Syntheses and structural characterizations of three WOX_2L_3 type complexes: crystal structures of *cis-mer*-$WOBr_2(PMe_2Ph)_3 \cdot 0.5C_7H_8$ and $WOBr_2(PR_3)_3$, where $PR_3 = PMe_2Ph$ or $PMePh_2$

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Abstract

Three new complexes of the type WOX_2L_3, where X= Br and L=PMe_2Ph, $PMePh_2$ are reported. All were structurally characterized by X-ray diffraction studies. Compound **1**, $WOBr_2(PMe_2Ph)_3 \cdot 0.5C_7H_8$, crystallizes in the monoclinic space group $P2_1/c$ with a = 15.378(3), b= 11.281(2), c = 18.984(3) Å, β = 105.84(2)°, V=3167(2) Å^3 and Z=2. Compound 2, $WOBr_2(PMe_2Ph)_3$, crystallizes in the orthorhombic space group *Pbca* with a = 17.624(5), b = 28.240(6), c = 11.480(3) Å, V=5714(4) Å^3 and Z = 8. Compound 3, $WOBr_2(PMePh_2)_3$, crystallizes in the triclinic space group $P\bar{1}$ with a = 10.473(2), b = 18.969(2), c = 9.954(3) Å, a= 95.41(2)°, β = 106.75(2)°, γ=79.43(1)°, V=1860(1) Å^3 and Z=2. In each case, the coordination of the W atom is distorted octahedral. In these compounds the phosphines are arranged meridionally and one of the bromine atoms is *trans* to the oxygen atom. The W=O distances are 1.70(1), 1.784(6) and 1.701(4) for **1**, **2** and 3, respectively, while the W-Br (*trans* to oxygen atom) distances are 2.668(2), 2.676(1) and 2.655(1) Å for **1**, **2** and 3, respectively. The IR spectra of 2 and 3 as solids show peaks due to ν(W=O) at 943 and 958 cm^{-1}, respectively. The $^{31}P\{^1H\}$ NMR spectrum of 2 consists of a doublet at δ -20.446 ppm and a triplet at δ -28.826 ppm in a 2:1 intensity ratio, and the ^1H NMR spectrum of 2 is also consistent with its structure in the crystal.

Introduction

There have been claims in the literature that co-ordination compounds may exist in forms that are identical in composition and have the same overall geometry but differ in specific bond lengths. These have been called either 'distortional isomers' [1] or 'bond-stretch isomers' [2]. The first alleged examples of such compounds were molecules of the type $MoOX_2L_3$, where X= halogen, pseudohalogen or mixed halogen and L = phosphine or arsine [3]. Such complexes were said to be either blue or green in color while some of them were said to show both colors [4]. Chatt *et al.* invoked this concept to account for the similarities and differences between the blue and green forms of cis-mer-$MoOCl_2(PR_3)_3$ complexes [1]. With the help of X-ray crystallography they found that both forms of this type of complex had identical ligand arrangements around the metal center. They and other workers also found that the blue *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ [5] has a short Mo=O distance (1.676(6) Å) while the green *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ [6] and *cis-mer*-$MoOCl_2(PEt_2Ph)_3$

[7] have long Mo=O distances (1.80(2) and 1.803(11) Å, respectively). These differences were described as distortional isomerism. There are several other reports where distortional isomerism was invoked to explain the long M=O distances in such complexes [8]. On the other hand, Cotton et *al.* found that both green *cis-mer*-$MoOCl_2(PMePh_2)_3$ and blue *cis-mer*-$MoO(NCO)_2(PEt_2Ph)_3$ have short Mo=O distances (1.667(4) and 1.684(8) A, respectively) [9].

A few similar complexes of W(IV), namely WOX_2L_3, were first reported by Chatt and co-workers [10a] and recently by Carmona *et al.* [lob]. These complexes are either blue or purple in color. Prior to our work there was no crystal structure reported for this type of W(IV) complex, but Parkin has recently [11] determined that of $WOCl_2(PMe_2Ph)_3$. Distortional isomers of $[WOCl_2L']^+$, where L' is the cyclic tridentate ligand 1,4,7-trimethyl-1,4,7-triazacyclononane have recently been claimed to exist [12]. The W=O bond distance in the blue substance (1.729(11) Å) is shorter than that in the green one (1.893(20) A).

There have been doubts raised as to whether some (if not all) alleged distortional isomers (of the M=O bond stretch type at least) are in fact erroneous. Parkin

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and co-workers in a recent communication [13] have reinvestigated the molecular structures of *cis-mer*-$MoOCl_2(PR_3)_3$ complexes and have reported that the long and short Mo=O bond distances in these complexes observed by others is a consequence of compositional disorder of *cis-mer*-$MoOCl_2(PR_3)_3$ with *mer*-$MoCl_3(PR_3)_3$. Other experimental evidence refuting the original Chatt proposal is also available [14]. From the theoretical side, there has been one discussion in support of the authenticity of 'bond-stretch' isomerism [15], but another, more rigorous, examination of the Chatt type compounds finds no support for it [16].

Because of the wide interest in this question, structural data and other information concerning MOX_2L_3 type compounds is now of more interest than it might otherwise have been. For that reason, we would like to present our data on three tungsten compounds of this class. All of these were prepared unintentionally several years ago as undesired products or by-products in the attempted syntheses of other tungsten compounds, and the structures did not, at the time, seem to be worth publishing. We report them now, along with some spectroscopic data, because they contribute not only data *per se* but the comparison of one pair of structures shows that the interpretation of structural data may not be entirely straightforward.

