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Mononuclear tungsten(VI) complexes with methylenebis(6-alkylphenol)s

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Abstract

Reaction of monomeric tungsten(VI) complex [W(eg)$_3$] (**1**) (eg = 1,2-ethanediolate dianion) with either one or 2 equiv. of 2,2′-methylenebis(6-alkylphenol) [alkyl = Me (H$_2$L^1), ^{i}Pr (H$_2$L^2), ^{t}Bu (H$_2$L^3)] provides heteroleptic complexes [W(eg)$_2$(L^n)] (**2**) and [W(eg)(L^n)$_2$] (**3**), respectively. Sterically hindered ligand precursor H$_2$L^3, which bear bulky *tert*-butyl groups in *ortho*-positions, can form only a complex corresponding to formula **2**.

Keywords: Alkoxide complexes; Phenolate ligands; Tungsten; Crystal structures

1. Introduction

Transition metal complexes bearing chelating aryloxide ligands have recently attained increasing interest due to their purpose as accessories in metal-directed organic reactions [1]. The hard Lewis-base character of the phenoxide group makes these ligands ideal for attaching to the metal ions having high oxidation states (thus hard Lewis-acids). In addition, sterically hindered substituents on *ortho*-positions on the bis(phenolato) ligands allow the close environment of the central metal ion to be tuned without significantly altering the electronic properties of the ligands. As a result, several 1,1′-coupled biphenolates and binaphtholates of W(VI), often with other ligands, have been used productively as catalyst precursors in olefin metathesis reactions [1c,2]. However, reports on tungsten complexes with bridged bis(phenolate)s are scarce. Heppert's group has reported preparation and spectral characterisation of tungsten(VI) complexes [W(=X)Cl$_2$(mmp)] and [W(=X)Cl$_2$(ebp)] [X = O, NPh-2,6-Me$_2$; H$_2$mmp = 2,2′-methylenebis(4,6-dimethylphenol); H$_2$ebp = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)] [3]. Nakamura's group has studied complexes of sulfur-bridged bis(phenol)s, and has characterised several crystal structures e.g. [W(η^2-EtC = CEt)(tbp)Cl$_2$] (H$_2$tbp = 2,2′-thiobis(4,6-dimethylphenol) [4].

We have earlier prepared several heteroleptic tungsten(VI) complexes employing the reaction of [W(eg)$_3$] (**1**) (eg = 1,2-ethanediolate dianion) with methylene-bridged bis(phenol)s and found that the composition of complexes depends on the presence of the *ortho*-substituents of phenoxide moieties. For example, bulky 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) can replace only one eg group from **1** to form [W(biphe)(eg)$_2$], whereas less hindered 2,2′-dihydroxy-1,1′-dinaphtylmethane can substitute two ethanediolato ligands forming [W(dinap)$_2$(eg)]. Furthermore, these complexes can be activated by Et$_2$AlCl to obtain catalyst for olefin metathesis polymerisation of cyclic alkenes [5]. To have a more detailed knowledge about the preparation and chemical manipulation of tungsten bis(phenoxide) com-

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plexes, we have now studied the syntheses of new monomeric tungsten(VI) complexes with selected *ortho*-substituted methylenebis(phenolato) ligands.

2. Results and discussion

2.1. Synthesis and spectroscopy

The reaction of the ligand precursor H_2L^n with 1 equiv. of tungsten precursor **1** in refluxing toluene solution affords heteroleptic compounds **2** (Scheme 1). The yellow–orange products were purified by column chromatography to obtain air stable orange crystalline solids. These solids are soluble in chlorinated hydrocarbons, ethers and aromatic solvents and can be recrystallised from hot toluene to obtain single crystals for X-ray analyses. Chromatographic purification of **2a** and **2b** leads also to the isolation of minor amounts of red compounds, which were characterised as **3a** and **3b** (see below), respectively. Even so, the formation of these further substituted complexes can be prevented carrying out the reactions using slight excess (ca. 10%) of tungsten precursor. In addition, these reactions can be promoted by fractionating out the liberated ethanediol, which makes compounds **2** available in practically quantitative yields (based on ligand).

