

On the Reactions of Bisdiolatotungsten(VI) Phenoxides. Syntheses, Characterizations, and Molecular Structures of *trans*-[WCl₂(Diol)(OAr)₂]

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Coordinated phenoxide groups in [W(eg)₂(mephe)₂] (**2a**) and [W(eg)₂(prphe)₂] (**2c**) (eg = ethanediolate dianion; mephe = OC₆H₃Me₂-2,6; prphe = OC₆H₃Pr₂-2,6) undergo reaction with Br₂, leading to substitution at the *para* position of the phenyl rings and formation of the complexes [W(eg)₂(OC₆H₂R₂-2,6-Br-4)₂] (**2b**, R = Me; **2d**, R = 'Pr). The reaction of complexes **2a–2d** and [W(eg)₂(buphe)₂] (**2e**) (buphe = OC₆H₃tBu₂-2,4) with HCl leads to the displacement of one bidentate diolato ligand from the complex unit and formation of the corresponding *trans* dichloro diolato bis(phenoxide) tungsten(VI) complex [WCl₂(eg)(OAr)₂] (**3**). The X-ray crystal structure determinations of these compounds confirmed that all complexes **3** have a similar gross structure in which the chloro ligands are arranged at *trans* positions.

Introduction

Early transition metal alkoxides have been widely studied due to their applications in organometallic and catalytic chemistry, and a number of these studies have been stimulated by the demonstrated ability of various tungsten compounds containing alkoxide and aryloxy ligands to catalyze metathesis reactions of cyclic and acyclic alkenes.^{1–5} For example, tungsten phenoxides of the type [WCl_{6–x}(OAr)_x] and [WOCl_{4–y}(OAr)_y] are used as precursors for two-component catalyst systems, typically in the presence of an organometallic activator.² A standard procedure for the preparation of these complexes is the reaction of WCl₆ or WOCl₄ with a phenolic compound, which often results in a mixture of species with varying numbers of phenoxide substituents, some of which may also carry positional isomers with respect to the tungsten center.^{6,7} Previously, we reacted [W(eg)₃] (**1**) (eg = 1,2-ethanediolate dianion) with substituted phenyl acetates to prepare heteroleptic W(VI) phenoxides of the type [W(eg)₂(OAr)₂] (**2**) and have used these complexes as catalyst precursors in a two-component system for the ring opening metathesis polymerization of dicyclopentadiene and norbornene.^{8,9} To attain a greater degree of understanding of the chemistry of these complexes, we have now examined chloride-for-alkoxide substitution and prepared complexes of the type [WCl₂(eg)(OAr)₂] (**3**) by treating **2** with HCl.

Complexes **3** are the first examples of tungsten(VI) alkoxide phenoxides which carry a *trans*-dichloro moiety. Furthermore, bromination of the coordinated phenoxide group in the complexes **2** was also studied as an example of aromatic substitution in a ligand. Our long-term goal is to employ these functionalities in the preparation of polymer- or silica-supported tungsten catalysts.

Experimental Section

General Information. Solvents were dried over CaH₂ and distilled prior to use. Other chemicals were of reagent grade and used as purchased. Complexes **1**, **2a**, **2c**, and **2e** were prepared according to the literature procedures.^{8,9} ¹H NMR spectra were recorded using a Bruker AM 200 spectrometer in CDCl₃ solutions and were referenced internally to SiMe₄. IR spectra were recorded as KBr disks, using a Mattson Galaxy FTIR spectrometer. Elemental analyses were obtained using a Perkin–Elmer CHNS-Analyzer 2400. Analytical samples were dried in vacuo at 40 °C for 2 h prior to elemental and spectral analyses.