Experimental

Materials and methods

All manipulations were carried out under an atmosphere of argon by using standard Schlenk tube techniques. The solvents were freshly distilled under nitrogen from the appropriate drying agents. Chemicals were obtained from the following sources: PMe_2Ph and $PMePh_2$, Strem Chemical Company; WBr_5, $NaB(C_2H_5)_3H$, Aldrich Chemical Company; 2 M Na/Hg was prepared by adding 2 mmol of metallic sodium to a Schlenk tube containing 1 ml of dry mercury in a dry box.

Physical measurements

IR spectra from 4000–200 cm^{-1} were recorded on a Perkin-Elmer 783 spectrophotometer by using Nujol mulls between CsI or KBr plates. Electronic spectra were recorded as CH_2Cl_2 solutions in quartz cells on a Cary 17 UV–Vis spectrophotometer. The $^{31}P\{^1H\}$ NMR spectrum of 2 in benzene was run on a Varian XL-200 spectrometer at 81 MHz in a tube containing a sufficient amount of C_6D_6. The ^{31}P shifts are reported relative to external 85% H_3PO_4 by using the chemical shift difference, δ − 128.23. The ^1H NMR spectrum of 2 in C_6D_6 was recorded on a Varian XL-200 spectrometer at 200 MHz.

Preparation of $WOBr_2(PMe_2Ph)_3 \cdot 0.5C_7H_8$ (1)

To a suspension of WBr_5 (584 mg, 1.0 mmol) in 30 ml toluene, 1 ml 2 M Na/Hg was introduced by syringe. After stirring the mixture for half an hour 0.22 ml PMe_2Ph was added, and the stirring was continued for a further 2 days. A brown solid was separated from a red–brown solution by filtration under an atmosphere of argon. The red–brown solution was layered with hexane and afforded red crystals in three weeks. The red crystal was found to be $W_2Br_6(PMe_2Ph)_3$ and this compound will be reported elsewhere [17]. The brown solid was dissolved in methanol, transferred to a vial and the vial was kept in a refrigerator. Purple crystals were found within 3 days. One of these crystals was used for X-ray diffraction studies. The yield of this compound was c. 20% with respect to WBr_5.

Preparation of $WOBr_2(PMe_2Ph)_3$ (2)

A Schlenk tube containing the crystals of $W_2Br_6(PMe_2Ph)_3$ (verified by unit cell measurement) in a mixture of toluene and hexane was kept undisturbed and a second batch of crystals were found to grow in this tube in three weeks. These purple crystals were isolated as compound 2. Electronic spectrum (CH_2Cl_2 solution), λ_{max} (nm): 690, 430. IR spectrum (Nujol mull) (cm^{-1}): 943, 905, 837, 490, 417.

Preparation of $WOBr_2(PMePh_2)_3$ (3)

Toluene (30 ml) was added to a three-neck flask charged with 1 mmol (584 mg) of WBr_5. To this suspension 2 ml 1 M $NaB(C_2H_5)_3H$ in THF were introduced via a syringe. After stirring for 20 min a green solution was formed and 0.3 ml $PMePh_2$ was added to this solution. The mixture was stirred for a further 24 h and a red–brown solution was filtered from a black precipitate through Celite under an atmosphere of argon. The filtrate was layered with hexane and large blue–green crystals were formed in two weeks. Yield: 35% with respect to WBr_5. Electronic spectrum (CH_2Cl_2 solution), λ_{max} (nm): 575. IR spectrum (Nujol mull) (cm^{-1}): 958, 900, 700, 520, 490, 445.

X-ray crystallography

In each case a crystal of suitable size and quality was mounted on the tip of a thin glass fiber with the use of epoxy cement. X-ray data were collected on an automated four-circle diffractometer equipped with monochromated Mo $K\alpha$ radiation, following the general procedures and practices of this laboratory [18]*. Axial lengths and Laue class were confirmed with oscillation photographs. Lorentz, polarization and empirical ab-

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*Calculations were done on a Local Area VAX Cluster (VMS V4.6) with the programs SHELXS-86, and the commercial package SDP/V V 3.0.

sorption corrections based on azimuthal scans of several reflections with setting angles (χ) near 90° were applied to the data [19].

Crystal structure of 1

A small purple crystal was selected and shown to be of good quality by polarized light microscopy. The crystal was mounted on a goniometer head of a Nicolet P3/F equivalent diffractometer. Twenty five reflections in the range $20 \leqslant 2\theta \leqslant 28°$ were centered to refine the reduced cell parameters corresponding to the monoclinic crystal system. The monoclinic space group $P2_1/c$ was uniquely determined by the systematic absences. The ω scan technique was used to scan data points over a quadrant of reciprocal space. Three reflections were monitored periodically during the data collection; these showed an overall -4% change in intensity during 128.9 h of X-ray exposure. Positions of all atoms heavier than carbon were obtained from a Patterson synthesis and the remainder of the molecule was located and refined by alternating difference Fourier maps and least-squares cycles. Anisotropic displacement parameters were assigned to all atoms of the neutral molecule. At

this stage several peaks in the Fourier map were found and were treated as carbon atoms of a toluene molecule with constrained C–C (1.395 Å), C–CH$_3$ (1.48 Å) distances as well as with fixed ideal angles between the atoms. The methyl carbon atom was disordered because the molecule was located on an inversion center. The carbon atoms of the solvent molecule were refined isotropically. Hydrogen atoms were not included in the model. The crystal parameters and basic information related to data collection and structure refinement are summarized in Table 1. The last cycle of refinement included the fit of 296 parameters to unique 2679 data with $F_o^2 > 3\sigma(F_o^2)$ and gave residuals of $R = 0.048$ and $R_w = 0.060$. The final positional and thermal parameters for this structure are listed in Table 2.