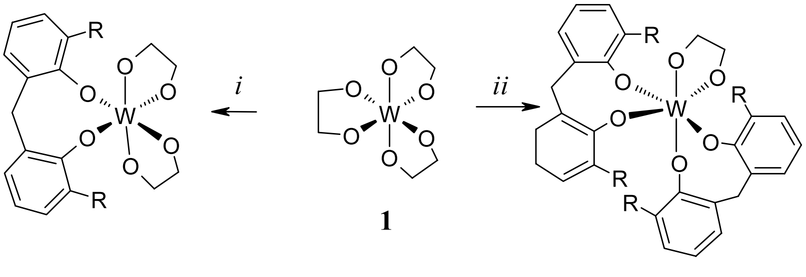
Complexes **3a** and **3b** were prepared in quantitative yields by reacting 1 equiv. of **1** with 2.2 equiv. of appropriate bis(phenol)s in refluxing toluene. However, ligand precursor H_2L^3 can replace only one of eg ligands around tungsten centre leading to the formation of **2b**. We tried to carry out this reaction also in other high-boiling solvents, e.g. chlorobentsene and *p*-chlorotoluene, but bulky *tert*-butyl groups in the *ortho*-positions of phenoxide rings can obviously prevent further substitution of eg ligands, which complies with our earlier observations [5]. Red, air-stable, crystalline solids of **3** were obtained by column chromatography followed by crystallisation from acetonitrile-toluene (**3a**) or acetonitrile (**3b**).

The ^1H NMR spectra of complexes **2** and **3** show typical resonances for ethanediolato groups in addition to the signals for aromatic protons and alkyl substituents of phenolic ligands. As puckered eight-membered rings in 2,2′-methylenebis(phenoxide) chelates can undergo slow flipping on the NMR timescale, the methylene protons in the chelate backbone are typically diastereotopic at ambient temperature [6–8]. The diastereotopic methylene protons in the chelate rings of studied compounds are separated by ca. 1.5 ppm showing doublets at ca. 3.3 and 5.0 ppm for **2** at ca. 3.5 and 5.0 ppm for **3**, respectively.

2.2. Crystallography

The solid-state structures of four new compounds were verified by X-ray studies. Complexes **2a** and **2b** (shown in Fig. 1(a and b), respectively; for **2b** only one of two molecules in the asymmetric unit is presented) have rather similar overall structure, which can be compared with other $[W(biphe)(eg)_2]$ compounds (see Table 1.) [5]. As bonding parameters of the aliphatic eg ligands are not so sensitive to the distortions than are those for the phenolato ligands, the eg ligand has only a minor role in the following discussion.

The W–O(1) and W–O(2) distances, the O(1)–W–O(2), W–O(1)–C_{arom} and W–O(2)–C_{arom} angles seem to be the most sensitive parameters for the ligand geometry variations. For example, the W–O(1) and W–O(2) distances are 1.887 (4) and 1.907(4) Å for **2a** and 1.879(4) and 1.912(4) Å for **2b** while the relevant distances in $[W(bino)(eg)_2]$ (bino = 1,1′-coupled binaphtholato) are 1.930(8) and 1.908(2) Å. Apparently, the methylene bridge can act as a hinge between phenyl groups in **2a** and **2b**, which makes these ligands more flexible, whereas if phenyl groups are directly bonded to each other as in $[W(bino)(eg)_2]$ the ligand is more rigid and it normally distorts the coordination sphere around W(VI). Related effect is also clearly seen when comparing the O(1)–W(1)–O(2) and W–O–C_{aryl} bond angles in **2a** and **2b** and $[W(bino)(eg)_2]$. The O(1)–W(1)–O(2) angles are 86.20(17) and 87.8(2)°, the W(1)–O(1)–C(1)



2a: R = Me
2b: R = ^iPr
2c: R = ^tBu

3a: R = Me
3b: R = ^iPr

Scheme 1. (i) H_2bisphenol/PhMe/reflux; (ii) $2H_2$bisphenol/PhMe/reflux.