Bromination of 2a and 2c. To a solution of **2a** or **2c** (0.20 mmol, 110 mg or 130 mg, respectively) in CCl₄ (10 mL) was added Et₃N (1.0 mmol, 0.14 mL) and Br₂ (0.50 mmol, 25 μ L) at room temperature. The reaction mixture was stirred for 2 h, filtered, and dried under reduced pressure. The yellow, solid crude product was purified by column chromatography using CH₂Cl₂ as eluent. **2b** and **2d** were also prepared from **1** and the appropriate phenyl acetates using literature methods.⁹

[W(eg)₂(OC₆H₂Me₂-2,6-Br-4)₂] (2b**).** Yield, 120 mg (85%). ¹H NMR (CDCl₃): δ 7.15 (4H, s, aromatics), 5.50 (2H, m, CH₂), 5.30 (6H, m, CH₂), 2.45 (12H, s, CH₃). IR (KBr): 1469 vs, 1380 vs, 1360 w, 1320 w, 1269 s, 1200 vs (br), 1070 vs (br), 1005 w, 930 s, 905 s, 900 s, 860 s, 850 m, 794 vs, 725 m, 652 s, 625 vs, 580 m, 568 s, 560 m, 525 s, 444 m, 415 w cm⁻¹. Anal. Calcd for C₂₀H₂₄Br₂O₆W: C, 34.1; H, 3.4. Found: C, 34.3; H, 3.4.

[W(eg)₂(OC₆H₂Pr₂-2,6-Br-4)₂] (2d**).** Yield, 145 mg (89%). ¹H NMR (CDCl₃): δ 7.16 (4H, s, aromatics), 5.55 (2H, m, CH₂), 5.30 (6H, m, CH₂), 3.60 (4H, m, CHMe₂), 1.18 (24H, s, CH₃). IR (KBr): 1470 vs, 1385 vs, 1360 w, 1340 w, 1320 w, 1270 w, 1200 vs (br), 1070 vs (br), 1005 w, 990 w, 930 s, 905 s, 900 s, 860 s, 850 m, 795 vs, 725 m, 650 s, 625 vs, 580 m, 568 s, 560 m, 525 s, 442 m, 415 w cm⁻¹. Anal. Calcd for C₂₈H₄₀Br₂O₆W: C, 41.2; H, 4.9. Found: C, 41.0; H, 4.8.

General Procedure for the Syntheses of 3a–3e. To a solution of **2** (0.250 mmol) in CH₂Cl₂ (20 mL) was introduced a slow stream of

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Table 1. Crystallographic Data for Compounds **3**

	3a'	3a''	3b	3c'	3c''	3e
formula	C ₁₈ H ₂₂ Cl ₂ O ₄ W	C ₁₈ H ₂₂ Cl ₂ O ₄ W	C ₁₈ H ₂₀ Br ₂ Cl ₂ O ₄ W	C ₂₆ H ₃₈ Cl ₂ O ₄ W	C ₂₆ H ₃₈ Cl ₂ O ₄ W	C ₃₀ H ₄₆ Cl ₂ O ₄ W
<i>M_r</i>	557.11	557.11	714.91	669.31	669.31	725.42
cryst syst	triclinic	triclinic	monoclinic	monoclinic	tetragonal	orthorhombic
space group (no.)	<i>P</i> -1 (2)	<i>P</i> -1 (2)	<i>C</i> 2/c (15)	<i>P</i> 2 ₁ (4)	<i>I</i> -4 (82)	<i>Pbca</i> (60)
<i>a</i> /Å	11.3504(14)	8.391(4)	24.634(3)	9.712(2)	26.657(6)	22.506(3)
<i>b</i> /Å	11.3636(10)	15.909(6)	11.508(4)	10.0849(14)	26.657(6)	27.700(6)
<i>c</i> /Å	8.3205(11)	8.117(4)	16.465(2)	14.7712(16)	10.304(10)	10.729(2)
α°	104.248(8)	109.50(4)	90	90	90	90
β°	94.583(12)	109.50(4)	101.295(13)	90.437(13)	90	90
γ°	73.150(9)	87.03(4)	90	90	90	90
<i>U</i> /Å ³	995.5(2)	997.8(7)	4577.1(17)	1446.8(4)	7322(7)	6689(2)
<i>Z</i>	2	2	8	2	8	8
<i>D_c</i> /g cm ⁻³	1.859	1.854	2.075	1.536	1.214	1.441
μ (Mo K α)/mm ⁻¹	6.089	6.075	8.793	4.204	3.322	3.643
obs. reflns	3510	3498	4028	2700	3552	5892
<i>R</i> _{int}	0.0187	0.0399	0.0229	0.0181	0.0456	—
parameters	226	226	244	299	298	328
<i>R</i> 1 ^a	0.049 (0.031)	0.074 (0.033)	0.121 (0.043)	0.038 (0.027)	0.1162 (0.0521)	0.201 (0.053)
<i>wR</i> 2 ^a	0.064 (0.060)	0.087 (0.075)	0.094 (0.078)	0.057 (0.055)	0.1385 (0.1188)	0.123 (0.093)