Crystal structure of 2

A purple crystal of 2 was selected from the product and was mounted on the goniometer head of an Enraf Nonius CAD-4 diffractometer. The unit cell determination gave the orthorhombic crystal system with a

TABLE 1. Crystal data for 1, 2 and 3

	1	2	3
Formula	$W_2Br_4P_6O_2C_{55}H_{74}$	$WBr_2P_3OC_{24}H_{33}$	$WBr_2P_3OC_{39}H_{39}$
Formula weight	1640.4	774.1	960.3
Space group	$P2_1/c$	$Pbca$	$P\bar{1}$
Systematic absences	$h0l, l \neq 2n;$	$hk0, h \neq 2n;$	$none$
	$0k0, k \neq 2n$	$h0l, l \neq 2n;$	
		$0kl, k \neq 2n$	
a (Å)	15.378(3)	17.624(5)	10.473(2)
b (Å)	11.281(2)	28.240(6)	18.969(2)
c (Å)	18.984(3)	11.480(3)	9.954(3)
α (°)	90.0	90.0	95.41(2)
β (°)	105.84(2)	90.0	106.75(2)
γ (°)	90.0	90.0	79.43(1)
V (Å^3)	3167(2)	5714(4)	1860(1)
Z	2	8	2
D_{calc} (g/cm^3)	1.720	1.800	1.715
μ(Mo Kα) (cm^{-1})	63.881	70.822	54.575
Data collection instrument	Nicolet P3	Enraf-Nonius CAD 4	Nicolet P3
Radiation (monochromated in incident beam)		Mo Kα ($\lambda\alpha = 0.71073$ Å)	
Temperature (°C)	21 ± 1	20 ± 1	21 ± 1
Scan method	ω–2θ	ω	ω–2θ
Data collection range, 2θ (°)	4–50	4–50	4–50
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3911, 2679	5005, 3487	6612, 5697
No. parameters refined	296	280	415
Transmission factors: max., min. (%)	99.92, 65.48	99.88, 68.49	99.89, 62.55
R^a	0.048	0.040	0.031
R_w^b	0.060	0.058	0.046
Quality-of-fit indicator^c	1.170	1.648	1.406
Largest shift/e.s.d., final cycle	0.06	0.01	0.10

$^aR = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

TABLE 2. Positional and isotropic equivalent displacement parameters and their e.s.d.s for $WOBr_2(PMe_2Ph)_3 \cdot 0.5C_7H_8$

Atom	x	y	z	B $(\text{Å}^2)^a$
W(1)	0.23590(4)	0.18915(6)	0.16172(4)	2.35(1)
Br(1)	0.2545(1)	0.1442(2)	0.0305(1)	4.53(6)
Br(2)	0.3472(1)	0.3741(2)	0.1740(1)	3.93(5)
P(1)	0.2255(3)	0.2354(4)	0.2873(2)	2.9(1)
P(2)	0.1202(3)	0.3415(4)	0.0993(2)	3.2(1)
P(3)	0.3826(3)	0.0782(4)	0.2108(3)	3.0(1)
O(1)	0.1632(7)	0.077(1)	0.1643(6)	3.3(3)
C(1)	0.305(1)	0.344(2)	0.3447(9)	3.9(5)
C(2)	0.243(1)	0.102(2)	0.345(1)	4.9(6)
C(3)	0.116(1)	0.282(1)	0.2955(9)	3.0(4)
C(4)	0.105(1)	0.388(2)	0.332(1)	5.1(6)
C(5)	0.015(1)	0.412(2)	0.338(1)	5.3(6)
C(6)	−0.059(1)	0.337(2)	0.307(1)	5.5(7)
C(7)	−0.047(1)	0.235(2)	0.271(1)	4.4(6)
C(8)	0.041(1)	0.209(2)	0.264(1)	4.4(5)
C(9)	0.110(1)	0.476(2)	0.149(1)	4.3(5)
C(10)	0.134(1)	0.400(2)	0.011(1)	5.3(6)
C(11)	0.007(1)	0.281(2)	0.073(1)	4.1(5)
C(12)	−0.063(1)	0.326(2)	0.100(1)	4.7(6)
C(13)	−0.148(1)	0.270(2)	0.080(1)	5.5(7)
C(14)	−0.165(2)	0.175(2)	0.031(1)	5.8(7)
C(15)	−0.098(2)	0.135(2)	0.002(1)	7.1(8)
C(16)	−0.009(1)	0.185(2)	0.022(1)	4.6(5)
C(17)	0.466(1)	0.130(2)	0.293(1)	4.2(5)
C(18)	0.455(1)	0.058(2)	0.147(1)	4.6(5)
C(19)	0.357(1)	−0.078(1)	0.231(1)	3.4(5)
C(20)	0.308(1)	−0.147(2)	0.168(1)	5.0(6)
C(21)	0.285(1)	−0.260(2)	0.177(2)	5.6(7)
C(22)	0.310(2)	−0.308(2)	0.249(2)	6.3(8)
C(23)	0.356(2)	−0.238(2)	0.310(1)	5.5(7)
C(24)	0.379(1)	−0.124(2)	0.299(1)	3.2(5)
C(25)	0.448(4)	0.740(2)	0.017(4)	12(2)*
C(26)	0.475(2)	0.617(1)	0.008(3)	19(2)*
C(27)	0.418(1)	0.524(2)	0.016(2)	11(1)*
C(28)	0.554(2)	0.593(2)	−0.011(2)	12(1)*

^{a}Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

primitive lattice. Data of a unique octant $(+h, +k, +l)$ were collected in the ranges $4 \leqslant 2\theta \leqslant 50°$ using the ω scan technique. The systematic absences were those of the *Pbca* space group. Three periodically monitored check reflections showed no significant change in intensity during the data collection. The crystal parameters and basic information related to data collection and structure refinement are summarized in Table 1. Tungsten, bromine and phosphorus atoms were located via Patterson maps. The rest of the structure was developed by alternating difference Fourier maps and least-squares cycles employing the Enraf-Nonius (1979) structure determination package. All of the atoms were anisotropically refined, giving a data to parameter ratio of 12.5. In the final difference Fourier map, there was a peak $(2.15 \text{ e}/\text{Å}^3)$, 0.95 Å away from the tungsten atom.

