structurally characterised adduct, $[WO_2F_2(2,2'\text{-bipy})]$, was isolated from the decomposition of $[WOF_4(2,2'\text{-bipy})]$.[12] The dark green WO_2I_2[13] is known, but no complexes have been reported. A small number of adducts of MO_2F_2 (M = Mo or W) with phosphane oxides have been prepared from MO_3/aqueous HF and the ligands,[7,14] and the structure of $[MoO_2F_2(OPPh_2Me)_2]$ determined, although spectroscopic data are limited. The structure of $[MoO_2F_2(thf)_2]$, obtained by hydrolysis of $[MoF_4(NCl)]$, has also been reported.[15] We are interested in developing the chemistry of high-valent, early transition metals with softer donors such as thio- or seleno-ethers, and have reported examples with MoO_2X_2 (X = Cl or Br),[16] TiX_4, $ZrCl_4$ and $HfCl_4$.[17] Currently we are exploring routes to W^{VI} complexes with these ligands, and because complexes of this type are very moisture sensitive and the ligands prone to oxidation or C–S(Se) bond fission under forcing conditions, many of the routes described above are not suitable. As a prelude to this work, we describe here the synthesis and characterisation of a series of phosphane oxide complexes of WO_2X_2 (X = Cl or Br) using anhydrous conditions and a route based upon $WX_6/(Me_3Si)_2O$. We also describe the (anhydrous) synthesis of fluorido analogues with both Mo^{VI} and W^{VI} using Me_3SnF[18] as fluorinating agent. Attempts to obtain $[MO_2I_2(OPR_3)_2]$ are also briefly discussed.

Results and Discussion

$[WO_2X_2(OPR_3)_2]$ (X = Cl or Br) Complexes

As expected, attempts to react commercial WO_2Cl_2 directly with OPR_3 (R = Me or Ph) in CH_2Cl_2 solution were unsuccessful, even after prolonged reflux. In contrast,

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"WO_2Cl_2" made in situ from reaction of WCl_6 with hexamethyldisiloxane, $(Me_3Si)_2O$, in anhydrous CH_2Cl_2, reacted readily with both phosphane oxides to produce $[WO_2Cl_2(OPR_3)_2]$ in good yields as white powders, moderately soluble in chlorocarbon solvents. Similar reactions using $WBr_6/(Me_3Si)_2O$ gave the corresponding cream $[WO_2Br_2(OPR_3)_2]$. To obtain pure products it is important to allow the $WX_6/(Me_3Si)_2O$ reaction to go to completion before adding the neutral ligand; similar observations were made by Dreisch et al.[10a] who examined the synthesis of $[WO_2Cl_2(dme)]$ (dme = $MeOCH_2CH_2OMe$) from $WOCl_4/(Me_3Si)_2O$ in some detail and observed significant amounts of W^V complexes under some conditions. Gibson et al.[10c] reported that WO_2Cl_2 could not be isolated from CH_2Cl_2 solution at ambient temperatures by this route, rather off-white tungsten siloxanes were formed. We obtained white materials, which although we did not isolate or characterise them, reacted in situ with OPR_3 to give high yields of $[WO_2Cl_2(OPR_3)_2]$, and the spectroscopic data showed no $-OSiMe_3$ present in the products. Extension of this route was also successful in affording diphosphane dioxide complexes $[WO_2X_2(L–L)]$ {L–L = $Ph_2P(O)CH_2P(O)Ph_2$, $Ph_2P(O)CH_2CH_2P(O)Ph_2$, and o-$C_6H_4[P(O)Ph_2]_2$} (Table 1), although these are only slightly soluble in chlorocarbons, and it is necessary to use larger volumes of solvent and longer reaction times, and also to recrystallise the products to obtain pure samples. The spectroscopic data on the $[WO_2X_2(OPR_3)_2]$ complexes (Table 1) are consistent with the limited literature data[9] and the geometries were confirmed by crystal structures of two examples (below). In particular two medium intensity features in the IR spectra in the range 900–965 cm^{-1} are the υ_{sym} and υ_{asym} vibrations of the *cis*-WO_2 group [for the $OPMe_3$ complexes $\rho(PMe_3)$ modes in the same region complicate the assignments – see Table 1], whilst the *trans*-WX_2 units have single bands at ca. 310 cm^{-1} (X = Cl) or ca. 240 cm^{-1} (X = Br). The $\upsilon(PO)$ modes occur as broad features typically shifted to low frequency by 40–70 cm^{-1} from the values in the parent OPR_3. Trends in the spectroscopic data with changes in halogen and between corresponding Mo and W complexes are discussed further in a later section.

The structures of $[WO_2Br_2(OPPh_3)_2]$ and $[WO_2Cl_2(OPMe_3)_2]$ are shown in Figure 1 and Figure 2 and selected bond lengths and angles are in Table 2 and Table 3. Both structures show distorted octahedral coordination at tungsten with *trans*-halides and with the phosphane oxide *trans* to W=O and with the X–W–X bent towards the neutral ligands and away from the WO_2 groups. The data can be compared with that for $[WO_2Cl_2(OPPh_3)_2]$[9b] which has W=O 1.706(8), 1.702(9) Å, W–Cl 2.385(3), 2.366(3) Å, and W–O(P) 2.175(8), 2.163(7) Å, P–O 1.499(8), 1.500(7) Å, O=W=O 102.2(4)° and Cl–W–Cl 163.5(1)°. Thus for $[WO_2X_2(OPPh_3)_2]$ (X = Cl or Br), the W=O, W–O(P) and P–O distances are the same within experimental error. The same basic features are present in the structure of $[WO_2Cl_2(OPMe_3)_2]$. The structures are also very similar to those of the molybdenum analogues reported previously.[6,7] As noted before, the M–O–P angle is rather variable. Within each structure, the M–O–P angles at the two phosphane

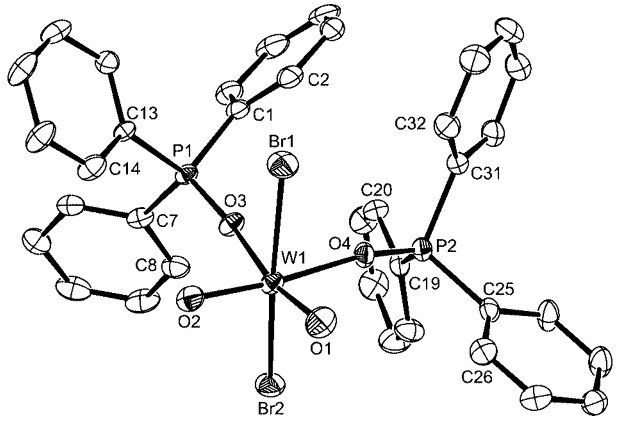

Figure 1. View of the structure of $[WO_2Br_2(OPPh_3)_2]$ with numbering scheme adopted. H atoms have been omitted for clarity and the ellipsoids are drawn at the 50% probability level.

