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Phosphine and diphosphine complexes of tungsten(VI) oxide tetrafluoride

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ABSTRACT

The reaction of $[WOF_4(MeCN)]$ with the diphosphines, $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(PMe_2)_2$, in anhydrous Et_2O produced high yields of [WOF_4(diphosphine)], the X-ray crystal structures of which reveal seven-coordinate pentagonal bipyramidal molecules with axial O/F. In contrast, the reaction of $[WOF_4(MeCN)]$ and PMe_3 forms the six-coordinate $[WOF_4(PMe_3)]$. These unusual W(VI) complexes have been characterised by microanalysis, IR, ^{1}H, $^{19}F\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectroscopy. The second-order $^{19}F\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of the [WOF_4(diphosphine)] have been analysed. Similar complexes do not form with the other o-phenylene-linked bidentate ligands, o-$C_6H_4(PPh_2)_2$, o-$C_6H_4(AsMe_2)_2$ or o-$C_6H_4(SMe)_2$.

1. Introduction

Soft-donor neutral ligand complexes of early d-block metal oxide fluorides are very rare, even more so than the corresponding binary fluoride complexes [1]. Very unstable $[VOF_3(RSCH_2CH_2SR)]$ (R = Me, Et, ^{i}Pr) have been isolated, but decompose in a few hours, whilst phosphines, arsines and selenoethers reduce VO_2F or VOF_3 to lower oxidation states [2,3]. Complexes of $NbOF_3$ with hard N- or O-donors can be prepared from NbF_5, $(Me_3Si)_2O$ and the ligand in anhydrous MeCN, but attempts to isolate phosphine, arsine or thioether complexes failed, with only (polymeric) $NbOF_3$ being formed [4]. In contrast, complexes of NbF_5 with soft (P, As, S or Se) donors have been fully characterised [5–7]. We recently reported a general route to complexes of WOF_4 with nitrogen- or oxygen-donor ligands, including $[WOF_4(L)]$ (L = py, Me_3PO, Ph_3PO, Me_2SO) using substitution of the MeCN in $[WOF_4(MeCN)]$ [8] with the neutral ligand in MeCN or CH_2Cl_2 solution. $[WOF_4(MeCN)]$ is a convenient synthon, easily prepared from WF_6 and $(Me_3Si)_2O$ in a 1:1 molar ratio in anhydrous MeCN solution. Reaction of $[WOF_4(L)]$ with more ligand, together with a second equivalent of $(Me_3Si)_2O$, produced the distorted octahedral $[WO_2F_2(L)_2]$ [8]; the complexes $[WO_2F_2(L–L)]$ (L–L = $Ph_2P(O)CH_2P(O)Ph_2$ or 1,10-phenanthroline) were also obtained. Attempts to prepare analogues with soft-donor ligands such as thioethers, selenoethers or arsines were unsuccessful, with these soft-donor ligands failing to displace the MeCN ligands.

Here we report examples of phosphine complexes of the mono-oxido tetrafluorido tungsten, WOF_4, the successful syntheses being very dependent upon the particular phosphine, the solvent and the reaction conditions. Two examples of type $[WF_6(PR_3)]$ ($R_3 = Me_3$, Me_2Ph) have been characterised as yellow and red crystals respectively, both seven-coordinate, the former a capped trigonal prism and the latter a capped octahedron [9]. Phosphine complexes of $WOCl_4$ have been described [10], but lack X-ray crystallographic authentication, although the structure of the green, pentagonal bipyramidal [$WOCl_4${o-$C_6H_4(AsMe_2)_2$}], which has axial O/Cl donors, has been reported [11,12].

2. Results and discussion

2.1. Synthesis and structures of [WOF_4(diphosphine)]

Reaction of $[WOF_4(MeCN)]$ with one equivalent of the diphosphines $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(PMe_2)_2$ in anhydrous Et_2O solution produced high yields of the complexes [WOF_4(diphosphine)] as white, highly moisture sensitive powders. Attempts to obtain these complexes using MeCN or CH_2Cl_2 as solvents were unsuccessful. The success of Et_2O as solvent, despite the fact that

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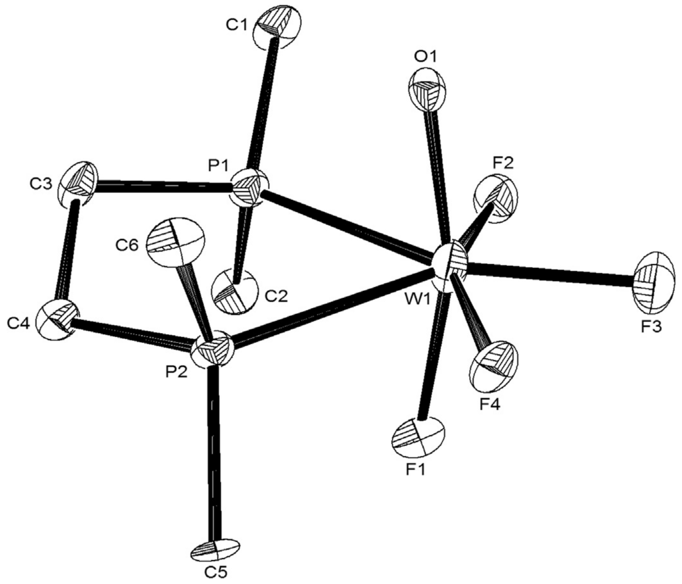