^a Values in parentheses for reflections with $I > 2.0\sigma(I)$. $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$, and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (2F_c^2 + F_o^2)/3$.

dry, gaseous HCl for 5 min, resulting in the solution changing from yellow to red in color. The mixture was allowed to stand at room temperature for 2 h (8 h were required for **3c** and **3d**). By TLC (silica gel using CH₂Cl₂ eluent), one major component and trace amounts of other components were present. Volatiles were then removed under reduced pressure, and the dark-red residue was column chromatographed over silica gel using CH₂Cl₂ as eluent. Crystals for X-ray measurements were grown from acetonitrile (**3a'**, **3c'**, and **3e**) or hexane (**3a''**, **3b**, and **3c''**) solutions. IR spectra for compounds **3a** and **3c** were measured on crystals obtained from hexane.

[W(eg)(OC₆H₂Me₂-2,6)Cl₂] (**3a**). Yield, 53 mg (39%). ¹H NMR (CDCl₃): δ 7.12 (2H, s, aromatics), 7.08 (2H, s, aromatics), 6.85 (2H, m, aromatics), 5.93 (4H, m, CH₂), 2.69 (12H, s, CH₃). IR (KBr): 1468 s, 1450 m, 1380 w, 1320 m, 1300 w, 1279 m, 1200 vs, 1190 vs, 1088 s, 1037 vs, 1015 m, 914 vs, 788 s, 768 vs, 734 s, 725 m, 651 vs, 625 w, 575 m, 543 s, 426 m. Anal. Calcd for C₁₈H₂₂Cl₂O₄W: C, 38.8; H, 4.0. Found: C, 38.9; H, 4.2.

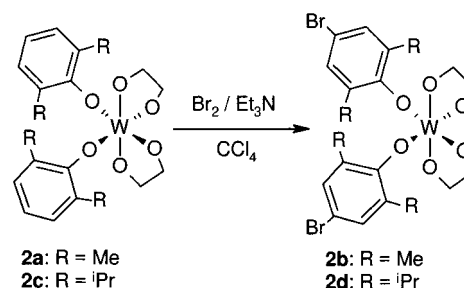
[W(eg)(OC₆H₂Me₂-2,6-Br-4)Cl₂] (**3b**). Yield, 82 mg (46%). ¹H NMR (CDCl₃): δ 7.17 (2H, s, aromatics), 7.13 (2H, s, aromatics), 5.90 (4H, m, CH₂), 2.70 (12H, s, CH₃). IR (KBr) 1470 s, 1450 m, 1380 w, 1320 m, 1300 w, 1280 m, 1200 vs, 1190 vs, 1088 s, 1035 vs, 1015 m, 912 vs, 788 s, 768 vs, 734 s, 725 m, 650 vs, 625 w, 575 m, 545 s, 425 m cm⁻¹. Anal. Calcd for C₁₈H₂₀Br₂Cl₂O₄W: C, 30.2; H, 2.8. Found: C, 30.0; H, 2.8.

