Oxygen, Sulphur, and Selenium Abstraction from WCl_4Y (Y = O, S, or Se) by Triphenylphosphine. Crystal and Molecular Structure of Tetrachlorobis(triphenylphosphine)tungsten(IV) *

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Excess of triphenylphosphine has been allowed to react with the series of compounds WCl_4Y (Y = O, S, or Se). The products from each reaction have been analysed and subjected to spectroscopic studies which have shown that in each reaction abstraction of the chalcogen atom took place thus reducing tungsten(VI) to tungsten(IV) and yielding $WCl_4{\cdot}2PPh_3$ and $P(Y)Ph_3$. With Y = O a second product, $WCl_4O{\cdot}P(O)Ph_3{\cdot}PPh_3$, was also isolated. The complex $WCl_4{\cdot}2PPh_3$ crystallises in the monoclinic space group $P2_1/n$, with a = 9.605(8), b = 21.320(13), c = 9.313(8) Å, β = 117.5(1)°, and Z = 2. The $WCl_4{\cdot}2PPh_3$ molecules are centrosymmetric with two equivalent W–Cl distances [2.320(5) and 2.344(6) Å] and a long W–P distance [2.629(6) Å].

There are a number of early reports of the reduction of high oxidation state halides and oxohalides of Groups 5A and 6A by nitrogen-containing Lewis bases.[1] In particular alkyl cyanides [2] and pyridine bases have been studied in some detail. The nature of the reduction process is of interest because with the oxohalide it is possible to envisage reduction *via* removal of halogen or oxygen. Of the systems already studied, halogen removal has been observed with VCl_3O and MCl_4O (M = Mo or W) which react with pyridine (py) to yield $VCl_2O{\cdot}3py$ [3] and $MCl_3O{\cdot}2py$ [4] respectively. With other Group 5B donors the mode of reduction is not so clear; thus PPh_3 with VCl_4 or WCl_4O is said to yield compounds which analyse approximately as $VCl_4{\cdot}2PPh_3$[5] and $WCl_4O{\cdot}2PPh_3$.[4] However, the former compound was believed to contain vanadium(III) and the latter tungsten(V), salts being proposed in each case. In contrast the reaction of an excess of L (L = PR_2Ph or $PRPh_2$; R = alkyl) with $ReCl_3O{\cdot}PPh_3$ is said to yield $ReCl_3{\cdot}3L$.[6] This latter redox process is of interest as, unlike those observed with nitrogen Lewis bases, reduction of the rhenium centre takes place *via* oxygen removal. This observation is all the more interesting because it has been shown that MCl_5 (M = Nb or Ta) and $P(O)Ph_3$ react to give $MCl_3O{\cdot}P(O)Ph_3$ [7,8] and presumably PCl_2Ph_3. It is against this background that the reaction of PPh_3 with WCl_4O has been reinvestigated and extended to include studies with WCl_4S and WCl_4Se. Preliminary experiments with the sulphido- and selenido-halides indicated that reduction was also taking place but some uncertainty existed about the nature of the compounds formed.[9]

Experimental

Tetrachloro-oxotungsten(VI) was prepared from the reaction of hexachlorotungsten(VI) with arsenic(III) oxide at 100 °C in a sealed tube. The product, WCl_4O, was obtained as an orange red solid and resublimed at 120 °C when orange crystals were formed (Found: Cl, 41.8; W, 53.4. Calc. for WCl_4O: Cl, 41.5; W, 53.8%). Tetrachlorosulphido- and tetrachloroselenidotungsten(VI) were prepared as previously described and sublimed before use [10] (Found: Cl, 39.8; W, 51.1. Calc. for WCl_4S: Cl, 39.6; W, 51.4%) (Found: Cl, 34.8; W, 45.3. Calc. for WCl_4Se: Cl, 35.0; W, 45.4%). Triphenylphosphine was recrystallised before use from light petroleum (b.p. range 100—120 °C).

Reaction of WCl_4Y (Y = O, S, *or* Se) *with* PPh_3.—All preparations and manipulations were executed on an all-glass vacuum line.

The reactants WCl_4Y (0.004 mol) and PPh_3 were added in a 1 : 5 mol ratio to an evacuated Pyrex glass ampoule containing a magnetic stirrer bar. The rigorously dried and outgassed solvent (toluene, CS_2, or CCl_4, *ca.* 30 cm^3) was distilled into the ampoule which was sealed whilst frozen under vacuum. The mixtures were allowed to warm to room temperature and stirred for a considerable period (see Table 1). In each reaction a dense yellow precipitate was formed and it was isolated by vacuum line filtration. The filtrates were pale yellow in colour and on removal of the solvent creamy yellow crystalline materials remained.