Table 1. Selected spectroscopic data.

Compound	$\delta(^{31}P\{^1H\})$/ppm[a]	$\delta(^{19}F\{^1H\})$/ppm[a]	$\upsilon(W=O)$ [cm^{-1}][b]	$\upsilon(P=O)$ [cm^{-1}][b]	$\upsilon(W–X)$ [cm^{-1}][b]
$[WO_2F_2(OPMe_3)_2]$	59.9	–65.9 (J = 110 Hz)	956,935,896[c]	1144, 1097	555
$[WO_2Cl_2(OPMe_3)_2]$	61.9	–	957, 937, 894[c]	1148, 1085	305
$[WO_2Br_2(OPMe_3)_2]$	63.9	–	956, 938, 891[c]	1155, 1100	235
$[WO_2F_2(OPPh_3)_2]$	40.2	–61.8 (J = 91 Hz)	963, 918	1164, 1096	584
$[WO_2Cl_2(OPPh_3)_2]$	42.1	–	959, 911	1156, 1140	310
$[WO_2Br_2(OPPh_3)_2]$	43.3	–	960, 914	1169, 1140	238
$[WO_2Cl_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$	40.3	–	963, 912	1156	324, 304
$[WO_2Br_2\{Ph_2P(O)CH_2P(O)Ph_2\}]$	43.7	–	961, 910	1150	239
$[WO_2Cl_2\{Ph_2P(O)(CH_2)_2P(O)Ph_2\}]$	47.1	–	957, 909	1173, 1145	317, 300
$[WO_2Cl_2\{o\text{-}C_6H_4[P(O)Ph_2]_2\}]$	44.7	–	959, 915	1174, 1148	313
$[WO_2Br_2\{o\text{-}C_6H_4[P(O)Ph_2]_2\}]$	45.9	–	958, 913	1169, 1160	234
$[MoO_2F_2(OPMe_3)_2]$	55.4	–57.2	955,943,906,892[c,d]	1141, 1092	566[e]
$[MoO_2F_2(OPPh_3)_2]$	38.5	–51.1	949, 915[d]	1141, 1083	587[e]
$[WO_2F_2(2,2'\text{-bipy})]$	–	–69.6 (J = 95 Hz)	962, 921	–	584
$[WO_2F_2(1,10\text{-phen})]$	–	–68.0 (J = 96 Hz)	961, 926	–	585

[a] In CH_2Cl_2 solution. [b] Nujol mull, $OPMe_3$ has $\upsilon(PO)$ = 1161 cm^{-1}, $OPPh_3$ has $\upsilon(PO)$ = 1195 cm^{-1}. [c] $\rho(PMe_3)$ in uncoordinated $OPMe_3$ occurs at 955, 937 and 867 cm^{-1} therefore assignment of $\upsilon(M=O)$ uncertain. [d] $\upsilon(Mo=O)$. [e] $\upsilon(Mo–F)$.

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oxides vary by 6° (Ph) and 9° (Me) with the mean angle for $OPMe_3$ some 25° smaller than that in the $OPPh_3$ complex.

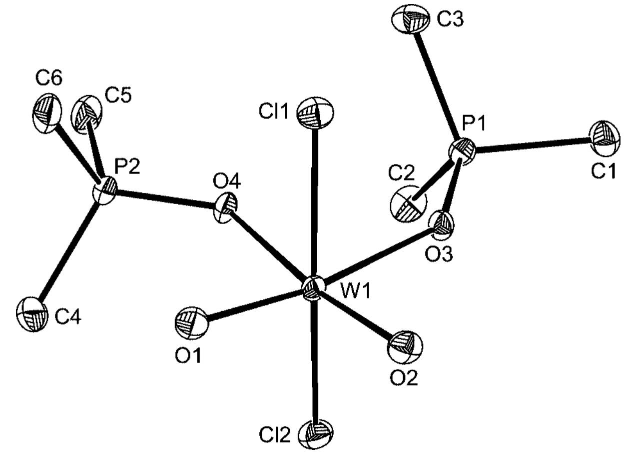

Figure 2. View of the structure of $[WO_2Cl_2(OPMe_3)_2]$ with numbering scheme adopted. H atoms have been omitted for clarity and the ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths [Å] and angles [°] for $[WO_2Br_2(OPPh_3)_2]$.

W1–O1	1.709(4)	W1–Br1	2.5469(7)
W1–O2	1.708(4)	W1–Br2	2.5398(7)
W1–O3	2.166(3)	P1–O3	1.511(4)
W1–O4	2.161(3)	P2–O4	1.508(4)
P–C	1.792(5)–1.809(5)		
O1–W1–O2	101.89(19)	O1–W1–O3	167.61(17)
O1–W1–O4	90.70(17)	O2–W1–O3	90.34(16)
O2–W1–O4	167.25(15)	O3–W1–O4	77.15(13)
Br1–W1–Br2	166.14(2)	O–P–C	108.6(2)–116.5(2)
W1–O3–P1	159.2(2)	O1/O2–W1–Br	92.93(13)–96.10(14)
W1–O4–P2	165.4(2)	O3/O4–W1–Br	83.65(10)–85.81(10)

Table 3. Selected bond lengths [Å] and angles [°] for $[WO_2Cl_2(OPMe_3)_2]$.