[W(eg)(OC₆H₃Pr₂-2,6)Cl₂] (**3c**). Yield, 32 mg (19%). ¹H NMR (CDCl₃): δ 7.28 (2H, s, aromatics), 7.24 (2H, s, aromatics), 7.05 (2H, m, aromatics), 5.90 (4H, m, CH₂), 3.93 (4H, m, CHMe₂), 1.26 (24H, m, CH₃). IR (KBr) 1461 s, 1430 m, 1380 m, 1360 m, 1322 s, 1245 s, 1200 s, 1174 vs, 1155 m, 1103 s, 1041 vs, 1016 w, 913 vs, 885 m, 823 w, 803 s, 788 s, 750 vs, 715 s, 655 vs, 625 w, 607 s, 545 vs, 445 w, 431 m, 426 m cm⁻¹. Anal. Calcd for C₂₆H₃₈Cl₂O₄W: C, 46.7; H, 5.7. Found: C, 46.5; H, 5.8.

[W(eg)(OC₆H₂Pr₂-2,6-Br-4)Cl₂] (**3d**). Yield, 60 mg (29%). ¹H NMR (CDCl₃): δ 7.27 (2H, s, aromatics), 7.23 (2H, s, aromatics), 5.90 (4H, m, CH₂), 3.95 (4H, m, CHMe₂), 1.25 (24H, m, CH₃). IR (KBr) 1465 s, 1430 m, 1382 m, 1360 m, 1320 s, 1245 s, 1203 s, 1174 vs, 1155 m, 1103 s, 1041 vs, 1016 w, 911 vs, 885 m, 823 w, 803 s, 785 s, 750 vs, 715 s, 655 vs, 625 w, 607 s, 544 vs, 445 w, 431 m, 426 m cm⁻¹. Anal. Calcd for C₂₆H₃₆Br₂Cl₂O₄W: C, 37.8; H, 4.4. Found: C, 38.0; H, 4.5.

[W(eg)(OC₆H₃Bu₂-2,4)Cl₂] (**3e**). Yield, 130 mg (72%). ¹H NMR (CDCl₃): δ 7.74 (1H, s, aromatics), 7.70 (1H, s, aromatics), 7.43 (4H, m, aromatics), 5.92 (4H, m, CH₂), 1.49 (18H, s, CH₃), 1.33 (18H, s, CH₃). IR (KBr) 1481 vs, 1461 s, 1430 m, 1390 m, 1361 s, 1322 m, 1300 m, 1270 w, 1245 s, 1215 vs, 1200 s, 1164 m, 1125 s, 1085 vs, 1046 vs, 1025 w, 917 vs, 885 m, 867 vs, 824 s, 759 s, 728 m, 759 s, 725 w, 665 vs, 625 w, 597 vs, 565 s, 537 vs, 445 w, 430 m, 425 w,

Scheme 1. Bromination of Coordinated Phenoxide in **2**



415 w cm⁻¹. Anal. Calcd for C₃₀H₄₆Cl₂O₄W: C, 49.7; H, 6.4. Found: C, 49.6; H, 6.2.

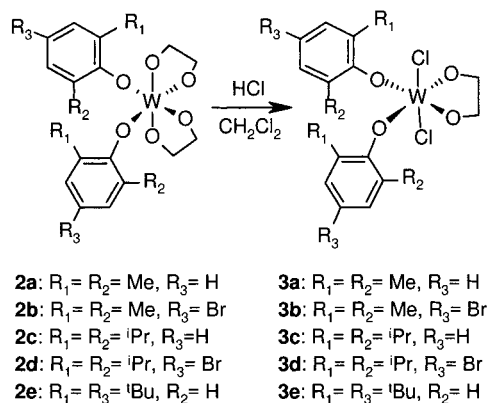
X-ray Crystal Determinations. Crystal data for all compounds along with other experimental details are summarized in Table 1. Single-crystal data collections, reduction, and subsequent calculations were performed essentially as described the previous papers.⁸ Three of the four *tert*-butyl groups in **3e** were refined in two positions.