Fig. 1. The structure of [$WOF_4(Me_2PCH_2CH_2PMe_2)$] showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. There was disorder in the axial F/O and only the major component is shown. Selected bond lengths (Å) and angles (°): W1–O1 = 1.757(12), W1–F1 = 1.923(9), W1–F3 = 1.924(3),W1–F2 = 1.960(4), W1–F4 = 1.959(4), W1–P1 = 2.5584(18), W1–P2 = 2.5714(17), O1–W1–F1 = 163.6(5), O1–W1–F3 = 100.4(5), F1–W1–F3 = 95.9(3), O1–W1–F4 = 90.7(5), F1–W1–F4 = 91.8(3), F3–W1–F4 = 76.30(16), O1–W1–F2 = 97.5 (5), F1–W1–F2 = 87.3(3), F3–W1–F2 = 77.72(16), O1–W1–P1 = 83.1(5), F1–W1–P1 = 84.5(3), F2–W1–P1 = 67.06(11), O1–W1–P2 = 86.5(5), F1–W1–P2 = 79.6(3), F4–W1–P2 = 66.99(10), P1–W1–P2 = 72.15(6).

the hard oxygen donor ether might be expected to be a better donor to a very hard Lewis acid than a soft phosphine, lies in the fact that the complexes precipitate from the reaction mixture immediately on formation. (We did not observe any evidence for diethyl ether adducts in the NMR spectra of the isolated phosphine complexes). CH_2Cl_2 fails as a solvent since the Lewis acidic tungsten centre promotes protonation/quaternisation of the phosphine by the solvent [1,5,6]. In the case of MeCN the phosphine complexes are soluble in this solvent and it is likely that a mixture of phosphine and nitrile complexes and "free" phosphine are present, and the latter can reduce the tungsten. In many high valent metal systems [1] there is some competition between complexation of the phosphine (fast) and redox chemistry (slower). Coordinated phosphine does not produce metal reduction, hence the Et_2O solvent system, from which the complex with bound phosphine precipitates is successful.

The isolated solid complexes appear stable under a dry dinitrogen atmosphere for several weeks. Colourless crystals of [$WOF_4(Me_2PCH_2CH_2PMe_2)$] were grown by evaporation of a solution in anhydrous CH_2Cl_2. The refinement revealed disorder of the axial O/F atoms which was satisfactorily modelled as two components in the ratio 68:32 (Section 3.4) (Fig. 1).

Several batches of crystals were grown from CH_2Cl_2 solutions of [$WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}$] and all showed a similar pentagonal bipyramidal geometry to [$WOF_4(Me_2PCH_2CH_2PMe_2)$], but also O/F disorder of the two axial ligands. Attempts to model the disorder were not successful in this case and the highest quality data set led to the structure in Fig. 2. The bond lengths in the pentagonal plane are not significantly different to those in [$WOF_4(Me_2PCH_2CH_2PMe_2)$], although because of the disorder present, comparisons of the metrical parameters should be made with due care.

The structure of the pentagonal bipyramidal [$WOF_4(py)_2$] was reported to show axial fluorides with an OF_2N_2 donor set in the pentagonal plane [13], but a subsequent NMR study showed the structure to contain axial O/F donors, and concluded that the crystal structure had contained unrecognised disorder of the axial O/F groups [14] and thus the bond length data are unreliable. The [$WOF_4(2,2'\text{-bipy})$] and [$WOF_4(napy)$] (napy = 1,8-naphthyridine, 2,7-Me_2-1,8-naphthyridine) [15,16], which are probably of similar structure to [$WOF_4(Me_2PCH_2CH_2PMe_2)$], were insoluble in most solvents precluding the growth of crystals. The structure of the pentagonal bipyramidal [$WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}$] is of low precision, but has axial O/Cl donors with d(W=O) = 1.89(4) Å [11]. In the [WOF_4(diphosphine)] species the axial O–W–F units are bent towards the diphosphine, O1–W1–F1 ~164°. Both the d (W=O) and the d(W–F) are longer in [$WOF_4(Me_2PCH_2CH_2PMe_2)$] than in the six-coordinate [$WOF_4(OPPh_3)$] and [WOF_4(F-py)] [8,13], which can largely be attributed to the higher coordination number.