W1–O1	1.718(2)	W1–Cl1	2.3888(9)
W1–O2	1.717(2)	W1–Cl2	2.3881(9)
W1–O3	2.125(2)	P1–O3	1.518(2)
W1–O4	2.190(2)	P2–O4	1.522(2)
P–C	1.769(4)–1.785(3)		
O1–W1–O2	102.66(10)	O1–W1–O3	166.53(9)
O1–W1–O4	88.70(9)	O2–W1–O3	90.80(9)
O2–W1–O4	168.43(9)	O3–W1–O4	77.87(8)
Cl1–W1–Cl2	164.08(3)	O–P–C	108.48(14)–112.77(14)
W1–O3–P1	141.87(13)	O1/O2–W1–Cl	93.58(7)–96.78(8)
W1–O4–P2	131.01(12)	O3/O4–W1–Cl	82.23(6)–84.54(6)

$[MO_2F_2(OPR_3)_2]$ (M = Mo or W) Complexes

The $[MoO_2Cl_2(OPR_3)_2]$[6] complexes were dissolved in anhydrous CH_2Cl_2 and stirred with a 50% excess of powdered Me_3SnF for ca. 24 h, which slowly dissolves as the reaction proceeds, to form $[MoO_2F_2(OPR_3)_2]$ and Me_3SnCl. The completion of the reaction is best monitored by checking the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture for complete loss of the resonance of the $[MoO_2Cl_2(OPR_3)_2]$ starting material, because we found that reaction times were quite variable, ranging from ca. 4–20 h. The polymeric Me_3SnF is insoluble in chlorocarbons and only dissolves as the reaction proceeds, and this solid-solution reaction probably accounts for the highly variable reaction times. It is also important to use sufficient solvent volume to prevent the product complexes from separating out on the suspended Me_3SnF. When reaction is complete, unreacted Me_3SnF was removed by filtration, the solvent and most of the Me_3SnCl pumped off in vacuo, and the residue washed thoroughly with *n*-hexane to remove any residual Me_3SnCl (Me_3SnCl is easily detected in the ^1H NMR spectra as singlet at $\delta = 0.62$ ppm with $^{119/117}Sn$ satellites). The corresponding reactions of $[WO_2Cl_2(OPR_3)_2]$ with Me_3SnF were carried out similarly, although the reaction times required are longer, and sometimes insoluble by-products are formed, which contain broad IR bands 850–700 cm^{-1} presumably due to W–O–W bridges. In attempts to overcome these problems we explored the effects of using $[WO_2Cl_2(OPR_3)_2]/Me_3SnF$ ratios of 1:2 (stoichiometric), 1:3 and 1:4, and also adding excess OPR_3 (ca. 2 mol. equiv.) to suppress oligomerisation, because it is known that the W=O groups exhibit a *trans* labilising effect.[14] In fact we find that the best route is to use rigorously anhydrous conditions, stoichiometric $[WO_2Cl_2(OPR_3)_2]/Me_3SnF$ ratio (1:2), without added OPR_3, and dilute solutions. Excess phosphane oxide forms adducts with the Me_3SnX (see below) making it harder to remove after the reaction is complete. After removing all volatiles in vacuo, the products were washed with anhydrous hexane, and the residue recrystallised from anhydrous CH_2Cl_2, discarding any insoluble material. The $^{31}P\{^1H\}$ NMR spectra obtained during the reactions show an additional resonance intermediate in chemical shift between those of the dichlorido- and difluorido-species, almost certainly due to $[WO_2ClF(OPR_3)_2]$ (although no attempt was made to isolate these), indicating that fluorination occurs stepwise. We also made $[WO_2F_2(OPMe_3)_2]$ by adding excess $OPMe_3$ in ethanol to a solution of "tungstic acid" (hydrated WO_3) in aqueous HF and allowing the solution to evaporate in air,[14] until very small colourless crystals separated (ca. 3 d). The products from the two routes were spectroscopically identical.

A small number of white crystals were isolated as a by-product from the $[WO_2Cl_2(OPPh_3)_2]/Me_3SnF$ reaction and were identified by a crystal structure determination as $[Me_3SnCl(OPPh_3)]$. The structure (Figure 3, Table 4) reveals a trigonal-bipyramidal tin centre with equatorial methyl groups. The structure of the parent molecule Me_3SnCl is also composed of distorted trigonal-bipyramidal units with axially disposed asymmetric chlorine bridges [Sn–Cl 2.430(2), 3.269(2) Å].[19] The Sn–C bonds are not significantly different between the parent [2.119 Å (av)] and the phosphane oxide adduct [2.120 Å (av)], and in the adduct the $OPPh_3$ simply replaces the longer Sn–Cl bridging interaction. The weak coordination of the phosphane oxide is evident in the long *d*(Sn–O) = 2.375(2) Å and short *d*(P–O) = 1.497(2) Å, which may be compared with values in $[SnX_4(OPPh_3)_2]$, which range from *d*(Sn–O) = 2.050(3) Å (X = F) to 2.13 Å (av) (X = I) and *d*(P–O) range from

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1.523(3)–1.485 Å.[20] The compound has been reported several times before[21] and the ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data in CH_2Cl_2 solution are little different from those of the constituents, suggesting only weak interaction in solution.

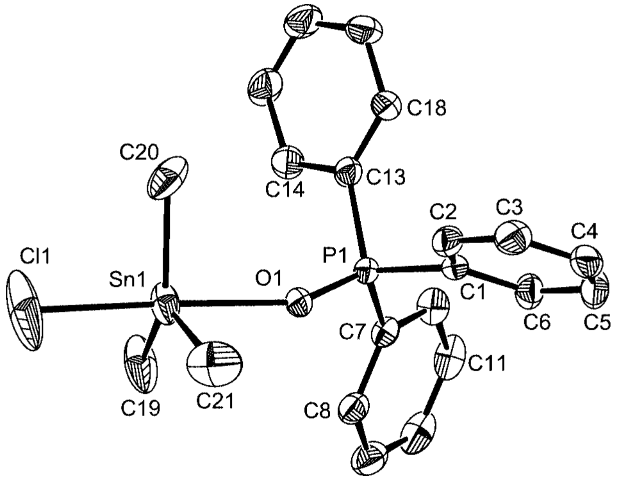

Figure 3. View of the structure of $[Me_3SnCl(OPPh_3)]$ with numbering scheme adopted. H atoms have been omitted for clarity and the ellipsoids are drawn at the 50% probability level.

Table 4. Selected bond lengths [Å] and angles [°] for $[Me_3SnCl(OPPh_3)]$.

