

# Improved synthetic routes to tungsten(IV) bromide complexes

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**Abstract** Convenient synthetic routes to the compounds  $WBr_4$  (1),  $WBr_4(MeCN)_2$  (2),  $WBr_4(THF)_2$  (3),  $WBr_4$  $(PPh_3)_2$  (4),  $WBr_4(bpy)$  (6), and  $WBr_4(dppe)$  (7) are described via the solution-phase oxidation of  $W(CO)_6$ using two equivalents of bromine. These one-pot syntheses use inexpensive and readily available starting materials and produce analytically pure compounds with high yields under mild conditions. Attempts to grow crystals of 1 by heating in a sealed tube at  $\sim 200$  °C resulted in formation of the previously reported compound WOBr<sub>4</sub>. Attempts to recrystallize 4 from dichloromethane solution produced [HPPh<sub>3</sub>]<sub>2</sub>[WBr<sub>6</sub>] (5). X-ray crystallographic studies showed that **5** consists of an array of  $[WBr_6]^{2-}$  anions and  $[HPPh_3]^+$  cations and that  $7 \cdot CH_2Cl_2$  has the expected sixcoordinate tungsten center. The synthesis of tungsten(IV) bromide compounds via oxidation of  $W(CO)_6$  is simple and provides better yields than previously reported methods. This synthetic route also has many advantages over the syntheses of similar tungsten(IV) chloride compounds which involve reduction of WCl<sub>6</sub>.

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### Introduction

Synthetic approaches to complexes that contain tungsten in the (II), (III), or (IV) oxidation states typically involve initial reduction of WCl<sub>6</sub> to WCl<sub>4</sub> by various methods [1]. Further reduction of WCl<sub>4</sub> to tungsten(II), in the form of the cluster compound (W<sub>6</sub>Cl<sub>8</sub>)Cl<sub>4</sub>, is possible via solidstate disproportionation of WCl<sub>4</sub> [2] or via direct reduction of  $WCl_6$  using Al [3, 4]. The majority of these reductions involve tube furnace reactions where high pressures and temperatures are used. Many require a two-zone furnace with careful temperature control, and irreproducibility has been a problem. To avoid such difficulties, a solution-phase route using tin as the reducing agent has been developed, which provides WCl<sub>4</sub> in high yield. However, the largescale version of this route involves 3 days of reaction time with repeated washing/centrifugation steps to remove the SnCl<sub>4</sub> by-product [1]. Early syntheses of tungsten(III) chloride complexes, in the form of the anionic cluster  $[W_3Cl_9]^{3-}$ , used WO<sub>3</sub> as the starting material [5].

Tungsten bromide complexes have received less attention, partly due to the limited commercial availability of tungsten(V) or (VI) bromides as compared with readily found WCl<sub>6</sub>. Preparations of WBr<sub>6</sub> have been reported through direct treatment of W(CO)<sub>6</sub> with liquid bromine [6–8] or via solid-state halide exchange reactions using WCl<sub>6</sub> and BBr<sub>3</sub> [9, 10]. Preparation of WBr<sub>5</sub> proceeds from direct oxidation of tungsten metal using Br<sub>2</sub> at high temperatures (~600 °C or higher) with subsequent isolation of the WBr<sub>5</sub> through repeated sublimation steps from a mixture that also contains WBr<sub>6</sub> [8, 11–13]. A more recent report indicates that heating of this mixed product under vacuum can yield pure WBr<sub>5</sub> [14]. A low-yield (~10 %) synthesis of WBr<sub>4</sub> has been reported from the high-temperature reduction of WBr<sub>5</sub> using W [15] or Al [2] in a

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uniform temperature gradient. McCarley and Brown [15] have reported the synthesis of WBr<sub>3</sub> using WBr<sub>2</sub> and Br<sub>2</sub> heated in a sealed tube at 50 °C for 2 weeks. When the WBr<sub>3</sub> was heated to higher temperature, it decomposed to form WBr<sub>2</sub> and Br<sub>2</sub>. Another preparation of WBr<sub>2</sub> involves disproportionation of WBr<sub>4</sub> in sealed tubes in a furnace with a temperature gradient [2]. As with the tungsten chloride compounds, the tungsten bromide syntheses involve sealed tubes where high pressures and temperatures, as well as careful temperature control, are necessary.

Our previous work with molybdenum(IV) bromide as a precursor to higher-oxidation-state molybdenum nitrido compounds [16] led us to investigate the solution-phase oxidation of W(CO)<sub>6</sub> using bromine. We report here improved synthetic routes and characterization of the known compounds  $WBr_4$  (1),  $WBr_4(MeCN)_2$  (2),  $WBr_4$  $(THF)_2$  (3),  $WBr_4(PPh_3)_2$  (4),  $WBr_4(bpy)$  (6), and  $WBr_4$ (dppe) (7). Although mentioned in the literature, several of these compounds (3, 4, and 7) have never been sufficiently characterized. Structural characterization of the tungsten(IV) compound WBr<sub>4</sub>(dppe)·CH<sub>2</sub>Cl<sub>2</sub> (7·CH<sub>2</sub>Cl<sub>2</sub>) is also discussed. The formation and structural characterization of the tungsten(IV) compound [HPPh<sub>3</sub>]<sub>2</sub>[WBr<sub>6</sub>] (5) are also addressed. The synthetic methods reported avoid the difficulties associated with previous approaches and provide analytically pure compounds with high yields under mild conditions using readily available starting materials.