Attempts to isolate analogous complexes with the softer and weaker σ-donor diphosphine $o\text{-}C_6H_4(PPh_2)_2$, the diarsine, o-

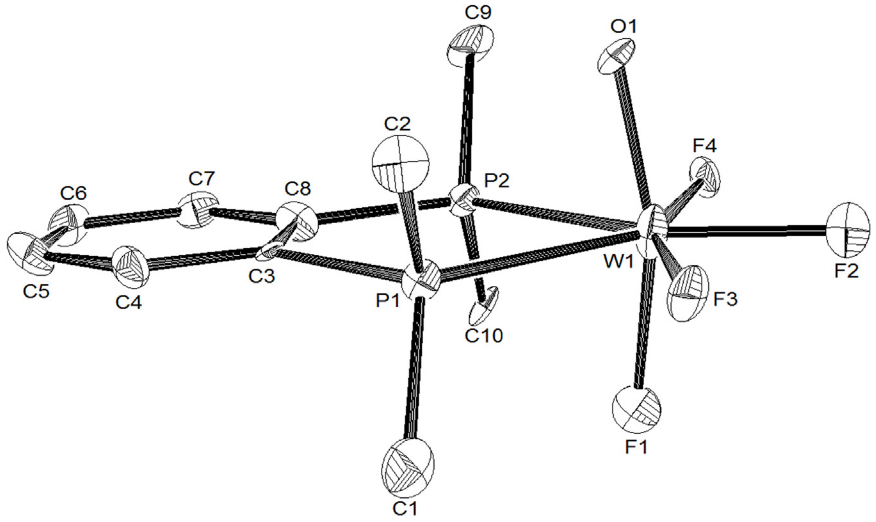


Fig. 2. The structure of [$WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Note that F1/O1 are disordered. Selected bond lengths (Å) and angles (°): W1–O1 = 1.792(7), W1–F1 = 1.843(6), W1–F3 = 1.959(6), W1–F2 = 1.891(7), W1–F4 = 1.957(6), W1–P1 = 2.554(3), W1–P2 = 2.554(3), O1–W1–F1 = 164.3(3), O1–W1–F2 = 99.5(3), F1–W1–F2 = 96.2(3), O1–W1–F4 = 92.2(3), F1–W1–F4 = 92.6(3), F2–W1 F4 = 76.8(3), O1–W1–F3 = 91.8(3), F1–W1–F3 = 90.3(3), F2–W1–F3 = 77.5(3), O1–W1–P2 = 84.9(2), F1–W1–P2 = 83.4(2), F4–W1–P2 = 66.32(19), O–1W1–P1 = 82.1(2), F1–W1–P1 = 84.5(2), F3–W1–P1 = 66.98(19), P2–W1–P1 = 72.49(9).

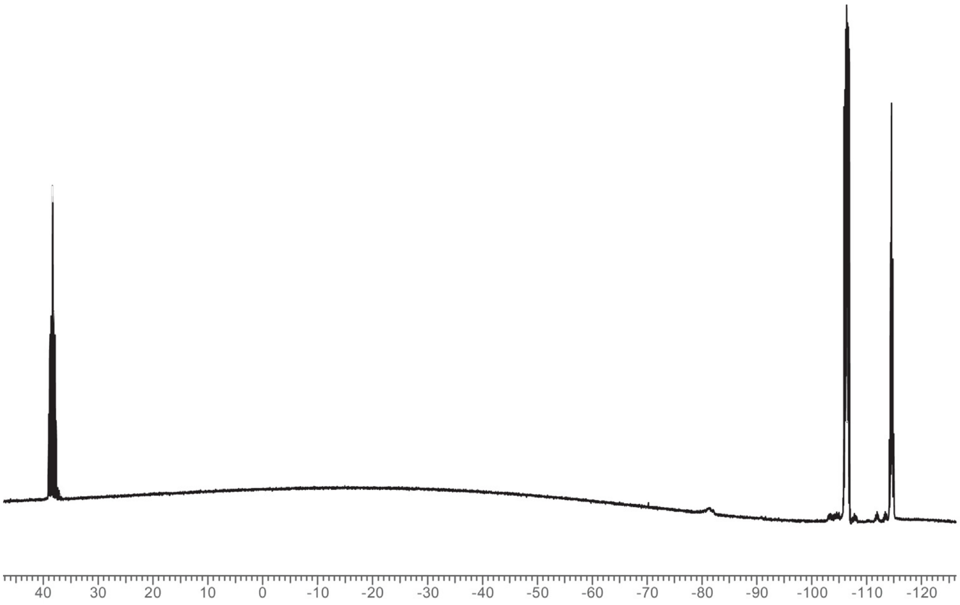


Fig. 3. $^{19}F\{^1H\}$ NMR spectrum of $[WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ in CH_2Cl_2/CD_2Cl_2 at 293 K.

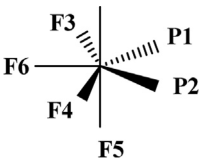
$C_6H_4(AsMe_2)_2$ or the dithioether, *o*-$C_6H_4(SMe)_2$, by reaction with $[WOF_4(MeCN)]$ in Et_2O failed, and there was no evidence from *in situ* NMR spectroscopy that such complexes formed. The synthesis of $[WOF_4(2,2'\text{-bipy})]$ has been described and was suggested to have a seven coordinate geometry, but attempts to grow crystals resulted in the isolation of $[WO_2F_2(2,2'\text{-bipy})]$ probably formed by disproportionation [16]. We re-prepared $[WOF_4(2,2'\text{-bipy})]$ and our IR spectrum is essentially identical with that reported [16], but we too were unable to obtain solution NMR spectra due to its insolubility in CH_2Cl_2, MeCN or $MeNO_2$, whilst dmso displaced the diimine.