Results and Discussion

Reactions. The coordinated phenoxide group can readily undergo some substitution reactions typical of the free ligands, e.g., [W(OPh)₆] is known to react in CCl₄ solution with bromine in the presence of CaCO₃ to form [W(OPh-4-Br)₆] in practically quantitative yield.¹⁰ Thus, treatment of either bisdiolate complex **2a** or **2c** with Br₂ in CCl₄ produced the analogous complex **2b** or **2d**, respectively, with *para*-brominated phenoxide groups in nearly quantitative yields (see Scheme 1). These bromophenoxides may be further derivatized to prepare building blocks for polymer- or silica-supported tungsten complexes. The presence of base is essential in this reaction (e.g., triethylamine) as otherwise a mixture of several products is obtained, resulting in lower yields and the requirement for a more extensive purification process. In the absence of a base, the liberated HBr from the reaction apparently results in (according to TLC and NMR analyses) the bromo analogue of **3** (see below).

Metal alkoxides can be transformed into mixed-ligand complexes composed of alkoxides and halides by various substitution reactions.¹¹ The direct addition of anhydrous HCl is the most straightforward method to the stepwise substitution

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Scheme 2. Chloride-for-alkoxide Substitution of **2**

of alkoxides but can be difficult to control.¹² Other successful reagents include AcOX , Me_3SiX , SOX_2 , and AlX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), where the reagent can react with proton sources, e.g., trace amounts of alcohol forming HX , the actual reacting species.^{13–15} Compounds of type **2** were successfully reacted directly with HCl in this study to yield dichlorocomplexes of type **3**, as indicated in Scheme 2.

The yellow–orange dichloromethane solutions of **2** were saturated with dry HCl forming intense red solutions, which were allowed to stand at room temperature for a few hours. Complexes **2c** and **2d**, which are substituted at both the 2 and 6 positions by bulky *iso*-propyl groups, required longer reaction times to produce notable yields. Significantly, **2e** reacted without difficulty, implying that steric hindrance is the reason and not inductive effects. Also, the best yield was achieved by **2e**. In all cases, purification by column chromatography was required to yield compounds **3** as dark-red crystalline solids. Complexes **3** are stable in air at room temperature and are very soluble in hydrocarbons, acetonitrile, chlorinated solvents, and ethers. They are also soluble in alcohols but decompose slowly in alcohol solutions. Identical products (by TLC and NMR) were also formed from the reactions of **2** with other chloride sources, e.g., AlCl_3 , AcOCl , or SOCl_2 , but the yields were lower due to the formation of many side-products which, moreover, made purification of the products more difficult. NMR and X-ray analysis of **3** verified that one eg ligand is displaced from **2** and replaced by two chlorides. This substitution results in the substantial rearrangement of the ligands, as the two newly introduced chlorides are oriented trans to one another but have replaced two oxygen atoms of one eg ligand which are, by necessity, in cis positions. The substitution reaction was shown to be reversible, as complexes **3** react with H_2eg in the presence of base to reform **2**, which indicates that the coordination sphere around W(VI) is quite flexible. Our attempts to eliminate the second eg ligand and prepare tetrachlorides of type $[\text{WCl}_4(\text{OAr})_2]$ by continuing the reaction further were unsuccessful. The prolonged treatment of complexes **2** with any of the abovementioned chloride sources did not result in the desired compound and only led finally to the formation of an uncharacterized dark solid and free phenol.

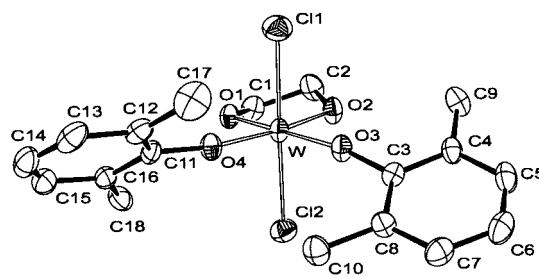


Figure 1. The ORTEP²⁰ drawing of complex $[\text{WCl}_2(\text{eg})(\text{mephe})_2]$ (**3a'**) showing 30% probability ellipsoids. The hydrogen atoms have been omitted for clarity. The crystals were grown from acetonitrile.