Hydrogen atoms were not included in the model. The final positional and thermal parameters are shown in Table 3.

Crystal structure of 3

A blue–green crystal of dimensions $0.75 \times 0.25 \times 0.15$ mm was mounted on a goniometer head of a Nicolet P3 diffractometer. Automatic search routines and autoindexing gave the unit cell parameters that are listed in Table 1 along with the data pertaining to the crystallographic procedures and refinement. During data collection three intensity standards were collected every 2 h. No significant decay was observed during the 137.7 h of exposure to X-rays. Data were collected according to the triclinic crystal system. Since this compound was crystallographically isomorphous with Mo-$OCl_2(PMePh_2)_3$, atomic coordinates of all atoms heavier than oxygen were taken from ref. 9 to initiate the refinement. The remainder of the molecule was located and refined by alternating difference Fourier maps and

TABLE 3. Positional and isotropic equivalent thermal parameters and their e.s.d.s for $WOBr_2(PMe_2Ph)_3$

Atom	x	y	z	B (Å^2)
W(1)	0.22300(2)	0.15042(1)	0.07880(3)	2.889(6)
Br(1)	0.34731(5)	0.20150(3)	0.07480(9)	4.35(2)
Br(2)	0.26877(7)	0.09539(4)	−0.09743(9)	5.16(2)
P(1)	0.1037(2)	0.1049(1)	0.0803(2)	5.00(6)
P(2)	0.3011(1)	0.09076(8)	0.1906(2)	3.50(5)
P(3)	0.1808(1)	0.20598(8)	−0.0799(2)	3.36(4)
O(1)	0.1771(4)	0.1800(2)	0.1967(5)	4.3(1)
C(1)	0.0771(9)	0.0705(5)	−0.046(1)	11.0(4)
C(2)	0.0229(7)	0.1467(5)	0.106(1)	8.8(3)
C(3)	0.0904(5)	0.0636(4)	0.1999(9)	4.9(2)
C(4)	0.1061(6)	0.0796(4)	0.3128(9)	5.1(2)
C(5)	0.0989(7)	0.0485(4)	0.407(1)	7.1(3)
C(6)	0.0727(7)	0.0002(4)	0.383(1)	7.4(3)
C(7)	0.0581(8)	−0.0143(4)	0.279(1)	7.4(3)
C(8)	0.0642(7)	0.0170(4)	0.184(1)	6.5(3)
C(9)	0.2755(6)	0.0273(3)	0.181(1)	5.3(2)
C(10)	0.4022(5)	0.0899(4)	0.1473(9)	5.0(2)
C(11)	0.3064(5)	0.1030(3)	0.3466(8)	3.6(2)
C(12)	0.3212(6)	0.1495(3)	0.3803(8)	4.1(2)
C(13)	0.3320(6)	0.1601(3)	0.4985(9)	5.0(2)
C(14)	0.3280(6)	0.1251(4)	0.5821(8)	5.3(2)
C(15)	0.3121(8)	0.0789(4)	0.547(1)	6.9(3)
C(16)	0.3037(7)	0.0673(4)	0.430(1)	6.6(3)
C(17)	0.1565(6)	0.2623(3)	−0.0131(9)	4.9(2)
C(18)	0.2539(6)	0.2209(4)	−0.1863(8)	4.6(2)
C(19)	0.1033(5)	0.1936(3)	−0.1761(7)	3.9(2)
C(20)	0.1118(7)	0.1581(3)	−0.2614(9)	5.4(3)
C(21)	0.0474(8)	0.1486(4)	−0.338(1)	7.0(3)
C(22)	−0.0189(6)	0.1716(5)	−0.325(1)	7.1(3)
C(23)	−0.0284(6)	0.2054(4)	−0.242(1)	6.8(3)
C(24)	0.0326(6)	0.2169(4)	−0.1664(9)	5.4(2)

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

least-squares cycles. Anisotropic displacement parameters were assigned to all atoms. Hydrogen atoms were not included in the model. The last cycle of refinement included the fit of 415 parameters to unique 5697 data with $F_o^2 > 3\sigma(F_o^2)$ and gave residuals of $R = 0.031$ and $R_w = 0.046$. The final positional and thermal parameters for this structure are listed in Table 4.