Attempts to obtain the corresponding $[WO_2F_2(\text{diphosphine})]$ by treatment of a suspension of $[WOF_4(\text{diphosphine})]$ in Et_2O, or as a solution in CH_2Cl_2 or in Et_2O containing 5% MeCN, with a further equivalent of $(Me_3Si)_2O$, were unsuccessful, the multinuclear NMR data showing that no reaction occurred. Over a longer period, the solution decomposed, but there was no evidence for the formation of $[WO_2F_2(\text{diphosphine})]$, which would be expected to have characteristic fingerprints in the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra [8].

2.2. Spectroscopic properties

The IR spectra of $[WOF_4(Me_2PCH_2CH_2PMe_2)]$ and $[WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ exhibit $\nu(W=O)$ at 957 and 961 cm^{-1}, respectively. The lower frequency compared to that in $[WOF_4(PMe_3)]$ ($\nu(W=O) = 982\ cm^{-1}$, below) reflects the higher coordination number; *cf.* $[WOF_4(2,2'\text{-bipy})]$ with $\nu(W=O)$ at 968 cm^{-1} [16], $[WOF_4(py)_2]$ at 973 cm^{-1} [13], and 964 cm^{-1} in $[WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ [12]. Despite the unsuitability of chlorocarbons as solvents for the synthesis, NMR spectra were readily obtained from *freshly prepared* CH_2Cl_2/CD_2Cl_2 solutions, since it is the free phosphine which reacts with the chlorocarbon; similar observations were made in the case of $[NbF_4(PR_3)_2][NbF_6]$ [6]. The complexes decompose slowly on standing in CH_2Cl_2 solution. The ^1H NMR spectra are consistent with the X-ray structures and indicate that the complexes are static on the NMR timescale in solution. In particular, the spectra of both complexes shows two CH_3 multiplet resonances of equal intensity, from CH_3 groups *syn* and *anti* to the W=O unit. The $^{19}F\{^1H\}$ NMR spectra contain three widely spaced multiplets with integrals 1:2:1 (Fig. 3), and the $^{31}P\{^1H\}$ NMR spectrum is a single multiplet. The weak ^{183}W satellites (^{183}W, $I = {}^1/_2$, 14.3%) were not clearly resolved.

2.3. Analysis of the NMR spectra



The six interacting nuclear spins in the proton-decoupled spectra form are conveniently divided into the set 1–4, which are described as an AA′XX′ second-order system, comprising P1, P2, F3 and F4, which has first-order coupling to F5 and F6. The partial spectra given by F5 and F6 can each be analysed as comprising a triplet of triplets of doublets, as shown in Figs. 4 and 5.

The four nuclei P1, P2, F3 and F4 do not have a first-order spectrum. The two ^{31}P nuclei are chemically, but not magnetically equivalent, as are F3 and F4. As a consequence, this part of the total spectrum is that of a AA′XX′ second-order spin system, which is

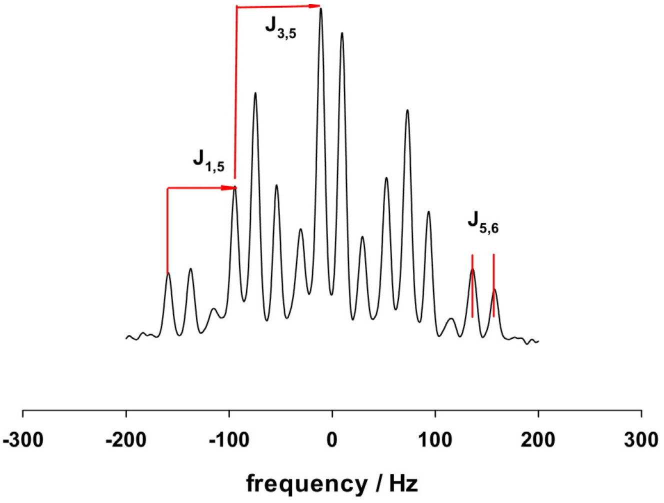


Fig. 4. $^{19}F\{^1H\}$ 376 MHz spectrum from F5 in $[WOF_4(Me_2PCH_2CH_2PMe_2)]$. The multiplet is centred on +36.7 ppm from external $CFCl_3$.