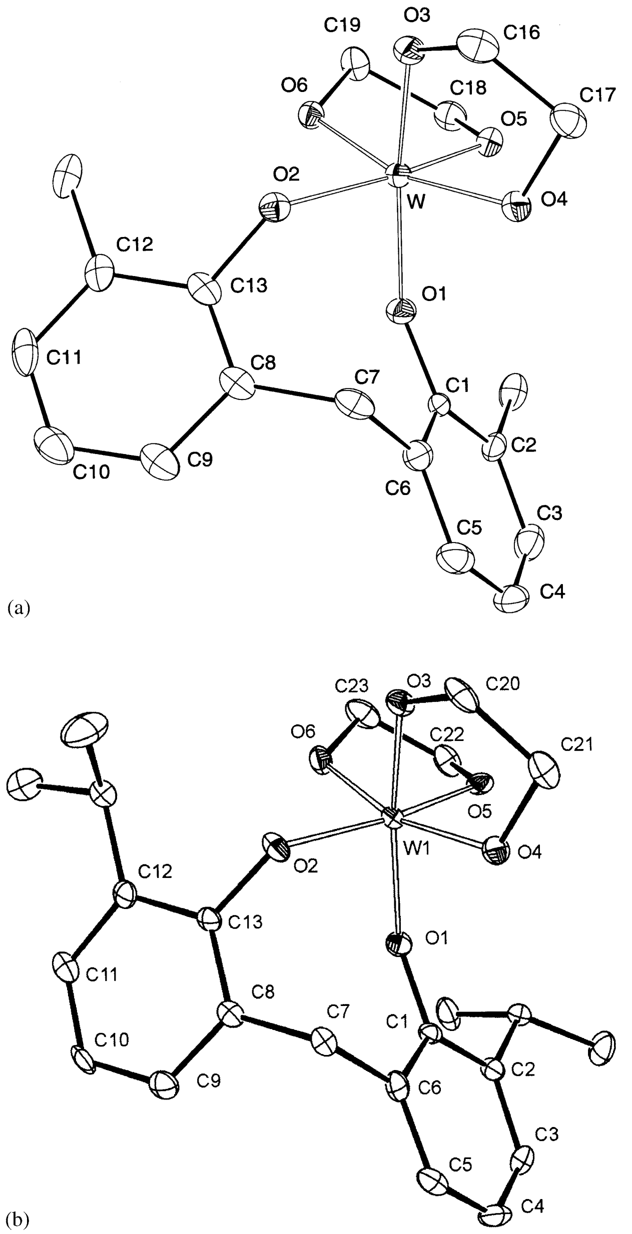


Fig. 1. Molecular structure of [W(eg)$_2$(L^1)] (**2a**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 30% probability level. (b) Molecular structure of [W(eg)$_2$(L^2)] (**2b**). Only one of the two molecules in the asymmetric unit is depicted. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 30% probability level.

angles are 146.3(4)° and 146.2(4)° and the W(1)–O(2)–C(13) angles are 138.9(4)° and 133.4(4)° for **2a** and **2b**, respectively. The relevant angles in [W(bino)(eg)$_2$] are 84.6(3)°, 130.1(7)° and 127.1(7)°, respectively (Table 1).

The data in Table 1 confirms, that the modification of the skeleton of the bis(phenolato) ligands (thus size of the chelate ring) results substantially more effects on the coordination sphere of the tungsten(VI) ion than altering the substituents in the aromatic ligand in the [W(biphe)(eg)$_2$] type compounds.

The angles of the dihedral planes described by atoms C(1)–C(6) and C(8)–C(13) are 75.9(2)° **2a** and 75.2(2)° for **2b** (75.3(2)° for the other molecule in the asymmetric unit).