TABLE 4. Positional and isotropic equivalent thermal parameters and their e.s.d.s for $WOBr_2(PMePh_2)_3$

Atom	x	y	z	B (Å^2)
W(1)	0.31852(2)	0.24454(1)	0.14342(2)	2.112(4)
Br(1)	0.20199(6)	0.34189(3)	0.29971(6)	3.49(1)
Br(2)	0.52973(5)	0.21693(3)	0.35879(6)	3.47(1)
P(1)	0.0996(1)	0.27500(7)	−0.0456(1)	2.43(3)
P(2)	0.2364(1)	0.15435(8)	0.2604(1)	2.67(3)
P(3)	0.4213(1)	0.35043(7)	0.1037(1)	2.62(3)
O(1)	0.3782(3)	0.1875(2)	0.0247(4)	2.87(8)
C(1)	−0.0541(5)	0.2952(4)	0.0123(6)	3.9(1)
C(2)	0.0566(5)	0.2050(3)	−0.1851(6)	3.0(1)
C(3)	−0.0668(6)	0.2199(4)	−0.2910(7)	4.2(2)
C(4)	−0.1102(7)	0.1677(4)	−0.3929(7)	5.0(2)
C(5)	−0.0295(7)	0.1017(4)	−0.3949(8)	5.3(2)
C(6)	0.0949(8)	0.0874(4)	−0.2954(8)	5.2(2)
C(7)	0.1388(6)	0.1390(4)	−0.1916(7)	4.1(1)
C(8)	0.0844(5)	0.3500(3)	−0.1542(5)	2.8(1)
C(9)	0.0037(6)	0.4164(3)	−0.1356(6)	3.9(1)
C(10)	0.0044(8)	0.4753(4)	−0.2132(8)	5.2(2)
C(11)	0.0790(8)	0.4663(4)	−0.3094(7)	5.8(2)
C(12)	0.1561(7)	0.3995(4)	−0.3290(7)	5.0(2)
C(13)	0.1598(6)	0.3414(4)	−0.2514(6)	3.9(1)
C(14)	0.2560(7)	0.1764(4)	0.4472(6)	4.1(1)
C(15)	0.3349(5)	0.0641(3)	0.2606(6)	3.2(1)
C(16)	0.3109(7)	0.0113(4)	0.3376(7)	4.9(2)
C(17)	0.3894(8)	−0.0576(4)	0.3418(8)	5.9(2)
C(18)	0.4847(7)	−0.0745(4)	0.2678(8)	5.0(2)
C(19)	0.5050(7)	−0.0231(4)	0.1880(8)	5.2(2)
C(20)	0.4308(7)	0.0455(4)	0.1876(7)	4.4(2)
C(21)	0.0632(5)	0.1366(3)	0.1951(6)	3.1(1)
C(22)	−0.0348(6)	0.1645(4)	0.2672(7)	4.9(2)
C(23)	−0.1679(6)	0.1514(5)	0.2087(8)	6.2(2)
C(24)	−0.2032(7)	0.1134(4)	0.083(1)	6.7(2)
C(25)	−0.1081(8)	0.0864(4)	0.0128(9)	6.0(2)
C(26)	0.0267(7)	0.0977(3)	0.0676(7)	4.3(2)
C(27)	0.3180(6)	0.4400(3)	0.0898(7)	3.8(1)
C(28)	0.5722(5)	0.3687(3)	0.2433(5)	2.9(1)
C(29)	0.5542(6)	0.4067(4)	0.3655(6)	4.1(1)
C(30)	0.6674(7)	0.4202(4)	0.4737(6)	5.0(2)
C(31)	0.7979(7)	0.3914(4)	0.4622(7)	5.2(2)
C(32)	0.8140(7)	0.3531(4)	0.3415(8)	5.3(2)
C(33)	0.7007(6)	0.3429(4)	0.2326(7)	4.4(2)
C(34)	0.4812(5)	0.3391(3)	−0.0523(5)	3.1(1)
C(35)	0.5387(6)	0.2713(4)	−0.0939(6)	4.2(1)
C(36)	0.5868(7)	0.2623(4)	−0.2127(7)	5.7(2)
C(37)	0.5727(7)	0.3218(4)	−0.2930(7)	5.2(2)
C(38)	0.5187(8)	0.3880(5)	−0.2522(7)	5.9(2)
C(39)	0.4721(7)	0.3976(4)	−0.1300(7)	4.9(2)

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Results

Compound **1** was obtained as a by-product in the synthesis of the dinuclear complex, $W_2Br_6(PMe_2Ph)_3$ while compound **2** was a degradation product of the dinuclear complex. Compound **3** was the only product isolated in a reaction that was intended to give the face-sharing dinuclear complex, $W_2Br_6(PMePh_2)_3$. We present the crystal structures of these compounds first and then the spectroscopic results.

Crystal structures

Compound 1

An ORTEP diagram of **1** is shown in Fig. 1, where the atom numbering scheme is also defined. Four molecules of this compound occupy the general position and two interstitial solvent molecules of toluene are at special positions. A unit cell diagram of **1** is shown in Fig. 2. Table 5 presents selected interatomic distances and angles. See also 'Supplementary material'.

The crystal structure of **1** consists of discrete monomeric units. The ligands have an *cis-mer* arrangement around the central tungsten atom. The coordination of the tungsten atom is distorted octahedral and this distortion is particularly notable for the P(2)–W(1)–P(3) angle, which is only 162.7(2)° due to the bending of P(2) and P(3) atoms away from P(1) atom. This can be attributed to the steric repulsions among the bulky phosphine ligands. The W–P distances are 2.488(5) Å (*trans* to bromine) and 2.523(4) and 2.524(4) Å (*cis* to bromine). The W–Br distance *cis* to O is c. 0.03 Å
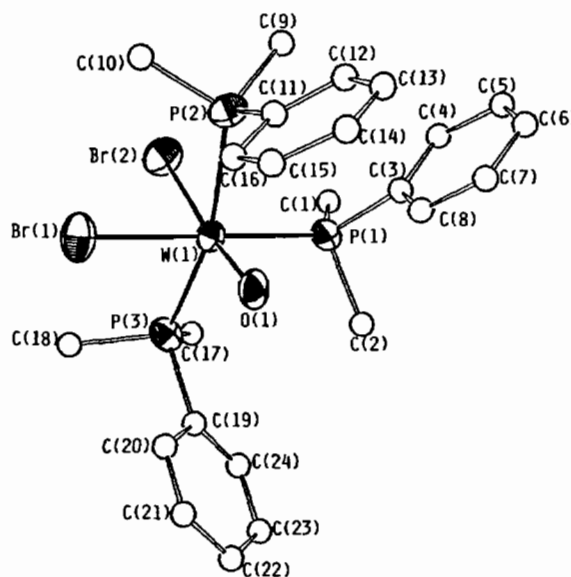