Sn1–Cl1	2.515(1)	Sn1–O1	2.375(2)
P1–O1	1.497(2)	Sn1–C19	2.125(4)
Sn1–C20	2.116(4)	Sn1–C21	2.119(4)
O1–Sn1–Cl1	177.57(7)	C19–Sn1–Cl1	94.71(10)
C20–Sn1–Cl1	93.39(11)	C21–Sn1–Cl1	94.84(12)
C19–Sn1–O1	85.43(11)	C20–Sn1–O1	88.64(11)
C21–Sn1–O1	83.03(12)	C–Sn1–C	117.4(2)–121.1(2)

The spectroscopic data on the four fluorido Mo^{VI} and W^{VI} complexes are given in Table 1. The *trans*-MF_2 units exhibit a strong IR vibration ca. 550–590 cm^{-1}. The $[MoO_2F_2(OPR_3)_2]$ exhibit sharp singlet ^{19}F NMR resonances at δ = –51.7 (R = Ph) or –57.2 (R = Me), and the ^{95}Mo resonances appear as broad triplets at δ = –114 (R = Ph) or –93 (R = Me) with $^1J(^{95}Mo\text{-}^{19}F)$ ca. 115–120 Hz. Literature data on molybdenum fluorides are sparse, and the only closely related species appears to be $[MoO_2F_2(acac)]^-$ which has $\delta(^{19}F)$ = –53.0, $\delta(^{95}Mo)$ = –76.3 (t) $^1J(^{95}Mo\text{-}^{19}F)$ = 114 Hz.[22] The $[WO_2F_2(OPR_3)_2]$ complexes exhibit ^{19}F NMR resonances in a similar region to the molybdenum analogues (Table 1), with ^{183}W satellites $^1J(^{183}W\text{-}^{19}F)$ ca. 90–110 Hz. The ^{19}F resonances are significantly to low frequency of those in WF_6 or WOF_4 adducts.[23]

As a further test of this method, the $[WO_2Cl_2(L–L)]$ (L–L = 2,2′-bipy, 1,10-phen), originally obtained from WO_2Cl_2 and the molten diimines,[9a] were prepared from $WCl_6/(Me_3Si)_2O$ and the appropriate diimine, and then fluorinated with Me_3SnF, in these cases under reflux for 48 h, due to the poor solubility of reagents and products. The $[WO_2F_2(L–L)]$ are poorly soluble, white powders (Table 1), with the data in good agreement with those reported[12] for $[WO_2F_2(L–L)]$ made from $[WOF_4(2,2′\text{-bipy})]$ or from $[WOF_2(OEt)_2]$. During this work two different crystalline forms of $[WO_2Cl_2(1,10\text{-phen})]$ were obtained, an unsolvated form (the structure of which has been reported previously)[24a] and a 1:1 CH_2Cl_2 solvate. The structures of both were determined (see Table 5 and Figure 4 and Figure 5). The distortions from regular octahedal angles at W are similar to those observed above for the phosphane oxides, but with the O=W=O angle ca. 4° larger and the Cl–W–Cl angle ca. 6° smaller in the 1,10-phenanthroline complexes. The tungsten residues in these two structures have very similar bond lengths and angles and they provide good examples of the effect of chemical environment on molecular geometry.[24b] The data on the unsolvated form agree well with that reported.[24a] Comparison of the data show that *d*(W=O) and *d*(W–Cl) differ little from the values in the phosphane oxide adduct, indicating that these are the dominant bonds to tungsten, with the neutral ligands filling the remaining coordination sites.

Table 5. Selected bond lengths [Å] and angles [°] for $[WO_2Cl_2(1,10\text{-phen})]$ species. (a) $[WO_2Cl_2(1,10\text{-phen})]\cdot CH_2Cl_2$. (b) $[WO_2Cl_2(1,10\text{-phen})]$.[a]

(a)			
W1–O1	1.717(2)	W1–Cl1	2.3623(10)
W1–O2	1.721(2)	W1–Cl2	2.3518(10)
W1–N1	2.318(3)	W1–N2	2.303(3)
N–C	1.321(4)–1.363(4)		
O1–W1–O2	106.23(11)	O1–W1–N1	92.55(10)
O1–W1–N2	163.21(10)	O2–W1–N1	161.20(10)
O2–W1–N2	90.56(10)	N1–W1–N2	70.67(9)
Cl1–W1–Cl2	157.93(3)		
O–W1–Cl	96.23(9)–96.96(8)	N–W1–Cl	80.29(7)–81.41(7)
(b)			
W1–O1	1.718(3)	W1–N1	2.298(3)
W1–Cl1	2.3586(12)	N1–C	1.340(5), 1.353(5)
O1–W1–O1a	106.7(2)	O1–W1–N1	91.27(12)
O1–W1–N1a	162.05(13)	N1–W1–N1a	70.81(16)
Cl1–W1–Cl1a	157.34(6)		
O1–W1–Cl	96.31(11), 97.17(10)	N1–W1–Cl	80.50(8), 81.07(8)

[a] Symmetry operation: a = 1–*x*, *y*, 1/2–*z*.

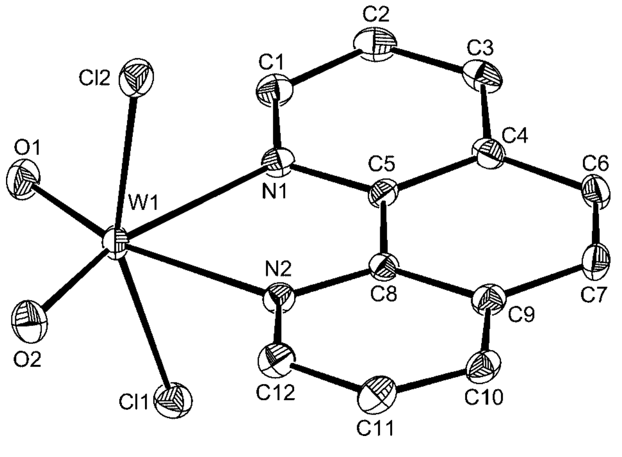

Figure 4. View of the structure of $[WO_2Cl_2(1,10\text{-phen})]\cdot CH_2Cl_2$ with numbering scheme adopted. The solvate molecule is not shown, H atoms have been omitted for clarity and the ellipsoids are drawn at the 50% probability level.