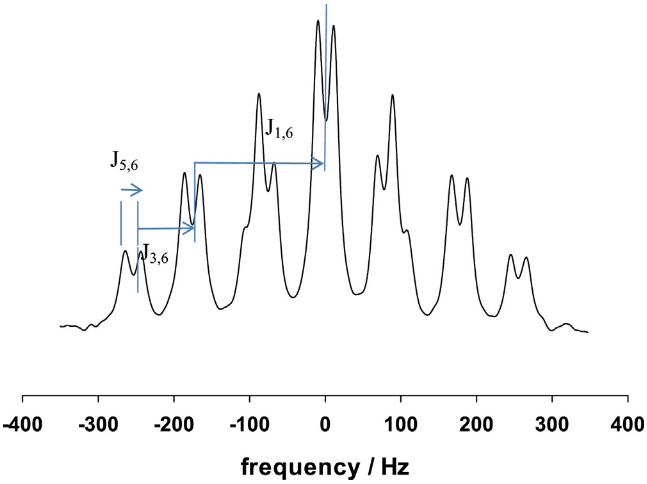


Fig. 5. $^{19}F\{^1H\}$ 376 MHz spectrum from F6 in [$WOF_4(Me_2PCH_2CH_2PMe_2)$]. The multiplet is centred on −117.0 ppm from external $CFCl_3$.

characterised by chemical shifts δ_A and δ_X, four coupling constants $J_{AA'} \equiv J_{1,2}$, $J_{XX'} \equiv J_{3,4}$, $J_{AX} \equiv J_{1,3} = J_{A'X'} \equiv J_{2,4}$, $J_{AX'} \equiv J_{1,4} = J_{A'X} \equiv J_{2,3}$. Analysis of an AA′XX′ spin system can yield values for all these coupling constants, but cannot distinguish between $J_{AA'}$ and $J_{XX'}$, nor between J_{AX} and $J_{AX'}$ [17]. This fundamental property of a one-dimensional AA′XX′ spectrum can be overcome by appropriate double-resonance, or two-dimensional correlation experiments, but these experiments were not possible on the two samples studied here, primarily because the compounds are not sufficiently stable for these long duration experiments. Figs. 6 and 7 show the resonances of P1 and P2 and F3 and F4.

The spectra were analysed using an iterative computer program ARCANA [19]. There are a total of 10 A and 10 X possible transitions, and coupling to F5 and F6 leads to a possible total 40 transitions for P1 and P2, and 40 for F3 and F4. The observed spectra for these four nuclei contain far fewer lines, and analysis of the spectrum requires assigning lines in the spectra of both groups P1, P2 and F3, F4 and iterating on the values of $J_{1,2}$, $J_{1,3} = J_{2,4}$, $J_{1,4} = J_{2,3}$ and $J_{3,4}$ whilst keeping $J_{1,5} = J_{2,5}$, $J_{1,6} = J_{2,6}$, $J_{3,5} = J_{4,5}$, $J_{3,6} = J_{4,6}$ fixed at the values obtained from separate analysis of the peaks from F5 and F6. The chemical shifts and coupling constants are listed in Table 2.

2.4. [$WOF_4(PR_3)$] complexes

The reaction of various tertiary phosphines with [$WOF_4(MeCN)$] was attempted using MeCN, CH_2Cl_2, Et_2O, toluene and chlorobenzene as solvents, of which only Et_2O proved suitable. The reaction of alkylphosphines with [$WOF_4(MeCN)$] in a 1: 1 molar ratio in anhydrous MeCN failed to displace the MeCN cleanly, whilst using excess phosphine produced intensely coloured solutions (blue or orange depending on the phosphine) which showed only small amounts of [$W_2O_2F_9$]$^-$ [15] and [HF_2]$^-$ in their ^{19}F NMR spectra. The deep colours suggest lower oxidation state paramagnetic (and hence NMR-silent) tungsten species had formed. In anhydrous CH_2Cl_2 similar reactions produced blue insoluble precipitates and the supernatant solutions contained the same tungsten fluoroanion, whilst the $^{31}P\{^1H\}$ NMR spectra showed some phosphine oxide, but mainly the phosphonium ([PR_3H]$^+$) cations. The promotion of quaternisation of the phosphine by strong Lewis acids in halocarbon solutions has been observed in other systems, including with NbF_5 and TiF_4 [5,6,18]. Successful use of Et_2O depends upon the phosphine complex being poorly soluble and hence its precipitation (see above) drives the reaction and removes the reducing free phosphine from the reaction.

[$WOF_4(MeCN)$] is poorly soluble in anhydrous Et_2O, but on addition of one molar equivalent of PMe_3 to a stirred suspension of [$WOF_4(MeCN)$], a clear solution formed, and concentration of the solution *in vacuo*, led to precipitation of a slightly bluish-white powder. The powder was identified as [$WOF_4(PMe_3)$] by microanalysis and multinuclear NMR spectroscopy. An excess of phosphine in the reaction immediately produced a deep blue oil. The ^1H NMR spectrum of a freshly prepared solution shows only coordinated PMe_3, whilst the $^{19}F\{^1H\}$ NMR spectrum contains a doublet at $\delta = +49.0$ ($^2J_{PF} = 93$ Hz) with weak ^{183}W satellites ($^1J_{WF} = 62$ Hz). The ^{19}F chemical shift is ~20 ppm to low frequency of those found in corresponding N- or O-donor complexes [8]. Confirmation of the identity of the complex comes from the $^{31}P\{^1H\}$ NMR spectrum which contains a binomial quintet at $\delta = +44.8$, a coordination shift of ~+107 ppm. The IR spectrum exhibits $\nu(W=O)$ at 982 cm^{-1}, similar to other six-coordinate complexes of WOF_4 [8]. The instability in solution prevented growth of crystals for an X-ray study, but the NMR data clearly confirm the pseudo-octahedral geometry with O *trans* to P, as expected.