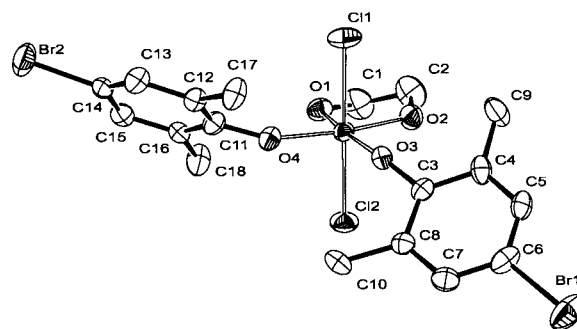


Figure 2. The ORTEP²⁰ drawing of complex $[\text{WCl}_2(\text{eg})(\text{Brmephe})_2]$ (**3b**) showing 30% probability ellipsoids. The hydrogen atoms have been omitted for clarity. The crystals were grown from hexane.

¹H NMR Studies. The ¹H NMR spectra of compounds **2b** and **2d** showed the typical resonances for substituted phenolato ligands. In the aliphatic region of the spectra, two distinct multiplets for the ethanediolato groups are observed (at ca. 5.3 and 5.5 ppm), implying that there are two different environments for these methylene protons. These portions of the spectra for the eg ligands are similar to the previously reported spectra of comparable complexes, e.g., $[\text{W}(\text{bino})(\text{eg})_2]$ (bino = 1,1'-bi-2-naphtholate).¹⁶ In the case of complexes **3**, the ¹H NMR spectra also showed typical resonances for the phenolato ligands but only one multiplet for the eg group (at ca. 5.9 ppm). In principle, the unsymmetrical phenolato ligands (buphe) in complex **3e** can adopt either of two different rotational isomers (syn and anti), which are similar to the imido ligand in the structurally comparable molybdenum bis imido complex $[\text{MoCl}_2(\text{dme})(\text{NPh}^t\text{-Bu-2})_2]$.¹⁷ However, the ¹H NMR spectrum of **3e** in CDCl_3 at room temperature contained only one signal for ¹Bu groups in the ortho position. Thus, on the NMR time-scale in solution at room temperature they are time averaged and yield only one signal. X-ray structure determination of **3e** verified that these asymmetric phenolato ligands adopted a syn conformation in the solid state (see below).

X-ray Crystal Structures. Compounds **3a–3c** and **3e** form monomeric molecules in which one diolato ligand (two oxygen donors), two phenolato oxygen atoms, and two chloro ligands bond to the central tungsten atom (Figures 1–4). The main features of the structures are the following: 1) the chloro ligands are in trans positions relative to one another (the Cl–W–Cl angle is ca. 180°), 2) the O(diolato)–W–O(diolato) angle is 79°, and 3) the O(phenolato)–W–O(phenolato) angle is about 100°. The distorted octahedral *trans*- WCl_2O_4 units are generally similar in all studied compounds, as indicated by the bond parameters presented in Table 2. The phenyl groups can adopt

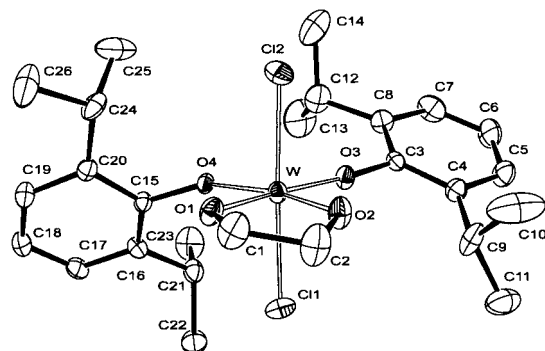
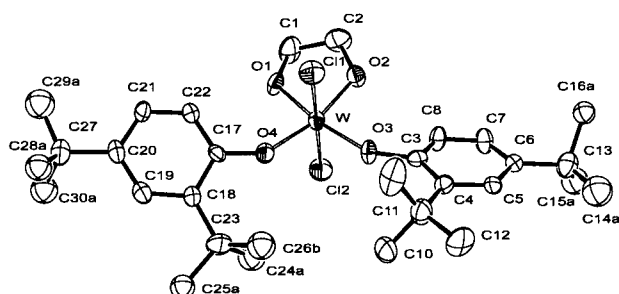
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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **3**