### Experimental

#### Materials and methods

Compounds were manipulated in an Innovative Technology System One glovebox under prepurified  $N_2$  or through use of standard Schlenk techniques. Dichloromethane, 1,2dichloroethane, and acetonitrile solvents were distilled from CaH<sub>2</sub> under nitrogen. Diethyl ether and tetrahydrofuran were distilled from purple Na/benzophenone ketyl under nitrogen. Deuterated chloroform was dried with CaH<sub>2</sub> and was vacuum-transferred to an airtight vessel containing activated molecular sieves. Tungsten hexacarbonyl, triphenylphosphine, 1,2-*bis*(diphenylphosphino)ethane (dppe), and 2,2'-bipyridine (bpy) were purchased from Aldrich Chemical Company and were dried under vacuum before transfer to the glovebox. Bromine was purchased from Aldrich and was distilled from CaO prior to use.

#### **Physical measurements**

Decomposition points were measured by a Mel-Temp II apparatus in sealed glass tubes and are uncorrected. Elemental analyses were performed by Columbia Analytical Services. Infrared spectra were obtained using Nujol mulls or KBr pellets on a Shimadzu Advantage FTIR-8900 or on a Perkin-Elmer 1600 FTIR spectrophotometer. <sup>1</sup>H-NMR data were collected on a Varian Unity INOVA instrument operating at 299.950 MHz. Chemical shifts were referenced to the residual protons of the solvent. Magnetic susceptibilities were measured with a Johnson-Matthey MS-1 Magnetic Susceptibility Balance.

#### Synthesis

#### Tungsten(IV) bromide, WBr<sub>4</sub> (1)

Tungsten hexacarbonyl (1.00 g, 2.84 mmol) was dried under vacuum for  $\sim 45$  min. Freshly distilled dichloromethane (40 mL) was added, and the mixture was placed in a cold bath at -18 °C (orthodichlorobenzene/liquid nitrogen bath). After ca. 10 min, Br<sub>2</sub> (0.28 mL, 5.70 mmol) was added dropwise via syringe over a period of 2 min. As the Br<sub>2</sub> reacted, bubbles of gas (CO) were seen, and the suspension turned black (Warning: This reaction should be performed in an efficient fume hood). After stirring the mixture for several minutes at -18 °C, the cold bath was removed, and a black solid formed at room temperature. After stirring for 3 h, the black solid was isolated by filtration, washed with  $3 \times 10$  mL portions of CH<sub>2</sub>Cl<sub>2</sub>, and was thoroughly dried under vacuum. Yield 1.35 g (94 % based on W). Decomposition point: ca. 190 °C (see text). IR (KBr pellet): No peaks observed from 4000 to 450 cm<sup>-1</sup>. Anal. Calcd. for WBr<sub>4</sub>: W, 36.52; Br, 63.48. Found: W, 36.50; Br, 63.43.

## Tungsten bis(acetonitrile) tetrabromide, $WBr_4(CH_3CN)_2$ (2)

To a flask containing WBr<sub>4</sub> (1) (4.55 g, 9.04 mmol) was added ca. 70 mL of freshly distilled acetonitrile. A dark red suspension formed instantly in an exothermic reaction. The mixture was degassed, placed under a nitrogen atmosphere, and was allowed to stir for 24 h. A dark reddish-brown solid was isolated by filtration and was dried under vacuum. Yield 3.40 g (64 % based on W). Decomposition point: 145–148 °C. IR (Nujol mull, cm<sup>-1</sup>): 2307(m), 2299(m), 2269(s), 1352(m), 1260(w), 1015(m), 802(b), and 662(w). Anal. Calcd. for C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>Br<sub>4</sub>W: C, 8.20; H, 1.03; N, 4.78; Br, 54.59. Found: C, 8.13; H, 1.02; N, 4.61; Br, 54.98.

*Tungsten tetrabromide bis(tetrahydrofuran),* WBr<sub>4</sub>(THF)<sub>2</sub> (3)

To a nitrogen-purged flask containing  $WBr_4(CH_3CN)_2$  (2) (1.00 g, 1.71 mmol) was added 35 mL of freshly distilled tetrahydrofuran. The flask was degassed, placed under

nitrogen, and the mixture was allowed to stir for 3 h. After this time, the mixture had turned brownish orange. The product was isolated by filtration and dried under vacuum. Yield 0.76 g (69 % based on W). IR (Nujol mull, cm<sup>-1</sup>): 1400(s), 1350(s), and 1240(s). Decomposition point: 130–132 °C. Anal. Calcd. for  $C_8H_{16}O_2Br_4W$ : C, 14.82; H, 2.49; N, 0.00; Br, 49.36. Found: C, 14.68; H, 2.33; N, 0.08, Br, 49.15.