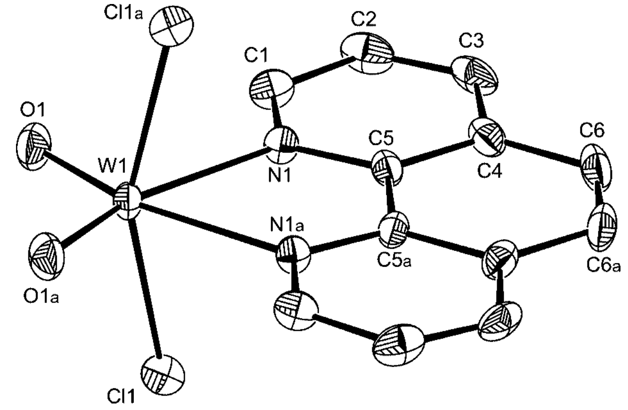

Figure 5. View of the structure of $[WO_2Cl_2(1,10\text{-phen})]$ with numbering scheme adopted. H atoms have been omitted for clarity and the ellipsoids are drawn at the 50 % probability level. The molecule has crystallographic twofold symmetry. Symmetry operation: $a = 1-x, y, 1/2-z$.

Attempted Preparation of $[MO_2I_2(OPR_3)_2]$

A CH_2Cl_2 solution of $[MoO_2Cl_2(OPPh_3)_2]$ treated with 2.5 equiv. of Me_3SnI, slowly developed a dark green colour. After ca. 24 h an in situ $^{31}P\{^1H\}$ NMR spectrum showed that the $[MoO_2Cl_2(OPPh_3)_2]$ had been completely consumed, and there were no new phosphorus resonances. Evaporation of the solution gave a paramagnetic green-brown solid which showed no evidence of $\upsilon(MoO_2)$ vibrations in the IR spectrum, and the UV/Vis spectrum contained, in addition to intense bands $> 25000\ cm^{-1}$, a broad, weak feature ca. $16000\ cm^{-1}$ assignable as a d–d transition, consistent with the reduction of the molybdenum to a lower oxidation state. The reaction of $[WO_2Cl_2(OPPh_3)_2]$ with Me_3SnI was very slow, but after 7 d a yellow solution formed and a $^{31}P\{^1H\}$ NMR spectrum of this solution showed that all the chlorido complex had reacted. However, neither the IR nor the $^{31}P\{^1H\}$ NMR spectra of the product(s) were consistent with the formation of $[WO_2I_2(OPPh_3)_2]$, and we conclude that the latter is not formed by this route.

Some Comparisons

The spectroscopic data on the $[MO_2X_2(OPR_3)_2]$ complexes show no systematic variation in $\upsilon(PO)$ or $\upsilon(MO_2)$, for which the broadness of the bands and probably some coupling to other modes are responsible. However, systematic trends are evident in the multinuclear NMR spectroscopic data. The $^{31}P\{^1H\}$ NMR chemical shifts of the coordinated phosphane oxides show high frequency shifts $F < Cl < Br$ (Table 1 and Table 6), the opposite of that expected on electronegativity grounds, and probably reflecting less effective $\pi(X)\rightarrow Mo$ donation as the halogen orbitals become larger. Similarly, the ^{95}Mo chemical shifts show an inverse halogen dependence, also seen in MoO_2X_2 (X = Cl or Br) complexes with N-donor ligands,[25] although this appears to be the first time data have been available for complexes containing F. (Our attempts to record ^{183}W NMR spectroscopic data for that series of compounds were unsuccessful due to the poor solubility of the complexes and the inherent insensitivity of the W nucleus.) The changes between the corresponding Mo and W complexes are also systematic for fixed OPR_3 and X, the $^{31}P\{^1H\}$ chemical shift is always slightly to higher frequency for M = W than Mo, whilst the ^{19}F chemical shifts in the fluorides are to lower frequency for the tungsten complexes.

Table 6. ^{95}Mo and $^{31}P\{^1H\}$ NMR spectroscopic data.[a]

Compound	$\delta(^{95}Mo)$ [ppm]		$\delta(^{31}P\{^1H\})$ [ppm]
$[MoO_2F_2(OPMe_3)_2]$	–95 (t)	$^1J(^{95}Mo\text{-}^{19}F) = 115$ Hz	55.4
$[MoO_2F_2(OPPh_3)_2]$	–114 (t)	$^1J(^{95}Mo\text{-}^{19}F) = 120$ Hz	38.5
$[MoO_2Cl_2(OPMe_3)_2]$[b]	149		59.1
$[MoO_2Br_2(OPMe_3)_2]$[b]	179		60.6
$[MoO_2Cl_2(OPPh_3)_2]$[b]	137		40.6
$[MoO_2Br_2(OPPh_3)_2]$[b]	171		42.0
$[Et_4N][MoO_2F_2(acac)]$[c]	–73.5 (t)	$^1J(^{95}Mo\text{-}^{19}F) = 114$ Hz	

[a] In CH_2Cl_2 solution. [b] Data from ref.[6] [c] Data from ref.[22]

Attempted Synthesis of Chromium(VI) Analogues

The extensive data obtained on the series of Mo^{VI} and W^{VI} $[MO_2X_2(OPR_3)_2]$ compounds, prompts the consideration of the 3d analogues containing Cr^{VI}. Chromyl fluoride, CrO_2F_2, is an orange gas and a powerful fluorinating agent,[26] whilst CrO_2Br_2 is very unstable, decomposing rapidly above ca. 210 K,[27] seemingly ruling out any coordination chemistry. However, the commercially available CrO_2Cl_2 was briefly examined. The UV/Vis spectrum of a solution of freshly distilled chromyl chloride in anhydrous CH_2Cl_2 exhibited a strong broad band at ca. $26000\ cm^{-1}$ and a weak broader feature at ca. $18000\ cm^{-1}$,[28] and these bands were unchanged on addition of dry $OPPh_3$, indicating no adduct formation. Over a few hours the initially deep orange-red solution turns red-brown and new weak features appear at low energy, which we assign to reduction to d^1 Cr^V. Decomposition is much faster in the presence of moisture or in bright light. The $^{31}P\{^1H\}$ NMR spectrum of a mixture of CrO_2Cl_2 and $OPPh_3$ in rigorously anhydrous CH_2Cl_2 also shows no reaction, but in the presence of traces of moisture a resonance at δ ca. +46 ppm appears due to the formation of Ph_3POH^+.[29] On a preparative scale, the reaction of CrO_2Cl_2 and $OPPh_3$ (1:1 mol. ratio) in anhydrous CH_2Cl_2 gave a deep red solution, which on removal of all volatiles in vacuo at 25 °C, left a sticky red-brown, paramagnetic solid. The IR spectrum of the solid showed no uncoordinated $OPPh_3$, but a broad feature at ca. $1140\ cm^{-1}$ was assignable to coordinated phosphane oxide, and features at ca. 970 and $875\ cm^{-1}$ may be $\upsilon(CrO)$ modes. The evidence points to the red-brown solid being a Cr^V species (or mixture of Cr^V compounds), and there is no evidence that CrO_2Cl_2 forms adducts with phosphane oxides. This contrasts with the behaviour of $VOCl_3$ which forms $[VOCl_3(OPPh_3)]$ and $[VOCl_3(OPMe_3)_2]$.[30] A few adducts of CrO_2Cl_2 with N-heterocycles, amines or amides have been claimed on the basis of analytical and IR spectroscopic data,[31] but it appears that these are chloridooxidochromate(V) species with protonated N-base cations.[32] A literature search failed to find any clearly established examples of Cr^{VI} compounds with coordination numbers > 4, except in the oxide-fluorides[26] or imido complexes.[33]