The principal structures of the compounds **3a** (1/2)C_7H_8 and **3b** (shown in Fig. 2(a and b)) are quite similar, although compound **3a** crystallizes with a half molecule of toluene. The overall bonding parameters are rather similar to those found earlier for other bis(phenoxide) derivatives of **1**, thus the influence of the substituents in bis(phenoxide) moieties is quite small [5]. However, large deviations are seen in several bonding parameters of comparable bonds. For example the W–O(3) bond distance in **3a** is 1.851(4) Å (the W–O(3)–C$_{aryl}$ angle is 161.1(4)°) and the W–O(2) bond distance in [W(binap)$_2$(eg)] is 1.942(4) Å (the W–O(2)–C$_{aryl}$ angle is 128.6(4)°) (Table 2).

The dihedral angle between the planes defined by atoms C(1)–C(6) and C(8)–C(13) is 77.9(2)° and the angle between the analogous planes of other ligand is 69.1(2)° for **3a**. In **3b**, there are two identical ligands in the complex and the dihedral angle between the planes is 68.0(2)°.

A bidentate ligand bond to the metal ion creates a puckered ring with two different conformations (δ and λ). Symbols Δ and Λ are used to describe the absolute configuration of dissymmetric complex, when dissymmetry is due to chelate ring distributions [9]. In the solid state, **2a** and both molecules of **2b** in the asymmetric unit adopt a $\Delta(\lambda\ \lambda\ \lambda)$ configuration and both **3a** (1/2)C_7H_8 and **3b** adopt a $\Delta(\lambda\ \lambda\ \delta)$ configuration (δ with eg). The simulated OCCO torsion angle in the phenolato ligands has been calculated using OC···CO unit, which for example in **2a** includes the atoms O(1), C(1), C(13), O(2). A general trend in all trisdiolato complexes of tungsten(VI) seems to be that the five-membered WOCCO ring (formed by eg ligand) distorts toward planar conformation as in now studied compounds the OCCO torsion angles vary from 24.1(10)° to 43.0(5)°. Comparable five-membered rings formed by neutral ligands are typically more puckered, e.g. in $Co(en)_3^{3+}$ (en = 1,2-diaminoethane) the ligand has a torsion angle of ca. 55° [9].

3. Conclusion

Reaction of monomeric tungsten(VI) complex [W(eg)$_3$] (eg = ethanediolate dianion) with either 1 or 2 equiv. of 2,2′-methylenebis(6-alkylphenol) [alkyl = Me (H$_2$L^1), ^{i}Pr (H$_2$L^2), ^{t}Bu (H$_2$L^3)] provides heteroleptic complexes [W(eg)$_2$(L^n)] and [W(eg)(L^n)$_2$], respectively. Sterically hindered ligand precursor H$_2$L^3, which bear bulky *tert*-butyl groups, can form only a complex corresponding to the former formula. Variation of the substituents does not show substantial effects on the

Table 1
Selected bond lengths [Å] and angles [°] for **2a**, **2b** and related compounds

	2a	**2b** [a]	$[W(mbp)(eg)_2]$ [b]	[W(cbp)(cg)] [c]	$[W(bino)(eg)_2]$ [d]
W–O(1)	1.887(4)	1.879(4)	1.8970(17)	1.891(6)	1.930(8)
W–O(2)	1.907(4)	1.912(4)	1.8848(16)	1.899(5)	1.908(8)
W–O(3)	1.893(4)	1.885(4)	1.9324(18)	1.923(11)	1.894(7)
W–O(4)	1.912(4)	1.917(5)	1.9049(18)	1.899(6)	1.891(8)
W–O(5)	1.903(4)	1.917(4)	1.9069(16)	1.925(7)	1.879(8)
W–O(6)	1.905(4)	1.915(5)	1.9143(17)	1.888(7)	1.925(8)
O(1)–W–O(2)	86.2(2)	87.8(2)	87.35(7)	88.7(3)	84.6(3)
O(1)–W–O(3)	161.9(2)	161.2(2)	165.66(7)	168.0(3)	164.7(4)
O(2)–W–O(5)	165.0(2)	164.0(2)	162.52(7)	167.5(3)	162.3(4)
C(1)–O(1)–W	146.3(4)	146.2(4)	148.82(15)	152.9(6)	130.1(7)
C(n)–O(2)–W	138.9(4)	133.4(4)	151.18(14)	158.7(6)	127.1(7)

[a] From one of two similar molecules in the asymmetric unit.
[b] Compound **2** in Ref. [5a].
[c] Compound **3** in Ref. [5a].
[d] Compound **5a** in Ref. [5b].