### Tungsten tetrabromide bis(triphenylphosphine), WBr<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> (**4**)

Method A To a nitrogen-purged flask containing WBr<sub>4</sub> (1) (0.500 g, 0.993 mmol) and PPh<sub>3</sub> (2.08 g, 7.94 mmol) was added ca. 40 mL of freshly distilled 1,2-dichloroethane at room temperature. An orange-red suspension formed immediately, and the mixture was allowed to stir for several hours under nitrogen. A dark orange-red solid was isolated by filtration, washed with  $3 \times 10$  mL portions of 1,2-dichloroethane, and dried under vacuum. Yield 0.555 g (54 % based on W).

Method B To a stirred suspension of  $W(CO)_6$  (1.01 g, 2.87 mmol) in 30 mL  $CH_2Cl_2$  at -18 °C (orthodichlorobenzene/liquid nitrogen bath) was added Br<sub>2</sub> (0.29 mL, 5.66 mmol) dropwise via syringe over a period of two minutes. Evolution of CO gas was evident as a black suspension formed. (Warning: This reaction should be performed in an efficient fume hood). The reaction mixture was allowed to stir for 1 h at room temperature, and then, PPh<sub>3</sub> (1.64 g, 6.26 mmol) was added using a solid addition funnel. As the PPh<sub>3</sub> reacted, the black suspension turned to an orange-red suspension. The reaction mixture was stirred for several hours, and the red-orange product was isolated by filtration, washed with  $3 \times 15$  mL portions of CH<sub>2</sub>Cl<sub>2</sub>, and extensively dried under vacuum. Yield 2.93 g (70 % based on W). Decomposition point: 152-156 °C. IR (KBr pellet, cm<sup>-1</sup>): 3150(w), 2017(b), 1940(b); 1896(b), 1601(m), 1435(s), 1088(s), 997(m), 519(s), 508(s), 492(w), 472(w), and 452(w). Magnetic susceptibility: Corrected molar susceptibility:  $1.11 \times 10^{-3}$  emu, Magnetic moment, 1.61  $\mu_{\rm B}$ . <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  12.4 (broad, 12H), 8.4 (broad, 12H), 7.8 (broad, 6H). Anal. Calcd. for  $C_{36}H_{30}P_{2-}$ Br<sub>4</sub>W: C, 42.04; H, 2.94; N, 0.00; P, 6.03. Found: C, 42.34; H, 2.99; N, <0.05; P, 5.64.

# Triphenylphosphonium hexabromotungstate(IV), [HPPh<sub>3</sub>]<sub>2</sub>[WBr<sub>6</sub>] (5)

Approximately 20 mL of the filtrate from Method A of the  $WBr_4(PPh_3)_2$  synthesis was placed in a Schlenk tube and layered with 10 mL of freshly distilled diethyl ether. After 10 days, shiny orange-red crystals had formed at the bottom of the tube. The supernatant liquid was removed, and

the crystals were partially dried under vacuum. Recrystallization of WBr<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> from dichloromethane solutions at -10 °C over a period of several weeks also yielded orange-red crystals of **5**, contaminated with deeper red crystals of WBr<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> (**4**). <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  11.4 (broad, 12H), 8.5 (broad, 12H), 8.0 (broad, 6H).

#### Tungsten tetrabromide (2,2'-bipyridine), $WBr_4(bpy)$ (6)

Method A A 100 mL Schlenk flask was charged with WBr<sub>4</sub> (1) (1.00 g, 1.99 mmol), and ~35 mL freshly distilled 1,2dichloroethane was added to form a black suspension. A separate solution of 2,2'-bipyridine (0.34 g, 2.18 mmol) in 35 mL of freshly distilled 1,2-dichloroethane was added to the flask containing the WBr<sub>4</sub>. The black suspension turned brown. The reaction mixture was allowed to stir for 24 h. The brown product was isolated by filtration, washed with  $3 \times 10$  mL portions of 1,2-dichloroethane, and was extensively dried under vacuum. Yield 0.806 g (61 % based on W).

Method B To a stirred suspension of  $W(CO)_6$  (1.00 g, 2.84 mmol) in ca. 30 mL of CH<sub>2</sub>Cl<sub>2</sub> at -18 °C was added  $Br_2$  (0.29 mL, 5.66 mmol) dropwise with a syringe over a period of 2 min. Gas evolution (CO) was observed as a black suspension formed (Warning: This reaction should be performed in an efficient fume hood). After 10 min, the cold bath was removed and the reaction was allowed to stir at room temperature for 7 h. At this point, 2,2'-bipyridine (0.598 g, 3.83 mmol) was added to the mixture using a solid addition funnel. The black suspension turned brown. The reaction mixture was allowed to stir for 24 h. The product was isolated by filtration, washed with  $3 \times 10$  mL portions of CH<sub>2</sub>Cl<sub>2</sub>, and extensively dried under vacuum. Yield 1.67 g (89 % based on W). Decomposition point: 330-334 °C. IR (KBr pellet, cm<sup>-1</sup>): 1601(s), 1442(m), 1315(s), 969(s), 765(s), 668(w), 647(w), 519(w), 503(w), 494(w), and 473(w). Magnetic susceptibility: Corrected molar susceptibility,  $1.16 \times 10^{-3}$  emu, effective magnetic moment, 1.65 µ<sub>B</sub>. Anal. Calcd. for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>Br<sub>4</sub>W: C, 18.19; H, 1.22; N, 4.25. Found: C, 17.87; H, 1.19; N, 4.08.