Fig. 1. An ORTEP drawing of $WOBr_2(PMe_2Ph)_3$ in **1**. Non-carbon atoms are drawn at the 50% probability level; carbon atoms are shown as spheres of arbitrarily small radius.
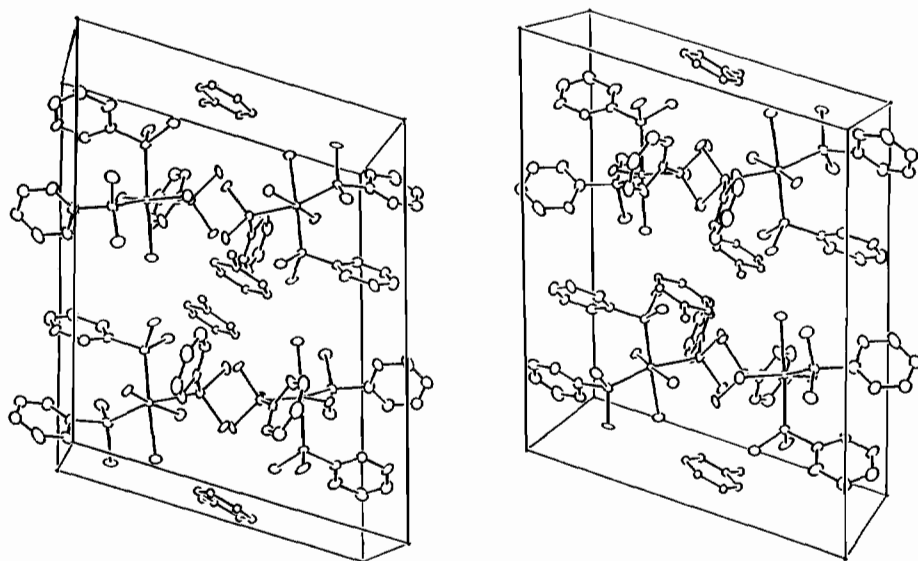
Fig. 2. Unit cell diagrams for **1**. Axes orientation: *c*, down; *a*, across; *b*, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

TABLE 5. Selected bond distances (Å) and bond angles (°) for $WOBr_2(PMe_2Ph)_3 \cdot 0.5C_7H_8$

Distances					
W(1)–Br(1)	2.634(2)	W(1)–P(1)	2.488(5)	W(1)–P(3)	2.524(4)
W(1)–Br(2)	2.668(2)	W(1)–P(2)	2.523(4)	W(1)–O(1)	1.70(1)
Angles					
Br(1)–W(1)–Br(2)	90.04(7)	Br(2)–W(1)–P(1)	87.7(1)	P(1)–W(1)–P(3)	92.0(2)
Br(1)–W(1)–P(1)	177.4(1)	Br(2)–W(1)–P(2)	82.0(1)	P(1)–W(1)–O(1)	85.1(4)
Br(1)–W(1)–P(2)	86.1(1)	Br(2)–W(1)–P(3)	82.4(1)	P(2)–W(1)–P(3)	162.7(2)
Br(1)–W(1)–P(3)	86.4(1)	Br(2)–W(1)–O(1)	172.7(4)	P(2)–W(1)–O(1)	97.9(4)
Br(1)–W(1)–O(1)	97.2(4)	P(1)–W(1)–P(2)	94.9(2)	P(3)–W(1)–O(1)	98.5(4)

Numbers in parentheses are e.s.d.s in the least significant digits.

shorter than that *trans* to O, and the W=O distance is 1.70(1) Å.

Compound 2

This compound contains the same metal complex as compound **1** except that there are no interstitial solvent molecules. A view of compound **2** is shown in Fig. 3. Important bond distances and angles for **2** are listed in Table 6. In compound **2**, the P(2)–W(1)–P(3) angle, 160.84(8)°, is very similar to that in **1**. The W–Br distance *trans* to O is *c.* 0.048 Å longer than that *cis* to O, and the W=O bond length is 1.784(6) Å.

Compound 3

Selected bond distances and angles for **3** are listed in Table 7. An ORTEP drawing of **3** is shown in Fig. 4. The crystal structure of **3** consists of discrete monomeric units. As in **1** and **2**, the ligands adopt an octahedral *cis-mer* configuration about a central tungsten atom. The most significant angular deviation from octahedral symmetry is again the bending of the P(2)

and P(3) atoms away from P(1), resulting in the P(2)–W(1)–P(3) angle being only 162.39(4)°. The orientations of the methyl and phenyl groups on each phosphorus atom are of some interest. One of the phenyl groups on each phosphorus atom is perpendicular to the plane of the phosphorus atoms while the other phenyl ring positions on the same side of this plane as the oxygen atom. The methyl group on each phosphorus atom lies on the same side of this plane as the bromine atom that is *trans* to the oxygen atom. All W–P distances are quite similar. The W–Br *cis* to O bond is *c.* 0.04 Å shorter than the W–Br *trans* to O bond, and the W=O distance is 1.701(4) Å.