Conclusions

A route to [$WO_2X_2(OPR_3)_2$] (X = Cl or Br) compounds using anhydrous conditions has been developed, and the (also anhydrous) fluorination of these and related complexes achieved using Me_3SnF. These routes should allow the synthesis of highly moisture sensitive WO_2X_2 (X = F, Cl or Br) complexes of soft ligands containing heavier groups 15 or 16 donors, and work is underway to test this approach in our laboratories.

Experimental Section

Infrared spectra were recorded as Nujol mulls between CsI plates with a Perkin–Elmer 983G spectrometer over the range 4000–200 cm^{-1}. ^1H and $^{19}F\{^1H\}$ NMR spectra were recorded with a Bruker AV300 spectrometer and referenced to TMS and $CFCl_3$, respectively. $^{31}P\{^1H\}$ and ^{95}Mo NMR spectra were recorded with a Bruker DPX400 spectrometer and are referenced to external 85% H_3PO_4 and aqueous Na_2MoO_4 at pH = 11, respectively. Microanalyses were undertaken by the University of Strathclyde microanalytical service. Solvents were dried prior to use and all preparations were undertaken using standard Schlenk techniques under N_2. WCl_6, $OPMe_3$ and $OPPh_3$ were obtained commercially (Alfa or Aldrich), while the other phosphane oxides were obtained by oxidation of the parent phosphane by the literature method.[34] The $OPMe_3$ was freshly sublimed in vacuo before use. WBr_6 was obtained by treatment of solid [$W(CO)_6$] with Br_2.[35] Me_3SnF was obtained by the literature methods.[36] CrO_2Cl_2 (Aldrich) was freshly distilled, and freeze/thaw degassed immediately before use.

[$WO_2Cl_2(OPMe_3)_2$]: WCl_6 (0.23 g, 0.58 mmol) and $(Me_3Si)_2O$ (0.19 g, 1.7 mmol) were stirred in anhydrous CH_2Cl_2 (30 cm^3) under N_2 when the red solution rapidly turned orange ($WOCl_4$) and then colourless. After 2 h, $OPMe_3$ (0.12 g, 1.3 mmol) in CH_2Cl_2 (10 cm^3) was added. The solution was stirred for a further ca. 2 h. The resulting colourless solution was filtered and the solvent removed in vacuo. The white solid was washed thoroughly with hexane (100 cm^3) and dried in vacuo. Yield 0.26 g, 95%. $C_6H_{18}Cl_2O_4P_2W$ (470.9): calcd. C 15.3, H 3.9; found C 15.2, H 4.1. ^1H NMR ($CDCl_3$): δ = 1.82 (d, $^2J_{PH}$ = 13.2 Hz, Me) ppm.

[$WO_2Cl_2(OPPh_3)_2$]: Method as above to give a white solid. Yield 91%. $C_{36}H_{30}Cl_2O_4P_2W \cdot CH_2Cl_2$ (928.2): calcd. C 47.9, H 3.5; found C 47.5, H 3.2. ^1H NMR ($CDCl_3$): δ = 7.30–7.75 (m, Ph) ppm.

[$WO_2Cl_2\{Ph_2P(O)CH_2P(O)Ph_2\}$]: Method as above to give a white solid. Yield 89%. $C_{25}H_{22}Cl_2O_4P_2W$ (703.2): calcd. C 42.7, H 3.1; found C 42.8, H 3.1. ^1H NMR ($CDCl_3$): δ = 3.86 (t, 2 H, CH_2), 7.35–7.90 (m, 20 H, Ph) ppm.

[$WO_2Cl_2\{Ph_2P(O)CH_2CH_2P(O)Ph_2\}$]: Method as above to give a white solid contaminated with WO_2Cl_2. The [$WO_2Cl_2\{Ph_2P(O)CH_2CH_2P(O)Ph_2\}$] was then re-dissolved in CH_2Cl_2 (10 cm^3) and filtered (to remove the WO_2Cl_2). Addition of Et_2O gave the complex as a white solid. Yield 64%. $C_{26}H_{24}Cl_2O_4P_2W$ (717.8): calcd. C 43.6, H 3.4; found C 44.3, H 3.4. ^1H NMR ($CDCl_3$): δ = 7.50–7.85 (m, 20 H, Ph), 2.67 (d, $^2J_{PH}$ = 10.5 Hz, 4 H, CH_2) ppm.

[$WO_2Cl_2\{o\text{-}C_6H_4[P(O)Ph_2]_2\}$]: Method as for [$WO_2Cl_2\{Ph_2P(O)CH_2CH_2P(O)Ph_2\}$] above to give a white solid. Yield 60%. $C_{30}H_{24}Cl_2O_4P_2W \cdot (C_2H_5)_2O$ (839.3): calcd. C 48.7, H 4.0; found C 49.6, H 4.3. ^1H NMR (CD_2Cl_2): δ = 7.30–7.90 (m, aromatic CH) ppm.

[$WO_2Br_2(OPMe_3)_2$]: WBr_6 (0.17 g, 0.26 mmol) with $(Me_3Si)_2O$ (0.08 g, 0.52 mmol) were stirred in CH_2Cl_2 (30 cm^3) under N_2 for 3 h until a pale cream solution was obtained and then $OPMe_3$ (0.05 g, 0.54 mmol) was added, and the solution was stirred overnight. The resulting solution was filtered and pumped to dryness. The white solid obtained was washed thoroughly with hexane (100 cm^3) and dried in vacuo. Yield 0.11 g, 76%. $C_6H_{18}Br_2O_4P_2W$ (559.8): calcd. C 12.9, H, 3.3; found C 13.5, H 4.4. ^1H NMR ($CDCl_3$): δ = 2.02 (d, $^2J_{PH}$ = 13.5 Hz, Me) ppm.