# *Tungsten tetrabromide [bis(diphenylphosphino)ethane], WBr*<sub>4</sub>(*dppe*) (7)

*Method A* A 100 mL Schlenk flask was charged with WBr<sub>4</sub> (1) (0.50 g, 0.99 mmol) and 1,2-*bis*(diphenylphosphino)ethane (0.435 g, 1.09 mmol). To the flask was added 80 mL of freshly distilled 1,2-dichloroethane via syringe. The resulting dark suspension was allowed to stir for 4 h at room temperature. The reaction mixture was placed in a freezer (-10 °C) for 16 h after which shiny, golden-brown crystals were isolated by filtration, washed with 10 mL of 1,2-dichloroethane, and dried under vacuum. Yield 0.479 g (54 % based on W).

Method B To a stirred suspension of  $W(CO)_6$  (2.02 g, 5.74 mmol) in ca. 40 mL CH<sub>2</sub>Cl<sub>2</sub> at -18 °C was added Br<sub>2</sub> (0.58 mL, 11.3 mmol) dropwise via syringe. Gas evolution (CO) was observed as a black suspension formed (Warning: This reaction should be performed in an efficient fume hood). The cold bath was removed after 10 min, and the suspension was allowed to stir at room temperature for 5 h. At this point, 1,2-bis(diphenylphosphino)ethane (2.97 g, 7.46 mmol) was added to the mixture with a solid addition tube. The black suspension turned brown and was allowed to stir for 16 h at room temperature. Golden-brown crystals were isolated by filtration, washed with 10 mL CH<sub>2</sub>Cl<sub>2</sub>, and were dried extensively under vacuum. Yield 4.04 g (78 % based on W). IR (KBr pellet,  $cm^{-1}$ ): 1262(w), 1097(b), 867(w), 707(w), 688(s), 516(s), 497(m), and 472(w). Decomposition point: 274-278 °C. Magnetic susceptibility: Corrected molar susceptibility,  $1.78 \times 10^{-3}$ emu, effective magnetic moment 2.04  $\mu_B$ . <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 16.430 (s, 8H), 14.762 (dd, 8H), 13.791 (t, 4H), -8.880 (s, 4H). Elemental analysis indicated the unsolvated form. Anal. Calcd. For C<sub>26</sub>H<sub>24</sub>P<sub>2</sub>Br<sub>4</sub>W: C, 34.61; H, 2.68; N, 0.00; P, 6.87. Found: C, 34.56; H, 2.49; N, <0.05; P, 6.49.

### X-ray data collection and refinement

Α crystal suitable for structure determination of  $[HPPh_3]_2[WBr_6]$  (5) was obtained from the filtrate illustrated in Scheme 1 after layering with diethyl ether. Crystals of  $WBr_4(dppe) \cdot CH_2Cl_2$  (7 · CH\_2Cl\_2) were produced by layering the filtrate obtained from the reaction illustrated in Scheme 2 with diethyl ether. Crystallographic data were obtained on a Bruker SMART diffractometer using the  $\omega$ -scan mode and graphite-monochromated Mo K $\alpha$  radiation. All crystals were mounted in grease on a glass fiber and were quickly placed in the cold stream (173 K) of the goniometer. Refinement was carried out with the full-matrix least-squares method based on  $F^2$ (SHELX-97) with anisotropic thermal parameters for all nonhydrogen atoms. The H atoms were geometrically placed and treated as riding atoms with C-H = 0.96 Å and  $U_{iso}(H) = (1.2) U_{iso}$  (parent C atom). The hydrogen atom

Scheme 1 Synthesis and reactivity of WBr<sub>4</sub> (1)

on the phosphorus atom in compound **5** was located on an electron density difference map as a Fourier peak appended to the least-squares refinement output file and was refined isotropically. Crystal data and selected details of the structure determinations are given in Table 1.

#### **Computational studies**

Calculations were performed using the GAUSSIAN 09 Rev A.02 programming package [17]. Geometry optimizations in the gas phase were performed using density functional theory (DFT) with the B3LYP hybrid functional [18–20]. The LANL2DZ basis set was used.

### **Results and discussion**

#### Synthesis

Using W(CO)<sub>6</sub> as the starting material, the synthesis of WBr<sub>4</sub> (1) involves a stoichiometric oxidation in dichloromethane solvent using Br<sub>2</sub>, as shown in Scheme 1. Due to the generation of CO gas, care should be taken to use an effective fume hood and to cool the reaction mixture before the bromine is added. The black product is easily isolated via filtration and was extensively dried under vacuum. Typical yields were over 90 %. Previous solid-state syntheses of WBr<sub>4</sub> via reduction of WBr<sub>5</sub> using W or Al involved sealed tubes, high temperatures, and 10-day reaction times [2, 15].