The reaction of [$WOF_4(MeCN)$] with P^nPr_3 or $PPhMe_2$, in a 1:1 molar ratio in anhydrous Et_2O, precipitated white solids, but these rapidly turned yellow and then brown. The white solids could be

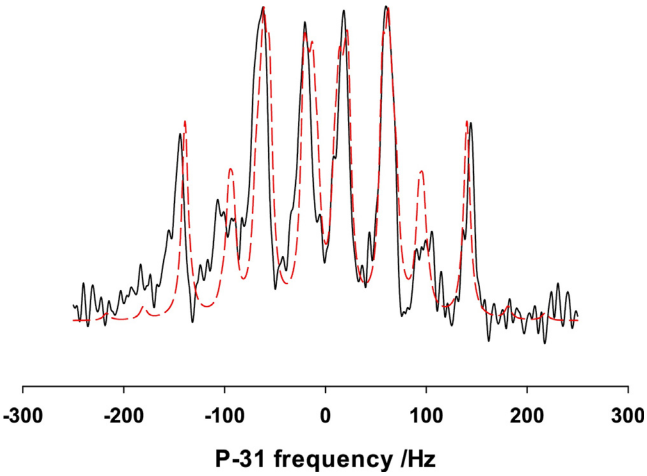


Fig. 6. 162 MHz $^{31}P\{^1H\}$ spectrum (black, continuous line) and calculated (red, dashed line) for [$WOF_4(Me_2PCH_2CH_2PMe_2)$],. The multiplet is centred on +80.3 ppm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

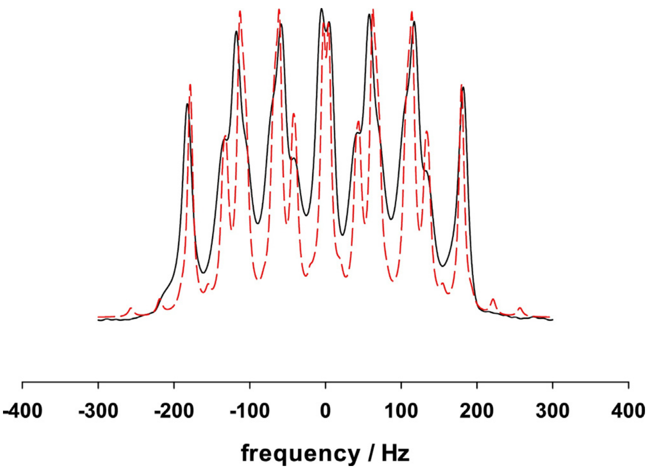


Fig. 7. $^{19}F\{^1H\}$ 376 MHz spectrum (black, continuous line) and calculated (red, dashed line) for F3 and F4 in [$WOF_4(Me_2PCH_2CH_2PMe_2)$]. The multiplet is centred on −107.7 ppm from external $CFCl_3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 1
X-ray crystallographic data.[a]

Compound	$[WOF_4(Me_2PCH_2CH_2PMe_2)]$	$[WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$
Formula	$C_6H_{16}F_4OP_2W$	$C_{10}H_{16}F_4OP_2W$
M	425.98	474.02
Crystal system	Monoclinic	Orthorhombic
Space group (no.)	$P2_1/c$ (14)	$P2_12_12_1$ (19)
a/Å	7.8096(10)	6.058(2)
b/Å	10.9262(10)	14.199(3)
c/Å	13.869(2)	16.071(3)
α/°	90	90
β/°	97.873(12)	90
γ/°	90	90
U/Å^3	1172.3(3)	1382.4(6)
Z	4	4
μ(Mo-K$_\alpha$)/mm^{-1}	10.147	8.618
F(000)	800	896
Total number reflns	6314	7254
R_{int}	0.081	0.064
Unique reflns	2306	2721
No. of params, restraints	150, 32	168, 7
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.038, 0.061	0.040, 0.098
R_1, wR_2 (all data)	0.061, 0.068	0.059, 0.109

[a] Common items: $T = 293$ K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°.
[b] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; w$R_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma wFo^4]^{1/2}$.