Table 2
Selected bond lengths [Å] and angles [°] for **3a**·$(1/2)C_7H_8$, **3b** and $[W(binap)_2(eg)]$

	3a·$(1/2)C_7H_8$	**3b**	$[W(binap)_2(eg)]$ [a]
W–O(1)	1.886(4)	1.883(3)	1.911(4)
W–O(2)	1.917(4)	1.919(3)	1.942(4)
W–O(3)	1.851(4)	1.883(3)	1.904(4)
W–O(4)	1.909(4)	1.919(3)	1.903(4)
W–O(5)	1.909(4)	1.921(3)	1.902(5)
W–O(6)	1.908(4)	1.921(3)	1.889(4)
O(1)–W–O(2)	86.89(15)	85.02(11)	84.7(2)
O(3)–W–O(4)	89.47(17)	85.02(11)	84.9(2)
O(1)–W–O(3)	170.73(16)	169.21(18)	162 9(2)
O(2)–W–O(5)	169.31(16)	167.17(12)	162.3(4)
O(4)–W–O(6)	164.91(15)	167.17(12)	161.3(2)
C(1)–O(1)–W	145.4(4)	146.9(3)	141.3(4)
C(*n*)–O(2)–W	134.0(3)	133.0(2)	128.6(4)
C(*n*)–O(3)–W	161.1(4)	146.9(3)	131.3(4)
C(*n*)–O(4)–W	141.9(3)	133.0(2)	138.7(4)

[a] Compound **4** in Ref. [5a].

overall solid-state structures of these new compounds. However, the different degrees of shielding (depends on the bulkiness of substituents) of WO_6 unit may lead to the different reactivity in further reactions.

4. Experimental

Starting materials **1** [10] and H_2L^n [11] were prepared according to the literature. Other chemicals and solvents were from commercial origins and were used without subsequent purification. NMR spectra were recorded on Bruker AM-200 spectrometer. IR spectra were measured on a Mattson Galaxy FTIR spectrometer as Nujol mulls. Elemental analyses were obtained using a Perkin–Elmer CHNS-Analyzer 2400. Analytical samples were kept in vacuo at 40 °C for 2 h prior to elemental and spectral analyses.

*4.1. Syntheses of **2a–2c***

Tungsten precursor **1** (1.10 mmol) was heated with H_2L^n (1.00 mmol) in 60 ml of toluene at reflux temperature for 4 h to form a red solution. The H_2eg that formed during reaction was removed as toluene azeotrope. Remaining solvent was evaporated and orange solid residue was column chromatographed (silica/CH_2Cl_2) to give complex **2** as orange crystalline solids. Single crystals for X-ray measurements were obtained from hot toluene.

*4.1.1. $[W(eg)_2(L^1)]$ (**2a**)*

Yield: 458 mg (87%, based on ligand). IR: 1262(s), 1221(s), 1201(s), 1175(m), 1059(vs), 1032(vs, br), 947(w), 924(m), 901(s), 887(vs), 812(vs), 799(w), 777(m), 758(s), 733(m), 716(m), 656(s), 625(vs), 586(s), 534(s), 515(m). ^1H NMR ($CDCl_3$): δ 7.12 (m, 4H, aromatics), 6.90 (m, 2H, aromatics), 5,60 (m, 4H, $-OCH_2CH_2O-$), 5,32 (m, 4H, $-OCH_2CH_2O-$), 5.30 (d, $J=12$, 1H, $-CH_2-$), 3.25 (d, $J=13$, 1H, $-CH_2-$), 2.19 (s, 12H, CH_3). Found: C, 39.1; H, 4.7. $C_{16}H_{22}O_6W$ requires C, 38.9; H, 4.5%.