Addition of acetonitrile to solid WBr<sub>4</sub> under an inert atmosphere produces WBr<sub>4</sub>(MeCN)<sub>2</sub> (**2**) as a dark red suspension in an exothermic reaction, as shown in Scheme 1. The mixture was filtered to collect the black product with yields of 65 %. Other syntheses of WBr<sub>4</sub>(-MeCN)<sub>2</sub> have been reported. Fowles reported that reaction of WBr<sub>5</sub> with excess acetonitrile produced WBr<sub>4</sub>(MeCN)<sub>2</sub>. No yield was given, but the elemental analysis (C, H, and N) was within acceptable range [12]. McCarley reports that oxidation of W(CO)<sub>6</sub> using bromine in acetonitrile gave WBr<sub>4</sub>(MeCN)<sub>2</sub> in yields of 70–80 %. Elemental analysis data for both W and Br were consistent, but no C, H, and N data were reported [21]. Marshalsea synthesized this compound in acetonitrile solvent according to Eq. (1):

$$W(CO)_{6} \xrightarrow{+ 2 \operatorname{Br}_{2}, \operatorname{CH}_{2}\operatorname{Cl}_{2}}_{-18^{\circ}\operatorname{C} \text{ to } \operatorname{R.T.}, - 6 \operatorname{CO}} \xrightarrow{+ L}_{R.T.} WBr_{4}(L)$$
$$L = 2 \operatorname{PPh}_{3}, \operatorname{bpy}, \operatorname{dppe}$$

Scheme 2 One-pot syntheses of compounds (4), (6), and (7)



#### Table 1 Crystallographic data for 5 and 7.CH<sub>2</sub>Cl<sub>2</sub>

	5	$7 \cdot CH_2Cl_2$
Reference	CCDC 902600	CCDC 902599
Empirical formula	$C_{36}H_{32}Br_6P_2W$	$C_{27}H_{26}Br_4Cl_2P_2W$
Formula weight	1189.87	986.81
Г (К)	173	173
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_{1}/c$
Unit cell dimensions		
7 (Å)	10.2295(3)	11.4017(4)
b (Å)	13.5330(5)	19.6307(6)
c (Å)	13.9489(5)	14.6629(5)
χ (°)	90.00	90.00
β (°)	91.283(1)	108.143(1)
y (°)	90.00	90.00
$V(Å^3)$	1930.5(1)	3118.7(2)
Ζ	2	4
$\mu (\mathrm{mm}^{-1})$	9.309	9.119
λ(Å)	0.71073	0.71073
$F(0 \ 0 \ 0)$	1124	1864
Crystal size (mm)	$0.15 \times 0.15 \times 0.10$	$0.35 \times 0.15 \times 0.15$
$D_{\text{calc}} (\text{g cm}^{-3})$	2.047	2.102
Theta range for data collection (°)	2.10–25.15	1.79–25.15
Index ranges	$-11 \le h \le 12, -16 \le k \le 15, -16 \le l \le 16$	$-13 \le h \le 13, -23 \le k \le 23, -17 \le l \le 17$
Reflections collected	18,926	35,937
Independent reflections	3460 [(R(int) = 0.0533])	5616 [( $R(int) = 0.0420$ ]
Reflections with $I > 2\sigma(I)$	2938	5030
Data/restraints/parameters	3460/0/209	5616/0/325
GOF on $F^2$	1.057	1.175
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0284$	$R_1 = 0.0271$
	$wR_2 = 0.0715$	$wR_2 = 0.0707$
R indices (all data)	$R_1 = 0.0364$	$R_1 = 0.0321$
	$wR_2 = 0.0715$	$wR_2 = 0.0729$
Largest difference in peak and hole (e $\mathring{A}^{-3}$ )	0.620 and -1.408	1.244 and -1.060

$$W(CO)_{6} \xrightarrow{\text{Reflux}} W(CO)_{3} (MeCN)_{3} \xrightarrow{+2 \operatorname{Br}_{2}, \operatorname{Reflux}} WBr_{4} (MeCN)_{2}$$
(1)

No yield was reported, and the elemental analysis data were not within the accepted level of  $\pm 0.4 \%$  [22]. Herrmann reports that oxidation of W(CO)<sub>6</sub> in acetonitrile using PBr<sub>5</sub> gives the product in 98 % yield with consistent elemental analysis data [23]. This method gives the best yield of those reported. The chloro analog of compound (2), WCl<sub>4</sub>(MeCN)<sub>2</sub>, was produced in a reaction analogous to Eq. (1) using a stream of chlorine gas in place of the bromine [22]. No yield was reported, and the elemental analysis results were not within an acceptable range. McCarley reported [21] the synthesis of  $WCl_4(MeCN)_2$  via the reaction shown in Eq. (2):

$$4WCl_5 + W(CO)_6 + 10MeCN \rightarrow 5WCl_4(MeCN)_2 + 6CO$$
(2)

The yield was 60–70 %, and elemental analysis data (W, Cl) were consistent. Messerle placed WCl<sub>4</sub> (prepared by reduction of WCl<sub>6</sub> with Sn) in MeCN to give WCl<sub>4</sub> (MeCN)<sub>2</sub> in 81 % yield [1]. Elemental analysis data (W, Cl) were consistent.