	3a'	3a''	3b	3c'	3c''	3e
W—O(1)	1.880(4)	1.886(6)	1.884(7)	1.877(6)	1.886(11)	1.869(8)
W—O(2)	1.888(4)	1.877(6)	1.876(7)	1.873(6)	1.880(11)	1.881(8)
W—O(3)	1.840(4)	1.849(5)	1.862(7)	1.845(5)	1.846(12)	1.857(8)
W—O(4)	1.847(4)	1.841(6)	1.849(7)	1.874(5)	1.842(12)	1.857(8)
W—Cl(1)	2.358(2)	2.363(3)	2.357(3)	2.367(3)	2.359(5)	2.362(3)
W—Cl(2)	2.398(2)	2.388(3)	2.371(3)	2.354(3)	2.385(5)	2.365(3)
O(3)—C(3)	1.380(6)	1.371(9)	1.362(11)	1.371(9)	1.41(2)	1.398(13)
O(4)—C(Ar)	1.379(6)	1.379(10)	1.365(11)	1.380(10)	1.42(2)	1.366(12)
O(1)—W—O(2)	79.13(16)	78.9(3)	79.5(3)	79.5(3)	79.4(5)	78.6(3)
O(1)—W—O(3)	169.92(17)	170.6(3)	169.5(3)	172.9(3)	170.7(6)	166.5(3)
O(1)—W—O(4)	88.92(16)	89.2(3)	90.9(3)	87.9(3)	87.3(5)	88.0(3)
O(2)—W—O(3)	91.85(17)	93.5(3)	90.8(3)	93.4(3)	92.2(6)	89.0(3)
O(2)—W—O(4)	168.02(16)	167.6(3)	169.9(3)	166.7(3)	166.7(5)	165.4(3)
O(3)—W—O(4)	100.14(17)	98.6(3)	99.0(3)	99.2(3)	101.1(5)	104.9(3)
Cl(1)—W—Cl(2)	178.27(6)	177.12(11)	179.25(13)	177.79(12)	177.2(2)	175.76(12)
C(3)—O(3)—W	166.0(4)	159.6(5)	157.0(6)	172.3(6)	158.0(11)	146.6(8)
C(Ar)—O(4)—W	167.4(4)	165.6(6)	156.8(7)	147.6(5)	159.0(11)	147.2(7)
O1—C1—C2—O2	29.6(7)	35(1)	29(2)	18(2)	—18(3)	16(2)
O ₄ vs τ_1^a	29.4(2)	30.9(3)	40.8(3)	28.3(4)	38.7(4)	23.5(4)
O ₄ vs τ_2^a	38.9(2)	43.5(3)	44.2(3)	60.3(3)	50.3(6)	22.2(5)
τ_1 vs τ_2^a	65.4(2)	74.1(3)	84.9(3)	86.9(3)	88.5(6)	42.9(4)
C(me)···C(me) ^b	4.02(1)	3.86(2)	4.47(2)	5.61(2)	5.56(4)	7.25(2)

^a The dihedral angle between the O₄ coordination plane and the phenyl ring bonded to O(3) (τ_1); τ_2 is the plane of the phenyl ring bonded to O(4). ^b The closest distance between the two central carbon atoms of the substituents located at the ortho positions of adjacent phenyl rings.

**Figure 3.** The ORTEP²⁰ drawing of complex [WCl₂(eg)(prphe)] (**3c'**) showing 30% probability ellipsoids. The hydrogen atoms have been omitted for clarity. The crystals were grown from acetonitrile.**Figure 4.** The ORTEP²⁰ drawing of complex [WCl₂(eg)(buphe)₂] (**3e**) showing 30% probability ellipsoids. The hydrogen atoms have been omitted for clarity. The crystals were grown from hexane.

different rotational positions, as shown by the dihedral angle parameters in Table 2