isolated by immediate decantation of the solvent, but darkened to brown and became sticky over a few hours at ambient temperature. The NMR spectra in CD_2Cl_2 of the freshly prepared complexes, *recorded immediately*, identify them as *containing* $[WOF_4(PR_3)]$ although even then, significant decomposition is evident, Despite numerous attempts, we have been unable to obtain spectra free from large amounts of decomposition products and thus the data are not presented. In contrast, the reaction of $[WOF_4(MeCN)]$ with PPh_3 in a 1:1 molar ratio in anhydrous Et_2O gave a large amount of unidentified insoluble blue precipitate, and the colourless supernatant solution showed $[W_2O_2F_9]^-$ ($^{19}F\{^1H\}$: 62.4 (d, [8F], $^2J_{FF}$ = 60 Hz); −144.8 (m, [F]), some $[WOF_4(OPPh_3)]$ [8], $OPPh_3$ (δ_P = +28.0) and $[PPh_3H]^+$ (δ_P = +3.5, d, $^1J_{HP}$ = 510 Hz). In this case there was no evidence for $[WOF_4(PPh_3)]$ being formed.

2.5. Molybdenum analogues

There appear to be no neutral ligand complexes derived from $MoOF_4$ in the literature [1] apart from a mention of $[MoOF_4(OPPh_3)]$ identified *in situ* by ^{19}F NMR spectroscopy [20]. The addition of PMe_3, $AsMe_3$, $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(SMe)_2$ to a suspension of $[MoOF_4(MeCN)]$ [21] in Et_2O gave dark sticky red-brown or black precipitates immediately and it seems that these soft-donor ligands reduce the $MoOF_4$ upon contact.

3. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000−200 cm^{-1}. ^1H, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded using a Bruker AV-II 400 spectrometer and are referenced to the residual proton resonance from the solvent, external $CFCl_3$ and 85% H_3PO_4 respectively. Microanalyses were undertaken by London Metropolitan University. Solvents were dried prior to use: Et_2O by distillation from sodium benzophenone ketyl, MeCN and CH_2Cl_2 from CaH_2. Phosphine ligands were obtained commercially (Aldrich or Strem) and used as received, except for *o*-$C_6H_4(PMe_2)_2$ which was made as described [22]. The *o*-$C_6H_4(AsMe_2)_2$ [23] and *o*-$C_6H_4(SMe)_2$ [24] were also made by literature methods and $[WOF_4(MeCN)]$ was made as described previously [8]. All reactions were carried out under dinitrogen in rigorously dry solvents, using Schlenk and glove box techniques.

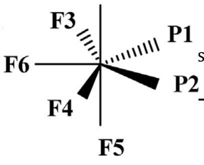
CARE: WF_6 is highly corrosive and causes serious burns on skin contact, and the complexes described below produce HF on hydrolysis. Appropriate safety equipment should be worn.

3.1. $[WOF_4(PMe_3)]$

Powdered $[WOF_4(MeCN)]$ (0.32 g, 1.0 mmol) was stirred in diethyl ether (10 mL) and PMe_3 (0.075 g, 1.0 mmol) in diethyl ether (5 mL) added dropwise, when a clear, colourless solution formed. After *ca.* 5 min a solid started to deposit and the solvent was concentrated to 3 mL *in vacuo*. The solid was filtered off, rinsed with diethyl ether (3 mL) and dried *in vacuo*. Yield: 0.28 g, 80% of a slightly bluish white solid. Calc. for $C_3H_9F_4OPW$ (351.9): C, 10.30; H, 2.54. Found: C, 10.90; H, 2.62%. IR (Nujol/cm^{-1}): 982 (*vs*) W=O, 570 (s), 536 (m) W−F. ^1H NMR (CD_2Cl_2, 293 K): δ = 1.98 (d, $^2J_{HP}$ = 16 Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = +49.0 (d, $^2J_{PF}$ = 93 Hz, $^1J_{WF}$ = 62 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = +44.8 (quintet, $^2J_{PF}$ = 93 Hz).

3.2. $[WOF_4(Me_2PCH_2CH_2PMe_2)]$

$[WOF_4(MeCN)]$ (0.20 g, 0.66 mmol) was suspended in diethyl ether (15 mL) and the mixture stirred whilst $Me_2PCH_2CH_2PMe_2$ (0.10 g, 0.66 mmol) was added, producing an immediate white precipitate. The stirring was continued for 2 h, then the very pale bluish white powder filtered off, rinsed with diethyl ether (2 mL) and dried *in vacuo*. Yield: 0.20 g, 71%. Calc. for $C_6H_{16}F_4OP_2W$ (426.0): C, 16.92; H, 3.65. Found: C, 16.78; H, 3.65%. IR (Nujol/cm^{-1}): 957 (*vs*) W=O, 568 (s), 525 (s), 507 (m), 490 (m) W−F. ^1H NMR (CD_2Cl_2, 293 K): δ = 1.83 (t, [3H], $^{2+5}J_{HP}$ = 10 Hz), 2.05 (t, [3H], $^{2+5}J_{HP}$ = 10 Hz), 2.58 (m, [2H], $J \sim 12$ Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = 36.7 (m, [F]), −107.7 (m, [2F]), −117.0 (m, [F]). $^{31}P\{^1H\}$



shifts, δ_i/ppm, and spin-spin coupling constants, $J_{i,j}$/Hz, obtained from analysis of the ^{31}P and ^{19}F spectra of samples dissolved in CH_2Cl_2 at 9.4 T.