[$WO_2Br_2(OPPh_3)_2$]: Method as [$WO_2Br_2(OPMe_3)_2$] to give a white solid. Yield 82%. $C_{36}H_{30}Br_2O_4P_2W$ (932.2): calcd. C 46.4, H 3.2; found C 47.3, H 3.2. ^1H NMR ($CDCl_3$): δ = 7.35–7.80 (m, Ph) ppm.

[$WO_2Br_2\{Ph_2P(O)CH_2P(O)Ph_2\}$]: Method as [$WO_2Br_2(OPMe_3)_2$] to give a light yellow solid. Yield 94%. $C_{25}H_{22}Br_2O_4P_2W$ (792.1): calcd. C 37.9, H 2.8; found C 38.0, H 2.9. ^1H NMR ($CDCl_3$): δ = 4.12 (t, 2 H, CH_2), 7.40–7.95 (m, 20 H, Ph) ppm.

[$WO_2Br_2\{o\text{-}C_6H_4[P(O)Ph_2]_2\}$]: Method as for [$WO_2Cl_2\{Ph_2P(O)CH_2CH_2P(O)Ph_2\}$] above to give a yellow solid. Yield 69%. $C_{30}H_{24}Br_2O_4P_2W \cdot (C_2H_5)_2O$ (928.3): calcd. C 43.9, H, 3.7; found C 44.1, H 3.0. ^1H NMR ($CDCl_3$): δ = 7.33–7.85 (m, aromatic CH) ppm.

[$MoO_2F_2(OPPh_3)_2$]: [$MoO_2Cl_2(OPPh_3)_2$][6] (0.22 g, 0.29 mmol) was dissolved in dry dichloromethane (10 cm^3), powdered anhydrous Me_3SnF (0.158 g, 0.87 mmol) added and the mixture stirred for 24 h. The solution was filtered, and the filtrate treated dropwise with hexane (5 cm^3) to precipitate the complex as a white solid. This was filtered off, rinsed with hexane (5 cm^3) and dried in vacuo. Yield 0.18 g, 86%. $C_{36}H_{30}F_2MoO_4P_2 \cdot CH_2Cl_2$ (807.5): calcd. C 55.0, H 4.0; found C 54.9, H 3.9. ^1H NMR ($CDCl_3$): δ = 7.20–7.80 (m, Ph) ppm.

[$MoO_2F_2(OPMe_3)_2$]: Was prepared similarly. Yield 91%. $C_6H_{18}F_2MoO_4P_2 \cdot CH_2Cl_2$ (471.1): calcd. C 19.3, H 4.6; found C 19.2, H 4.7. ^1H NMR ($CDCl_3$): δ = 1.65 (d, $^2J_{PH}$ = 13.0 Hz, Me) ppm.

[$WO_2F_2(OPPh_3)_2$]: [$WO_2Cl_2(OPPh_3)_2$] (0.18 g, 0.24 mmol) was dissolved in dry CH_2Cl_2 (20 cm^3), powdered Me_3SnF (0.088 g, 0.48 mmol) added and the mixture stirred for 24 h. The solution was taken to dryness in vacuo, the residue washed with anhydrous hexane (20 cm^3), filtered, and the solid dissolved in anhydrous CH_2Cl_2 (50 cm^3). Any insoluble material was filtered off and discarded, and the filtrate concentrated to ca. 5 cm^3 and treated dropwise with hexane (5 cm^3) to precipitate the complex as a white solid. This was filtered off, rinsed with hexane (5 cm^3) and dried in vacuo. Yield 0.13 g, 64%. $C_{36}H_{30}F_2O_4P_2W$ (810.4): calcd. C 53.4, H 3.7. (Repeated attempts to obtain carbon analyses on samples of this compound gave values 5–8% low and with poor reproducibility; we believe this is a combustion problem, since the samples appeared identical and spectroscopically pure). ^1H NMR ($CDCl_3$): δ = 7.20–7.80 (m, Ph) ppm.

[$WO_2F_2(OPMe_3)_2$]. Method 1: In a Teflon® beaker, tungstic acid ("$H_2WO_4 \cdot nH_2O$") (0.15 g, ca. 0.5 mmol) was dissolved in a mixture of 40% HF (5 cm^3) and water (5 cm^3) with gentle warming to give a colourless solution. The solution was cooled, decanted from any solid and a solution of $OPMe_3$ (0.184 g, 2.0 mmol) in ethanol (15 cm^3) added. The solution was stirred for 2 h, then allowed to evaporate at room temperature. After 3 d colourless small crystals formed, the mother liquor was decanted off, the crystals rinsed with diethyl ether (5 cm^3) and dried in vacuo. Yield 0.12 g 54%.

Method 2: $[WO_2Cl_2(OPMe_3)_2]$ (0.11 g, 0.24 mmol) was dissolved in dry CH_2Cl_2 (50 cm^3), powdered Me_3SnF (0.09 g, 0.50 mmol) and the mixture stirred for 48 h. The solution was taken to dryness in vacuo, the residue stirred with anhydrous hexane (50 cm^3) for 3 h, the solid filtered off and dissolved in anhydrous CH_2Cl_2 (20 cm^3). Any insoluble material was filtered off and discarded, and the filtrate concentrated to ca. 5 cm^3 and treated dropwise with hexane (5 cm^3) to precipitate the complex as a white solid. This was filtered off and dried in vacuo. Yield 0.06 g, 57% Spectroscopically the two methods gave identical products. $C_6H_{18}F_2O_4P_2W$ (438.0): calcd. C 16.5, H 4.1; found C 16.4, H 3.8. ^1H NMR ($CDCl_3$): $\delta = 1.65$ (d, $^2J_{PH} = 13$ Hz) ppm.

$[WO_2Cl_2(1,10\text{-phen})]$: WCl_6 (0.27 g, 0.68 mmol) was suspended in dry CH_2Cl_2 (10 cm^3) and $(Me_3Si)_2O$ (0.22 g, 1.4 mmol) added, and the mixture stirred for 2 h during which time it turned colourless. A solution of 1,10-phen (0.12 g, 0.68 mmol) in dry CH_2Cl_2 (20 cm^3) was added and the mixture stirred for 2 h. The solution was filtered, and the product precipitated from the filtrate by slow addition of hexane (100 cm^3), filtered off, washed thoroughly with hexane (100 cm^3) and dried in vacuo. Yield 0.32 g, 84%. ^1H NMR ($CDCl_3$): $\delta = 8.06$ (m, 4 H), 8.64 (m, 2 H), 9.83 (m, 2 H) ppm. IR (Nujol): $\tilde{\nu} = 936$, 919 $\upsilon(WO_2)$, 320 $\upsilon(WCl)$ cm^{-1}.