The crystals of compounds **3a** and **3c** were obtained from both acetonitrile (**3a'** and **3c'**) and from hexane (**3a''** and **3c''**) solutions. In each case, the structure of the crystals was dependent on the solvent. Compound **3a** crystallized out from both solvents as triclinic crystals with similar unit cell size, but there were some differences between the actual structures (see Table 2). Compound **3c** formed monoclinic crystals from acetonitrile and tetragonal ones from hexane. The crystals **3c''** are enantiomeric, and tubular cavities run through the entire

structure. The material is also quite soft and only poorly reflects the X-rays. The small residual electron density (0.80 e/Å³) and the poor quality of the data did not permit the refinement of any possible hexane molecules within the cavities of the structure. The packing efficiency of **3c'** is much greater than that of **3c''**, as the calculated density (D_c) for the former is 1.536 g cm⁻³ and the latter is 1.214 g cm⁻³, so the latter contains 21% more empty space than the former. The main differences between the two crystal forms of **3a** and **3c** are in the orientations of the phenyl rings, which is due to the packing forces. This also resulted in small changes in the bond parameters on the coordination sphere.

From the bond parameters presented in Table 2, it is seen that the W—O(diolato) bond lengths in **3a–c,e** vary from 1.869(8) to 1.888(4) Å, while the W—O(phenolato) bond lengths vary from 1.840(4) to 1.874(5) Å, i.e., the W—O(diolato) bond lengths are slightly longer than the W—O(phenolato) bond lengths. The *trans*-O(diolato)—W—O(phenolato) angles vary from 165.4(3) to 172.9(3)°. The smallest *trans*-O—W—O angle is present in **3e** where, in concert, the largest bond angle for the *cis*-phenolato ligands is observed (for **3e** the O(3)—W—O(4) bond angle is 104.9(3)°, for these other compounds it is ca. 100°). This suggests that the two bulky ArO⁻ ligands slightly distort the coordination sphere of the WCl₂(eg)(ArO)₂ unit, which is otherwise quite similar structurally to the other studied compounds.

The influence of the bulky phenolato ligands on the structure of these compounds is evident in the orientation of the phenyl groups with respect to the complex unit. In Table 2 a comparison between the dihedral angles of the O₄ coordination plane and the planes of phenyl rings and also the dihedral angles between two phenyl rings is presented. It can be seen that these values vary greatly from compound to compound and between polymorphs.

In the high-valent metal alkoxides and aryloxides the M—O distances are generally shorter than the values expected solely on the basis of σ bonding. This indicates that π bonding (electron donation from the p orbital of oxygen to the d orbitals of tungsten) is present. As a result, the relationship between the M—O bond distances and the degree of π bonding for the

terminal alkoxides and phenoxides has been widely discussed.^{11,18} The value of the M—O—C angle can also, in theory, reflect the degree of π donation to the metal, but it has been shown to be an extremely flexible parameter and primarily controlled by steric properties.^{18,19} In the newly prepared compounds, the W—O—C(phenyl) angles vary from 146.6(8)° (relevant W—O bond length 1.857(8) Å) to 172.3(6)° (1.845(5) Å). However, in **3a'** the W—O—C(phenyl) angle is 166.0(4)° and the W—O distance 1.840(4) Å. This indicates that the W—O distance is not responsive to the variation in the W—O—C(phenyl) angle, although some correlation is discernible. The crystal packing forces seem to have strong effects on the bending of these bonds.

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Conclusion

In conclusion, we have found that coordinated phenoxide groups in [W(eg)₂(OC₆H₃R₂-2,6)₂] (R = Me, ⁱPr) react with elemental bromine, resulting in *para*-bromination of the phenyl ring. The halide-for-alkoxide substitution of bisdiolatotungsten(VI) phenoxides [W(eg)₂(OAr)₂] was accomplished using HCl as the chloride source. This reaction leads to the displacement of one ethanediolato ligand and the formation of the dichloro complexes *trans*-[WCl₂(eg)(OAr)₂]. X-ray crystal structure determinations confirmed the general structural features of the complexes and *trans* orientation of the chloro ligands.

Supporting Information Available: Crystallographic information available as CIF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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