An attempted synthesis of  $WBr_4(THF)_2$  (3) via addition of tetrahydrofuran to solid  $WBr_4$  resulted in the formation of blue-green products, usually indicative of the presence of tungsten oxo compounds. Alternatively, the acetonitrile ligands of (2) could be replaced with THF as shown in Scheme 1. The brown-orange product was isolated via filtration in *ca*. 70 % yield. The chloro analog of (3),  $WCl_4(THF)_2$ , was synthesized by reduction of  $WCl_6$  in  $CH_2Cl_2$  using cyclopentene, followed by addition of THF. A low yield (36 %) was obtained [24].

The synthesis of WBr<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> (**4**) proceeds using 1,2dichloroethane as solvent, as shown in Scheme 1. The orange-red product was isolated by filtration in 54 % yield, but a one-pot synthesis provided better results. The separate reactions shown in Scheme 1 can be combined to yield compound (**4**) directly using dichloromethane as solvent, as shown in Scheme 2. Due to the generation of CO gas, care should be taken to use an effective fume hood and to cool the reaction mixture before the bromine is added. This method produced analytically pure (**4**) in 70 % yield. Cotton has reported an alternative synthesis of (**4**) using dibromomethane as solvent via Zn reduction of WBr<sub>5</sub> as shown in Eq. (**3**):

$$WBr_5 + excess PPh_3 \xrightarrow{Ln} WBr_4(PPh_3)_2$$
(3)

The reported yield was 61 %, but no characterization data of the product were included [25]. The chloro version of compound (4),  $WCl_4(PPh_3)_2$ , has been reported and is synthesized in dichloromethane via the reduction shown in Eq. (4):

$$WCl_6 + 2PPh_3 \xrightarrow{Zn} WCl_4 (PPh_3)_2 + ZnCl_2$$
 (4)

The product is isolated in low yield (34 %), and separation from the unused Zn can be problematic [26, 30].

Bidentate ligands can also be used. Synthesis of WBr<sub>4</sub>(bpy) (**6**) proceeds in 1,2-dichloroethane as shown in Scheme 1. The dark-brown product was filtered from the reaction mixture in 63 % yield. A one-pot synthesis using dichloromethane as solvent, as shown in Scheme 2, provided an increased yield. Since CO gas is generated, care should be taken to use an effective fume hood and to cool the reaction mixture before the bromine is added. This method produced analytically pure (**6**) in 98 % yield. Stiddard has reported the synthesis of compound (**6**) via the oxidation of W(CO)<sub>4</sub>(bpy) in dichloromethane, as shown in Eq. (**5**):

$$W(CO)_4(bpy) \xrightarrow{+2Br_2, \Delta} WBr_4(bpy) + 4CO$$
 (5)

A 68 % yield was reported along with acceptable element analysis results [27]. Stiddard also reported synthesis of the chloro version, WCl<sub>4</sub>(bpy), that was produced by replacing the Br<sub>2</sub> shown in Eq. (5) with a slow stream of Cl<sub>2</sub> gas. An 83 % yield was reported, but the elemental analysis results were not within acceptable range [27].

bidentate ligand 1.2-Another employed was bis(diphenylphosphino)ethane, (dppe). The synthesis of  $WBr_4(dppe)$  (7) proceeds in 1,2-dichloroethane as solvent as shown in Scheme 1. Golden-brown crystals of the product were isolated by filtration in 53 % yield. This yield could be increased by employing a one-pot synthesis using dichloromethane as solvent, summarized in Scheme 2. Since CO gas is generated, care should be taken to use an effective fume hood and to cool the reaction mixture before the bromine is added. This method produced analytically pure (7) in 95 % isolated yield. Lorenz has reported the synthesis of compound (7) using THF as solvent, as shown in Eq. (6):

$$W(dppe)_2 N_2 + 2SOBr_2 \xrightarrow{0^{\circ}C} WBr_4(dppe) + 2N_2 + SO + dppe$$
(6)

An 82 % yield is reported, but the elemental analysis results are outside acceptable limits [28]. A report on the synthesis of the chloro version of compound (7), WCl<sub>4</sub> (dppe), involved reaction of K<sub>2</sub>WCl<sub>6</sub> with fused dppe at 220 °C [29]. However, the elemental analysis of the compound was not within acceptable range. An alternative synthesis [30] is shown, using toluene as solvent, in Eq. (7):

$$WCl_4(PPh_3)_2 + dppe \xrightarrow{10^{\circ}C} WCl_4(dppe) + 2PPh_3$$
 (7)

The reported yield was 89 %, but this route requires the additional step of preparing  $WCl_4(PPh_3)_2$ , which in turn involves reduction of  $WCl_6$  as shown in Eq. (4).