Crystal Structure of $WCl_4{\cdot}2PPh_3$.—Crystals of $WCl_4{\cdot}2PPh_3$ were obtained by recrystallisation from CS_2 solution using the double ampoule technique. The crystals were orange needles.

Crystal data. $C_{36}H_{30}Cl_4P_2W$, M = 849.65, Monoclinic, a = 9.605(8), b = 21.320(13), c = 9.313(8) Å, β = 117.5(1)°, U = 1 691.3 $Å^3$, D_c = 1.67, Z = 2, D_m (flotation) = 1.65(5) g cm^{-3}, $F(000)$ = 836, Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 28.3 cm^{-1}. Space group $P2_1/n$ from systematic absences $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$.

Structure solution and refinement. The crystal was mounted on a Stoe STADI 2 diffractometer and data were collected *via* variable width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a scan width of (1.5 + sinμ/tanθ). Absorption and extinction corrections were not applied. The structure was determined from the Patterson function and Fourier methods were used to complete the determination of the atoms in the structure.

The structure was refined by full-matrix least squares.[11] The weighting scheme used was chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and (sinθ/λ). This was $w = 1/[\sigma^2(F) + 0.002F^2]$ with $\sigma(F)$ taken from counting statistics. The tungsten, chlorine, oxygen, phosphorus, and carbon atoms were refined anisotropically. Hydrogen atoms bonded to carbon were placed in trigonal positions. Their thermal parameters were allowed to refine but those in the same ring were constrained to be equivalent. Scattering factors were taken from International Tables.[12] Calculations were made

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* *Supplementary data available* (No. SUP 23453, 11 pp.): structure factors, thermal parameters, H-atom co-ordinates, PPh_3 bond lengths and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Reactions of WCl_4Y with PPh_3 (mol ratio 1 : 5): reaction conditions and products

Reaction	Solvents used	Reaction time	Colour of precipitate	Analysis * (%)		
				Cl	C	H
$WCl_4S + PPh_3$	Toluene, CS_2, or CCl_4	1 d	Yellow	16.9	50.1	3.3
$WCl_4Se + PPh_3$	Toluene, CS_2, or CCl_4	2 d	Yellow	17.0	49.7	3.2
$WCl_4O + PPh_3$	Toluene	2 d	Yellow	16.5	50.8	3.6

* No tungsten analyses as the presence of phosphorus leads to interference. Calc. for $WCl_4{\cdot}2PPh_3$: C, 50.8; H, 3.5; Cl, 16.7%.

Table 2. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W	5 000	5 000	5 000
Cl(1)	2 493(6)	5 199(3)	4 667(7)
Cl(2)	3 915(7)	4 420(3)	2 590(7)
P(1)	5 320(7)	4 004(3)	6 791(7)
C(11)	6 753(26)	4 086(11)	8 969(27)
C(12)	8 219(31)	4 249(13)	9 281(30)
C(13)	9 423(28)	4 294(15)	10 909(29)
C(14)	9 050(36)	4 153(15)	12 071(35)
C(15)	7 643(47)	3 969(15)	11 790(37)
C(16)	6 376(29)	3 956(13)	10 141(26)
C(21)	5 994(29)	3 293(12)	6 304(29)
C(22)	6 171(34)	3 194(13)	4 929(38)
C(23)	6 734(46)	2 642(15)	4 629(42)
C(24)	7 052(35)	2 148(14)	5 594(35)
C(25)	6 851(49)	2 222(17)	6 923(49)
C(26)	6 367(45)	2 768(15)	7 299(38)
C(31)	3 471(29)	3 805(11)	6 772(28)
C(32)	2 597(33)	3 261(13)	5 985(30)
C(33)	1 194(35)	3 160(15)	5 984(34)
C(34)	569(34)	3 551(16)	6 612(39)
C(35)	1 365(30)	4 092(16)	7 366(38)
C(36)	2 815(36)	4 225(13)	7 413(38)

Table 3. Distances (Å) and angles (°) for $WCl_4{\cdot}2PPh_3$ with estimated standard deviations in parentheses

W–Cl(1)	2.320(5)	P(1)–C(31)	1.817(25)
W–Cl(2)	2.344(6)	P(1)–C(11)	1.861(22)
W–P(1)	2.629(6)	P(1)–C(21)	1.787(26)
W–P(1)–C(31)	110.8(8)	Cl(1)–W–Cl(2)	89.61(21)
W–P(1)–C(11)	115.3(7)	Cl(1)–W–P(1)	92.47(19)
W–P(1)–C(21)	118.3(8)	Cl(2)–W–P(1)	92.94(20)

Table 4. Infrared and Raman spectra of $WCl_4{\cdot}2PPh_3$ (400—200 cm^{-1})

I.r. (cm^{-1})	Assignment [a]	Raman (cm^{-1})	Assignment [a]
325 (sh) 317.5vs	E_u [b]	354.5	A_{1g}
		322.5	B_{1g}

[a] All bands are assigned to W–Cl modes. [b] This mode is slightly split and may reflect deviation of the molecule towards D_{2h} symmetry.

using SHELX 76 [11] on the CDC 7600 computer at the University of Manchester Computer Centre. Atomic co-ordinates are listed in Table 2 and interatomic distances and angles in Table 3.