*4.1.2. $[W(eg)_2(L^2)]$ (**2b**)*

Yield: 480 mg (92%, based on ligand). 1264(s), 1229(s), 1207(s), 1185(m), 1172(s), 1055(vs), 1030(vs), 947(w), 924(m), 905(s), 881(s), 812(vs), 791(w), 770(m), 731(m), 716(m), 650(s), 625(vs), 566(s), 534(m), 515(m). ^1H NMR ($CDCl_3$): δ 7.10 (m, 4H, aromatics), 6.85 (m, 2H, aromatics), 5.59 (m, 4H, $-OCH_2CH_2O-$), 5.35 (m, 4H, $-OCH_2CH_2O-$), 5.28 (d, $J=12$, 1H, $-CH_2-$),3.44 (m, 2H, $-CH(CH_3)_2$), 3.28 (d, $J=12$, 1H, $-CH_2-$), 1.21 (m, 12H, CH_3). Found: C, 47.0; H, 5.3. $C_{23}H_{30}O_6W$ requires C, 47.1; H, 5.2%.

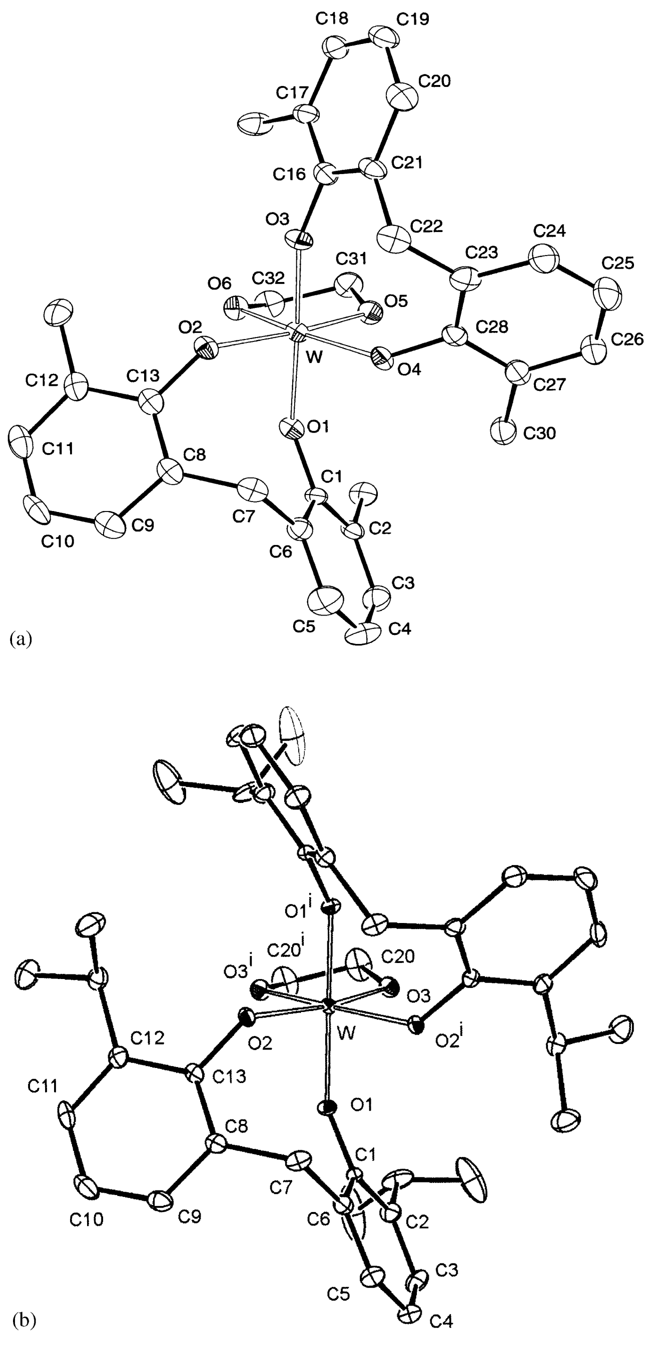


Fig. 2. Molecular structure of $[W(eg)(L^1)_2]\cdot(1/2)C_7H_8$ (**3a**·$(1/2)C_7H_8$). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 30% probability level. (b) Molecular structure of $[W(eg)(L^2)_2]$ (**3b**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids have been drawn at 30% probability level.