#### **Compound characterization**

Tungsten(IV) bromide (1) proved to be quite sensitive to hydrolysis and required an inert atmosphere for manipulation. Previous work indicates that WBr<sub>4</sub> is isomorphous with WCl<sub>4</sub> [2]. Messerle has shown that the WCl<sub>4</sub> structure consists of polymeric chains of edge sharing, distorted bioctahedra with alternating short (2.688 Å) and long (3.787 Å) distances between the tungsten centers [1]. More recent work has confirmed a similar structure for WBr<sub>4</sub> with alternating short (2.794 Å) and long (4.044 Å) W/W distances [8]. The black WBr<sub>4</sub> solid displayed slight solubility in dichloromethane and 1,2-dichloroethane.

An attempt to determine the decomposition temperature of solid WBr<sub>4</sub> in a sealed capillary tube led to observed sublimation and deposition of black, shiny crystals in the cooler portion of the tube. It was initially thought that WBr<sub>4</sub> might be decomposing to form a lower–oxidation-state bromide, as is observed with MoBr<sub>4</sub> [31–33]. Structural determination of the deposited crystals by X-ray diffraction revealed the known compound, WOBr<sub>4</sub>, and further refinement of the data was not pursued. Adventitious oxygen apparently reacted with WBr<sub>4</sub> to form the

**Fig. 1** ORTEP representation of [HPPh<sub>3</sub>]<sub>2</sub>[WBr<sub>6</sub>] (**5**) showing the atom numbering scheme



 Table 2 Bond distances (Å) and angles (°) for compound 5

W(1)–Br(1)	2.538(1)	Br(2)-W(1)-Br(3)	89.81(2)
W(1)-Br(2)	2.534(1)	Br(2)–W(1)–Br(4)	90.47(2)
W(1)-Br(3)	2.532(1)	Br(3)–W(1)–Br(4)	89.16(2)
P(1)–H(1)	1.341(4)	C(1)-P(1)-H(1)	105.3(4)

product. WOBr<sub>4</sub> has been previously synthesized by reaction of WBr<sub>5</sub> with SO<sub>2</sub> [34] or by a solid-state synthesis using WBr<sub>6</sub> and WO<sub>3</sub> [7]. The structure of WOBr<sub>4</sub> has been shown to consist of square pyramidal WOBr<sub>4</sub> units associated via the O atoms to form linear W/O chains [35].

The compound WBr<sub>4</sub>(MeCN)<sub>2</sub> (**2**) was sparingly soluble in dichloromethane or chloroform and was more soluble in polar solvents with which it can undergo ligand exchange (THF, DMSO, Pyridine). The infrared spectrum revealed the expected v(CN) frequency near 2300 cm<sup>-1</sup> for the coordinated acetonitrile. Earlier work with low-temperature far-infrared spectra identified both WCl<sub>4</sub>(MeCN)<sub>2</sub> and WBr<sub>4</sub>(MeCN)<sub>2</sub> as the *cis* isomers, based on the number of tungsten halide stretching modes [17].

The compound  $WBr_4(THF)_2$  (3) had similar solubility characteristics to compound 2. The infrared spectrum was typical of the coordinated tetrahydrofuran ligand. This compound has not been previously reported in the literature.

The compound  $WBr_4(PPh_3)_2$  (4) was soluble in both dichloromethane and 1,2-dichloroethane. The infrared spectrum was consistent with bound triphenylphosphine. Previous work identified  $WCl_4(PPh_3)_2$  as the *trans* isomer, based on single-crystal X-ray diffraction [37]. Compound 4 exhibited broadened and paramagnetically shifted peaks in the <sup>1</sup>H-NMR spectrum. Attempts to recrystallize 4 by



Fig. 2 ORTEP representation of  $WBr_4(dppe)$ , 7-CH<sub>2</sub>Cl<sub>2</sub> showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity

redissolving in dichloromethane or by layering of the reaction filtrate eventually led to isolation of crystals of the tungsten(IV) compound  $[HPPh_3]_2[WBr_6]$  (5), the structure of which is shown in Fig. 1. Bond distances and angles are given in Table 2. Compound 5 crystallizes in the

Table 5	вопа	distances (A) a	nd angles (*) for compo	build $h CH_2 CI_2$
W(1)–Br	(1)	2.512(1)	Br(1)-W(1)-Br(2)	92.15(2)
W(1)–Br	(2)	2.509(1)	Br(1)-W(1)-Br(3)	97.01(2)
W(1)–Br	(3)	2.451(1)	Br(1)-W(1)-Br(4)	95.11(2)
W(1)–Br	(4)	2.493(1)	Br(2)-W(1)-Br(3)	96.10(2)
W(1)-P(	l)	2.547(1)	Br(2)-W(1)-Br(4)	96.71(2)
W(1)–P(2)	2.561(1)	Br(3)–W(1)–Br(4)	161.98(2)	
		P(1)-W(1)-P(2)	81.47(4)	
		P(1)-W(1)-Br(2)	175.66(3)	
		P(2)–W(1)–Br(1)	172.85(3)	
		P(1)-W(1)-Br(3)	82.85(3)	
		P(1)-W(1)-Br(4)	83.42(3)	