Results and Discussion

The reactions of WCl_4S and WCl_4Se with an excess of PPh_3 in a variety of solvents yielded the same product, namely $WCl_4{\cdot}2PPh_3$. This complex has been prepared previously by ligand-exchange reactions on $WCl_4{\cdot}2NCPr^n$ [13] and by reduction of WCl_6 by zinc in the presence of PPh_3.[14,15] Attempts to prepare the complex directly from WCl_6 without reducing agents other than the phosphine were unsuccessful.[14]

The i.r. spectra of the products were in accordance with that expected from the formulation $WCl_4{\cdot}2PPh_3$ obtained by elemental analysis and showed no signs of unreacted WCl_4Y. The i.r. spectra of the soluble products revealed bands at 637 and 560 cm^{-1} attributed to ν(P=Y) of free $P(S)Ph_3$ and $P(Se)Ph_3$ respectively. The reactions therefore proceed according to equation (1) and involve total abstraction of chalcogen from WCl_4Y (Y=S or Se) with concomitant reduction of the tungsten atom by two oxidation states.

$$WCl_4Y + 3\,PPh_3 \longrightarrow WCl_4{\cdot}2PPh_3 + P(Y)Ph_3 \qquad (1)$$

Although reaction between WCl_4O and PPh_3 appeared visually to follow the path taken by the sulphur and selenium analogues, the i.r. spectrum of the yellow product obtained revealed bands at 970 and 1 149 cm^{-1} not present in $WCl_4{\cdot}2PPh_3$. These two absorptions are characteristic of terminal ν(W=O) and co-ordinated ν(P=O) of $P(O)Ph_3$, respectively. Close scrutiny of the i.r. spectrum of the soluble product from the WCl_4O–PPh_3 reaction showed no sign of free ν(P=O) (1 190 cm^{-1}) from $P(O)Ph_3$.

X-Ray powder diffraction patterns were recorded for the products from the three reactions. These showed the products from the WCl_4S and WCl_4Se reactions to be isomorphous but different from the product from the WCl_4O reaction.

Recrystallisation of the yellow powder obtained from the reaction from WCl_4S and PPh_3 yielded orange crystals which were confirmed to be $WCl_4{\cdot}2PPh_3$, the structure of which is described below. The major product from the WCl_4O–PPh_3 reaction yielded two types of crystals on recrystallisation, one orange and one green, in approximately equal amounts. Precession camera measurements showed the orange crystals to be $WCl_4{\cdot}2PPh_3$. Preliminary *X*-ray studies on the green crystals show that they consist of $WCl_4O\{P(O)Ph_3\}$ molecules together with unco-ordinated PPh_3 in the lattice giving an overall formulation of $[WCl_4O\{P(O)Ph_3\}]{\cdot}PPh_3$. This complex is therefore responsible for the additional bands observed in the i.r. spectrum of the original mixture. The overall reaction can therefore be formulated according to equation (2).

$$2\,WCl_4O + 4\,PPh_3 \longrightarrow [WCl_4O\{P(O)Ph_3\}]{\cdot}PPh_3 + WCl_4{\cdot}2PPh_3 \qquad (2)$$

Description of the Structure of $WCl_4{\cdot}2PPh_3$.—The structure of $WCl_4{\cdot}2PPh_3$ is depicted in the Figure from which it can be seen that the molecule exists in the *trans* configuration. The formation of a *trans* isomer is in agreement with predictions made previously on the basis of ^1H n.m.r. and i.r. studies.[14,16] The space group only requires the molecule to have a centre of symmetry. However, the tungsten–chlorine distances [2.320(5) and 2.344(6) Å] are within experimental error equivalent and so the co-ordination sphere can be visualised as having D_{4h} symmetry. The tungsten–chlorine distances are

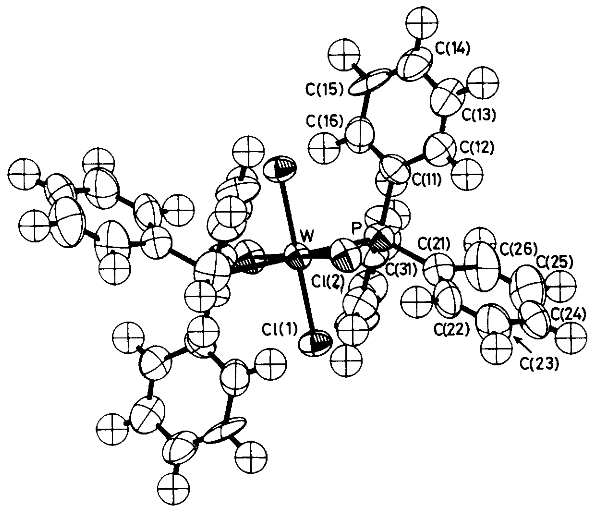

Figure. The structure of $WCl_4{\cdot}2PPh_3$ showing atomic numbering [apart from C(32)—C(36), omitted for clarity]

similar to those observed in $WCl_4{\cdot}2PMe_2Ph$[16] [2.339 (3) Å] but the mean distance [2.332(5) Å] is somewhat shorter than that in $WCl_4{\cdot}2py$ [2.347(1) Å].[17]