NMR spectra

The $^{31}P\{^1H\}$ NMR spectrum of **2** is shown in Fig. 5. It consists of a doublet at δ −20.446 ppm and a triplet at δ −28.826 ppm in the intensity ratio 2:1 corresponding to the two *trans* phosphorus atoms and to the single phosphorus atom *cis* to other two phosphorus atoms. Tungsten satellites are also observed due
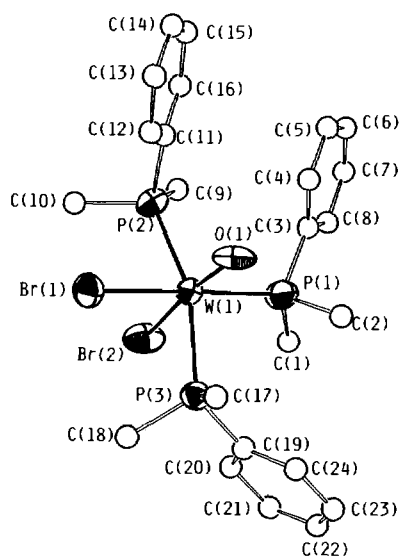
Fig. 3. An ORTEP drawing of $WOBr_2(PMe_2Ph)_3$ in **2**. Non-carbon atoms are drawn at the 50% probability level; carbon atoms are shown as spheres of arbitrarily small radius.

to the one bond tungsten to phosphorus couplings (^{183}W has a nuclear spin of 1/2 and a natural abundance of 14%); the ^1J(P–W) values are 336.59 and 437.95 Hz. The ^2J(P–P) value of 5.48 Hz is surprisingly small in this mononuclear complex. The ^1H NMR spectrum of bulk crystalline material of **2** in C_6D_6 shows two triplets centered at $\delta = 2.069$ (J(P–H) = 4.1 Hz) and 1.846 (J(P–H) = 4.2 Hz) ppm and a doublet centered at 1.344 (J(P–H) = 8.2 Hz) ppm for the methyl protons as the structure requires. The intensity ratios are 1:1:1.

The IR spectrum of **2** shows a strong band at 943 cm^{-1} which is the characteristic of the W=O stretch while that stretch produces a strong band at 958 cm^{-1} in the IR spectrum of **3**.

Discussion

Because all three complexes reported here were obtained unintentionally in the course of a synthetic

program directed towards the synthesis of bromo complexes of W(III), the methods used are not, to put it mildly, optimum preparative procedures. No doubt straightforward methods can be devised. We have no specific idea about the source of oxygen in these reactions although the problem of eliminating completely all sources of oxygen from reaction solutions (and during workup) when attempting the preparation of lower-valent tungsten compounds is a notoriously difficult and persistent one.

The general structural features of these complexes are not unusual and are very similar to those of the known molybdenum complexes of this type. The most interesting question to ask of these structures is, what do they tell us about the lengths to be expected for W=O bonds in such compounds? An associated question of equal importance is, how reliable and reproducible are such results? Had we determined only the structures of **1** and **3** the answer to both questions would appear to be simple, namely, the bond lengths should be about 1.70 ± 0.01 Å and this appears to be a very reliable result. Compound **2** sows the seeds of doubt. Is its greater W=O distance (by c. 0.08 Å) real? If not, what is the source of error? The structure of **2** shows no indication that anything is amiss. Neither the oxygen atom, nor any of the other atoms has an anomalous thermal ellipsoid. If the lengthening is really an artifact of the presence of a small amount of the $WBr_3(PMe_2Ph)_3$ molecule being present, there is no other indication of this. The two W–Br distances are practically the same in both **1** and **2**. Of course, a small amount of $WBr_3(PMe_2Ph)_3$ impurity, just sufficient to cause an apparent 0.08 Å lengthening of the W=O bond (perhaps a few %) would probably have no detectable effect on anything else.

It should be noted that the W=O stretching frequency in **2** is lower (943 cm^{-1}) than that in **3** (958 cm^{-1}), consistent with the different bond lengths. It is unfortunate that we did not record the IR spectrum of **1**. It should also be noted that the average of the W=O bond lengths in **1** and **2** is close to the value found by Parkin [11] in $WOCl_2(PMe_2Ph)_3$. Is it possible that

TABLE 6. Selected bond distances (Å) and bond angles (°) for $WOBr_2(PMe_2Ph)_3$

Distances

W(1)–Br(1)	2.624(1)	W(1)–P(1)	2.464(3)	W(1)–P(3)	2.516(2)
W(1)–Br(2)	2.676(1)	W(1)–P(2)	2.526(2)	W(1)–O(1)	1.784(6)

Angles

Br(1)–W(1)–Br(2)	93.12(3)	Br(2)–W(1)–P(1)	87.68(7)	P(1)–W(1)–P(3)	94.50(8)
Br(1)–W(1)–P(1)	177.99(7)	Br(2)–W(1)–P(2)	80.36(6)	P(1)–W(1)–O(1)	81.5(2)
Br(1)–W(1)–P(2)	85.44(6)	Br(2)–W(1)–P(3)	84.48(6)	P(2)–W(1)–P(3)	160.84(8)
Br(1)–W(1)–P(3)	83.75(6)	Br(2)–W(1)–O(1)	169.1(2)	P(2)–W(1)–O(1)	100.0(2)
Br(1)–W(1)–O(1)	97.7(2)	P(1)–W(1)–P(2)	96.51(8)	P(3)–W(1)–O(1)	97.1(2)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 7. Selected bond distances (Å) and bond angles (°) for $WOBr_2(PMePh_2)_3$