	Chemical shifts, ppm			
	$\delta_1 = \delta_2$	$\delta_3 = \delta_4$	δ_5	δ_6
$[WOF_4(Me_2PCH_2CH_2PMe_2)]$	+80.3	−107.7	+36.7	−117.0
$[WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$	+75.5	−106.4	+38.3	−111.0

	Coupling constants/Hz			
	$|J_{1,2}|$ (or $J_{3,4}$)	$|J_{3,4}|$ (or $J_{1,2}$)	$J_{1,3} = J_{2,4}$ (or $J_{1,4} = J_{2,3}$)	$J_{1,4} = J_{2,3}$ (or $J_{1,3} = J_{2,4}$)
$[WOF_4(Me_2PCH_2CH_2PMe_2)]$	20.3 ± 1.2	104.6 ± 1.2	±19.7 ± 0.9	±97.8 ± 0.9
$[WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$	28.3 ± 3.1	115.4 ± 3.1	±22.5 ± 0.3	±108.1 ± 0.3

	$J_{1,5} = J_{2,5}$	$J_{3,5} = J_{4,5}$	$J_{1,6} = J_{2,6}$	$J_{3,6} = J_{4,6}$	$J_{5,6}$
$[WOF_4(Me_2PCH_2CH_2PMe_2)]$	±78.0 ± 0.3	±175.0 ± 0.3	±83.5 ± 0.4	±65.0 ± 0.3	±20.0 ± 0.5
$[WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$	±79.3 ± 0.9	±177.0 ± 0.7	±82.9 ± 0.8	±64.5 ± 0.7	±20.2 ± 0.3

NMR (CD_2Cl_2, 293 K): δ = +80.3 (m). Colourless crystals were grown by slow evaporation from a CH_2Cl_2 solution of the complex in the glove box.

3.3. [$WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}$]

[$WOF_4(MeCN)$] (0.20 g, 0.66 mmol) was suspended in diethyl ether (15 mL) and the mixture stirred whilst *o*-$C_6H_4(PMe_2)_2$ (0.13 g, 0.66 mmol) was added, producing an immediate off-white precipitate. The stirring was continued for 1 h, then the very pale bluish-white powder filtered off and rinsed with diethyl ether (2 mL). It was redissolved in CH_2Cl_2 (10 mL), the solution filtered to remove some insoluble blue solid, and the solvent removed *in vacuo*. Yield: 0.25 g, 82%. Calc. for $C_{10}H_{16}F_4OP_2W{\cdot}CH_2Cl_2$ (559.0): C, 23.6; H, 3.3. Found: C, 23.5; H, 3.0%. IR (Nujol/cm^{-1}): 961 (*vs*) W = O, 584 (*vs*), 537 (*vs*), 517 (m), 496 (m) W—F. ^{1}H NMR (CD_2Cl_2, 293 K): δ = 2.04 (t, [3H], $^{2+5}J_{HP}$ = 7 Hz), 2.29 (t, [3H], $^{2+5}J_{HP}$ = 7 Hz), 5.3 (s, CH_2Cl_2), 7.76 s, ([2H]), 8.00 (s, [2H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = 38.3 (m, [F]), −106.4 (m, [2F]), −111.0 (m, [F]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ = +75.5 (m). Crystals were grown by slow evaporation from a CH_2Cl_2 solution of the complex in the glove box.

3.4. X-ray experimental

Crystals of the two diphosphine complexes were grown from CH_2Cl_2 solution as described above. 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 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2013 or SHELX-2014/7 [25]. The axial O/F disorder in [$WOF_4(Me_2PCH_2CH_2PMe_2)$] was modelled by splitting the disordered atom into two positions and allowing the occupancy to refine. The data converged with ratio 0.68:0.32. The axial O/F disorder in [$WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}$] could not be modelled satisfactorily, however. H atoms bonded to C were placed in calculated positions using the default C–H distance, and refined using the riding model. Details of the crystallographic parameters are given in Table 1. CCDC reference numbers in cif format are [$WOF_4(Me_2PCH_2CH_2PMe_2)$] CCDC 1525769 and [$WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}$] CCDC 1525768.

4. Conclusions

Two rare examples of soft donor phosphine complexes with a hexavalent early d-block oxide fluoride, [WOF_4(diphosphine)], have been prepared and characterised both structurally (single crystal X-ray) and spectroscopically (IR and multinuclear NMR). The second-order ^{19}F and ^{31}P NMR spectra have been satisfactorily analysed. The pentagonal bipyramidal molecules are rigid in solution, contrasting with the fluxional [$WF_6(PR_3)$]. Tertiary alkyl phosphines form related six-coordinate complexes [$WOF_4(PR_3)$], but only that of PMe_3 appears to be sufficiently stable to isolate in a pure form. Analogous complexes are not formed by the corresponding aryl phosphine, alkyl arsine or thioether ligands.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2017.02.007.

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