The tungsten–phosphorus bond length [2.629(6) Å] is rather long compared with equivalent distances in related tungsten complexes of triphenylphosphine {*e.g.* 2.508(3) Å in $[W(CO)_2(dcq)_2(PPh_3)]$ (dcq = 5,7-dichloro-8-quinolinolate[18]) or 2.581(3) Å in $[NEt_4][WCl_2(\eta\text{-}C_3H_5)(CO)_2(PPh_3)]$[19]}. This is ascribed to the combined effects of the *trans* influence exerted by the PPh_3 groups and steric interactions between the phenyl groups and the equatorial chlorine atoms. Two very short non-bonded Cl ··· H contact distances [H(22) ··· Cl(2) 2.50(3) Å and H(12) ··· $Cl(1^I)$* 2.65(3) Å] support this latter view. Any attempt to alleviate the strain by twisting of the phenyl rings relative to the WCl_4 plane is prevented by the already noticeable inter-ring interactions [represented by C(21) ··· H(32) 2.68(4) Å and C(31) ··· H(16) 2.59(3) Å]. Steric effects have also been used to explain the lengthening of the W–P bond in $W(CO)_5{\cdot}PBu^t_3$ (W–P = 2.686 Å)[20] compared to that in $[W(CO)_5(PMe_3)]$ (2.516 Å).[21]

Some lengthening of the W–P bond can also be expected to arise from the *trans* influence of the co-ordinated phosphine groups, a phenomenon which has also been observed previously in the complexes $MCl_3{\cdot}3PMe_2Ph$ (M = Re, Os, or Ir) and $WCl_4{\cdot}2PMe_2Ph$.[16] The W–P distance in the latter complex is slightly shorter (2.550 Å) than in $WCl_4{\cdot}2PPh_3$ which is consistent with the replacement of two bulky phenyl rings by the more compact methyl groups.

The different routes taken by the WCl_4Y–PPh_3 (Y = S or Se) and WCl_4O–PPh_3 reactions can be rationalised in terms of the relative strengths of the W=Y bonds. Results from gas-phase electron diffraction and vibrational spectroscopic studies on WCl_4Y (Y = O, S, or Se) led to an estimate of the ratios of the force constants for the ν(W=Y) modes which is given by $k(W{=}O)/k(W{=}S) = k(W{=}O)/k(W{=}Se) \simeq 1.8$. These values suggest that abstraction of sulphur or selenium would be thermodynamically more favourable than abstraction of oxygen. In the case of the WCl_4O–PPh_3 system a competing reaction is known to take place which involves adduct formation of WCl_4O by $P(O)Ph_3$ resulting in approximately equimolar yields of the products $WCl_4{\cdot}2PPh_3$ and $[WCl_4O\{P(O)Ph_3\}]{\cdot}PPh_3$. Experimental evidence suggests that adduct formation by $P(O)Ph_3$ may be more favourable than by $P(S)Ph_3$ or $P(Se)Ph_3$, and the reductive route involving complete chalcogen abstraction from WCl_4Y is favoured when Y = S or Se. In the case when Y = O the relatively stronger W = O bond, the complexing power of the $P(O)Ph_3$ ligand, and the ability of the more electronegative oxygen atom to stabilise higher oxidation states combine to prevent total oxygen abstraction and reduction of the tungsten atom.

Conclusion

Reaction of WCl_4Y (Y = S or Se) with PPh_3 leads to reduction and the formation of $WCl_4{\cdot}2PPh_3$. The observation is in contrast to the reaction of WCl_6 and PPh_3.[14] Reaction of WCl_4O with PPh_3 gives a mixture of products, namely $WCl_4{\cdot}2PPh_3$ and $[WCl_4O\{P(O)Ph_3\}]{\cdot}PPh_3$, neither of which were correctly identified by the use of spectroscopic and magnetic measurements.[4] The structural determination of $WCl_4{\cdot}2PPh_3$ confirms the formation of a *trans* isomer as has been previously predicted.[14,16]

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* Roman numeral superscript I refers to atoms related by the symmetry element 1–*x*, 1–*y*, 1–*z*.