Table 3 Bond distances (Å) and angles (°) for compound 7.CH2Cl2

**Table 4** Effective magnetic moment  $(\mu_{eff})$  values, units of Bohr magnetons

Compound	X = Br	X = Cl	
WX <sub>4</sub> (MeCN) <sub>2</sub>	1.89 <sup>a</sup>	1.78 <sup>a</sup>	
WX <sub>4</sub> (bpy)	1.65 <sup>b</sup> ; 1.69 <sup>c</sup>	1.64 <sup>c</sup>	
$WX_4(PPh_3)_2$	1.61 <sup>b</sup>	1.72 <sup>d</sup>	
WX <sub>4</sub> (dppe)	2.04 <sup>b</sup>	1.74 <sup>e</sup>	

<sup>a</sup> Ref. [12], <sup>b</sup> this work, <sup>c</sup> ref. [27], <sup>d</sup> ref. [21], <sup>e</sup> ref. [29]

monoclinic space group  $P2_1/n$  and consists of two triphenylphosphonium cations and the octahedral  $[WBr_6]^{2-1}$ dianion. It was initially thought the compound was cocrystallized, neutral molecules of triphenylphosphine and tungsten(VI) hexabromide, WBr<sub>6</sub>. Further analysis revealed paramagnetically shifted peaks in the <sup>1</sup>H-NMR spectrum, and a hydrogen atom was located on the phosphorus atom via an electron density difference map. Also, the average W(IV)-Br length of 2.535(1) Å in 5 is significantly longer (0.081 Å) than the reported W(VI)-Br length in WBr<sub>6</sub> of 2.454(3) Å [38]. Calculated W–Br bond distances in the gas phase at the B3LYP/LANL2DZ level of theory show a difference of 0.115 Å between  $[W(IV)Br_6]^{2-}$  (average W–Br of 2.656 Å) and  $[W(VI)Br_6]$ (W-Br of 2.541 Å). The structure of 5 shows the closest approach between cation and anion (along Br...H-P) is over 2.8 Å.

Bidentate ligands can also be attached to the WBr<sub>4</sub> moiety. The compound WBr<sub>4</sub>(bpy) (**6**) was insoluble in dichloromethane, but dissolved in acetonitrile. The infrared spectrum of **6** revealed the expected peaks due to the coordinated 2,2'-bipyridine ligand.

The compound WBr<sub>4</sub>(dppe) (7) was soluble in both dichloromethane and 1,2-dichloroethane. The infrared spectrum displayed peaks due to the 1,2-bis(diphenylphosphino)ethane ligand. The <sup>1</sup>H-NMR spectrum had sharp,

paramagnetically shifted peaks that retained the expected splitting pattern. Crystals of  $7 \cdot CH_2Cl_2$  were grown from the reaction mixture. Compound 7 crystallizes in space group  $P2_1/c$ , and the structure is shown in Fig. 2. The structure revealed a distorted octahedral tungsten center, as well as a noninteracting molecule of dichloromethane solvent. Bond distances and angles are given in Table 3. The two *trans* Br atoms [Br(3) and Br(4)] appear to be bent toward the cleft formed by the two phenyl rings of the chelating phosphine ligand. The Br(3)–W(1)–Br(4) angle is 161.98(2)°, while the Br(1)–W(1)–Br(2) angle is 92.15(2)°. The average W–Br bond distance is 2.491 Å, between the values of 2.445(2) Å from the tungsten(IV) compound (WOBr<sub>4</sub>) and 2.535(1) Å from the tungsten(IV) compound **5** [HPPh<sub>3</sub>]<sub>2</sub>[WBr<sub>6</sub>].

#### Magnetic measurements

Effective magnetic moments from this and previous work are presented in Table 4. All values fall within the range  $(1.5-2.2 \ \mu_B)$  previously reported for a variety of tung-sten(IV) compounds [21].

### Conclusion

In summary, the solution-phase oxidation of  $W(CO)_6$  using bromine is a simple, high yield route to a number of tungsten(IV) bromide compounds. One-pot syntheses have been described that avoid several difficulties involved with the preparation of similar tungsten(IV) chloride compounds that involve reduction of WCl<sub>6</sub>. Our approach is also superior to previously reported syntheses of tungsten bromide compounds that involve sealed tubes, high temperatures, and the requirement of careful temperature control. The methods described here are easily modified to allow incorporation of other ligands. We are currently investigating the electrochemistry and reactivity of various tungsten(IV) bromide compounds and will report our findings in due course.

### Supplementary data

CCDC 902599 and 902600 contain the supplementary crystallographic data for **5** and **7**·CH<sub>2</sub>Cl<sub>2</sub>. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retriev ing.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or email: deposit@ccdc.cam.ac.uk.

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