$[WO_2Cl_2(2,2'\text{-bipy})]$: This was made analogously to the 1,10-phenanthroline complex above. Yield 85%. ^1H NMR ($CDCl_3$): $\delta = 7.08$ (m, 2 H), 8.30 (m, 4 H), 9.60 (m, 2 H) ppm. IR (Nujol): $\tilde{\nu} = 952$, 915 $\upsilon(WO_2)$, 338 $\upsilon(WCl)$ cm^{-1}.

$[WO_2F_2(1,10\text{-phen})]$: $[WO_2Cl_2(1,10\text{-phen})]$ (0.16 g, 0.34 mmol) was suspended in anhydrous $CHCl_3$ (80 cm^3), powdered anhydrous Me_3SnF (0.18 g, 0.98 mmol) added and the mixture refluxed for 48 h. The mixture was filtered and the filtrate concentrated to ca. 5 cm^3, then treated with hexane (5 cm^3) to precipitate the product, which was separated and dried in vacuo. Yield 0.10 g, 73%. ^1H NMR ($CDCl_3$): $\delta = 8.07$ (m, 4 H), 8.68 (m, 2 H), 9.85 (m, 2 H) ppm.

$[WO_2F_2(2,2'\text{-bipy})]$: Was made similarly to the above. Yield 78%. ^1H NMR (CD_2Cl_2): $\delta = 7.78$ (m, 2 H), 8.24 (m, 4 H), 9.43 (m, 2 H) ppm.

X-ray Crystallography: Details of the crystallographic data collection and refinement parameters are given in Table 7. Colourless crystals of $[WO_2Cl_2(OPMe_3)_2]$ and light-yellow crystals of $[WO_2Br_2(OPPh_3)_2]$ were obtained by cooling a solution of the appropriate complex in CH_2Cl_2. Crystals of $[WO_2Cl_2(1,10\text{-phen})]\cdot CH_2Cl_2$ were obtained by layering *n*-hexane onto a CH_2Cl_2 solution of the complex and the non-solvated complex isolated from an attempted synthesis of $[WO_2F_2(1,10\text{-phen})]$. Colourless crystals of $[Me_3SnCl(OPPh_3)]$ were obtained from the reaction mixture used to prepare $[WO_2F_2(OPPh_3)_2]$. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with Mo-K_α radiation ($\lambda = 0.71073$ Å) and either a graphite monochromator or confocal mirrors. The crystals were held at 120 K in a nitrogen gas stream. Structure solution and refinement were routine[37–39] with H atoms introduced into the models in calculated positions. The choice of space group for $[Me_3SnCl(OPPh_3)]$ depended on a few *0k*0 reflections. The reflections in this group were weaker than other zones and the choice of $P2_1/c$ or Pc-$P2/c$ was not as clear cut as one would wish. Both $P2_1/c$ and Pc were explored and $P2_1/c$ used on the basis of providing as good a fit to the data with less parameters and avoiding the high correlations found in Pc with two molecules in the asymmetric unit. The structure agrees with unpublished work.[40] Selected bond lengths and angles are given in Table 2, Table 3, Table 4 and Table 5.

CCDC-615946 (for W/Br/Ph), -615947 (for W/Cl/Me), -615949 (for W/Cl/N/CH_2Cl_2), C-615948 (for W/Cl/N), and -615950 (for Sn/Cl) contain the supplementary crystallographic data for this paper (the atoms in parentheses indicate the species in the compounds). These

Table 7. Crystal data and structure refinement details.[a]

Compound	$[WO_2Br_2(OPPh_3)_2]$	$[WO_2Cl_2(OPMe_3)_2]$	$[WO_2Cl_2(1,10\text{-phen})]\cdot CH_2Cl_2$	$[WO_2Cl_2(1,10\text{-phen})]$	$[Me_3SnCl(OPPh_3)]$
Formula	$C_{36}H_{30}Br_2O_4P_2W$	$C_6H_{18}Cl_2O_4P_2W$	$C_{13}H_{10}Cl_4N_2O_2W$	$C_{12}H_8Cl_2N_2O_2W$	$C_{21}H_{24}ClOPSn$
M	932.21	470.89	551.88	466.95	477.51
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)
a [Å]	18.883(3)	10.521(2)	8.9590(10)	13.718(4)	12.7036(10)
b [Å]	9.9430(15)	11.485(2)	13.389(3)	9.794(3)	8.5432(10)
c [Å]	19.043(3)	12.256(3)	13.226(3)	11.500(4)	20.293(2)
α [°]	90	90	90	90	90
β [°]	110.937(7)	92.338(8)	95.385(13)	121.752(15)	98.892(5)
γ [°]	90	90	90	90	90
U [$Å^3$]	3339.4(8)	1479.8(5)	1579.5(5)	1313.8(7)	2175.9(4)
Z	4	4	4	4	4
μ [mm^{-1}]	5.987	8.376	7.995	9.195	1.376
F(000)	1808	896	1040	872	960
Total no. of observations (R_{int})	43216 (0.059)	12465 (0.031)	21531 (0.038)	8473 (0.038)	22531 (0.039)
Unique observations	7650	3387	3604	1497	4980
Min., max. transmission	0.796, 1.000	0.723, 1.000	0.702, 1.000	0.599, 1.000	0.768, 1.000
No. of parameters, restraints	406, 0	143, 0	199, 0	87, 0	226, 0
Goodness-of-fit on F^2	1.04	1.07	1.05	1.02	1.04
Residual electron density [e $Å^{-3}$]	–0.99 to +1.15	–1.31 to +0.57	–0.68 to +0.65	–1.54 to +0.71	–0.82 to +0.92
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.039, 0.081	0.021, 0.043	0.022, 0.044	0.024, 0.058	0.036, 0.081
R_1, wR_2 (all data)	0.062, 0.088	0.026, 0.044	0.026, 0.046	0.028, 0.060	0.048, 0.087

[a] Common items: temperature = 120 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \Sigma\| F_o| - |F_c\|/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$.

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data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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