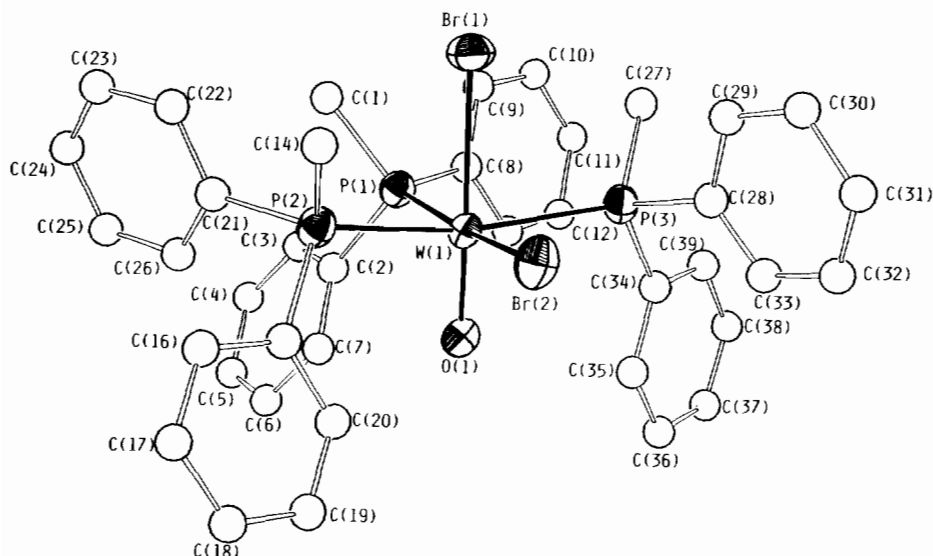| Distances					
W(1)–Br(1)	2.6545(6)	W(1)–P(1)	2.523(1)	W(1)–P(3)	2.557(2)
W(1)–Br(2)	2.6108(5)	W(1)–P(2)	2.553(2)	W(1)–O(1)	1.701(4)
Angles					
Br(1)–W(1)–Br(2)	89.99(2)	Br(2)–W(1)–P(1)	173.74(4)	P(1)–W(1)–P(3)	95.29(4)
Br(1)–W(1)–P(1)	84.51(3)	Br(2)–W(1)–P(2)	80.74(3)	P(1)–W(1)–O(1)	88.4(1)
Br(1)–W(1)–P(2)	84.60(3)	Br(2)–W(1)–P(3)	86.96(3)	P(2)–W(1)–P(3)	162.39(4)
Br(1)–W(1)–P(3)	82.83(3)	Br(2)–W(1)–O(1)	97.2(1)	P(2)–W(1)–O(1)	98.8(1)
Br(1)–W(1)–O(1)	172.4(1)	P(1)–W(1)–P(2)	95.74(4)	P(3)–W(1)–O(1)	95.2(1)

Numbers in parentheses are e.s.d.s in the least significant digits.

Fig. 4. An ORTEP drawing of $WOBr_2(PMePh_2)_3$ in **3**. Non-carbon atoms are drawn at the 50% probability level; carbon atoms are shown as spheres of arbitrarily small radius.
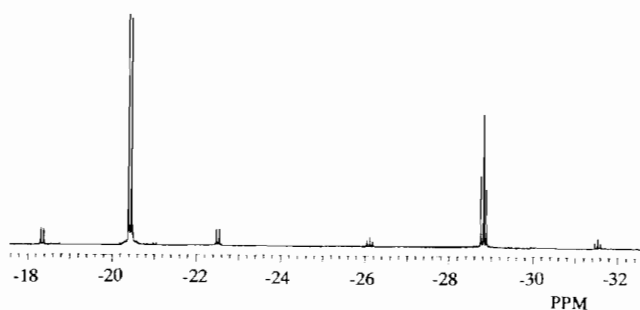

Fig. 5. $^{31}P\{^1H\}$ NMR spectrum of **2**.

the W=O bond lengths in **1** and **2** could really differ by 0.08 Å as a result of environmental influences? We find this hard to believe but, on the data at hand, impossible to rule out.

Table 8 compares the W=O stretches in the IR spectra and W–P and P–P coupling constants (wherever available) in the known WOX_2L_3 complexes. The W=O stretching frequencies are in the region 940–960 cm^{-1} and are sensitive to the ligands present in the complex.

The replacement of two Cl by two Br atoms in the $WOX_2(PMe_2Ph)_3$ complex causes little change in J(P–W) values.

Supplementary material

Full tables of crystallographic parameters and structure refinement, bond distances, bond angles and anisotropic displacement parameters for **1**, **2** and **3** (19 pages); and observed and calculated structure factors (63 pages) for **1**, **2** and **3**, may be obtained from author F.A.C.

Acknowledgement

TABLE 8. Comparison of W=O bond lengths, IR and $^{31}P\{^1H\}$ NMR data for WOX_2L_3 type complexes

Compound	r(W=O) (A)	ν(W=O)(cm^{-1})	δP(1) (ppm)	δP(2) (ppm)	^2J(P–P) (Hz)	^1J(P–W) (Hz)	Reference
$WOCl_2(P(OMe)_3)_3$		95.5	128.08d[a]	134.88t[a]	23.5	257.00 316.90	10b
$WOCl_2(PMe_2Ph)_3$	1.752(4)	960	128.30s"	135.80s"		343.00 442.00	10a, 11
$WOBr_2(PMe_2Ph)_3$	1.70(1)−1.784(6)	943	−20.45d	−28.83t	5.5	336.59 437.95	this work
$WOCl_2(PMePh_2)_3$		950					10a
$WOBr_2(PMePh_2)_3$	1.701(4)	958					this work

"Peaks are referenced to P_4O_6; s = singlet, d=doublet, t = triplet.

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