4.1.3. $[W(eg)_2(L^3)]$ (**2c**)

Yield: 532 mg (86%, based on ligand). 1263(vs), 1250(vs), 1223(vs), 1186(m), 1059(vs), 1113(w), 1072(vs), 1045(vs), 1024(vs), 943(w), 924(m), 901(vs), 846(w), 838(w), 791(m), 760(s), 756(m), 703(m), 650(vs), 611(vs), 561(m), 530(s), 507(m). ^{1}H NMR ($CDCl_3$) 7.08 (m, 2H, ArH), 6.71 (m, 4H, ArH), 5.60 (m, 2H, $-OCH_2-$), 5.50 (m, 4H, $-OCH_2-$), 5.30 (d, $J = 13$, 1H, $-CH_2-$), 5.08 (m, 2H, $-OCH_2-$), 3.26 (d, $J = 14$, 1H, $-CH_2-$), 1.30 (s, 9H, $C(CH_3)_3$), 1.24 (s, 9H, $C(CH_3)_3$). Found: C, 48.6; H, 5.6. $C_{25}H_{34}O_6W$ requires C, 48.9; H, 5.6%.

4.2. Syntheses of **3a** and **3b**

Tungsten precursor **1** (1.00 mmol) was heated with H_2L^n (2.20 mmol) in 60 ml of toluene at reflux temperature to form an intense red solution. The H_2eg that formed was removed by azeotropic distillation with toluene during 4 h. The solvent was evaporated and orange solid residue was column chromatographed (silica/CH_2Cl_2) to obtain red crystalline product. Single crystals were grown from acetonitrile–toluene (**3a**) or acetonitrile (**3b**).

4.2.1. $[W(eg)(L^1)_2]$ (**3a**)

Yield: 612 mg (88%, based on tungsten). 1269(s), 1211(vs), 1175(m), 1055(vs), 949(m), 901(s), 885(vs), 797(m), 771(m), 756(s), 733(m), 712(m), 625(vs), 594(m), 517(m). ^{1}H NMR ($CDCl_3$): δ 7.10 (s, 8H, aromatics), 6.72 (m, 4H, aromatics) 5.57 (m, 4H, $-OCH_2CH_2O-$), 4.95 (d, $J = 12$, 2H, $-CH_2-$), 3,45 (d, $J = 13$, 2H, $-CH_2-$), 2.36 (s, 6H, CH_3), 2.30 (s, 6H, CH_3). Found: C, 55.0; H, 4.7. $C_{32}H_{32}O_6W$ requires C, 55.2; H, 4.6%.

4.2.2. $[W(eg)(L^2)_2]$ (**3b**)

Yield: 757 mg (94%, based on tungsten). 1271(s), 1229(s),1213(vs), 1175(m), 1072(s), 1055(vs), 955(m), 901(s), 887(vs), 795(m), 771(m), 758(s), 739(m), 722(m), 621(vs), 590(m), 515(m). ^{1}H NMR ($CDCl_3$): δ 7.10 (8H, s, aromatics), 6.80 (4H, m, aromatics) 5.58 (m, 4H, $-OCH_2CH_2O-$), 5.10 (d, 2H, $J = 12$, $-CH_2-$), 3,48 (m, 4H, $-CH(CH_3)_2$), 3,44 (d, $J = 13$, 2H, $-CH_2-$), 1.21 (s, 12H, $-CH(CH_3)_2$), 1,19 (s, 12H, $-CH(CH_3)_2$). Found: C, 59.2; H, 5.8. $C_{40}H_{48}O_6W$ requires C, 59.4; H, 6.0%.

Crystal data for compounds **2a**–**3b**, along with other experimental details, are summarised in Table 3. The crystallographic data were collected at 173 K on a Nonius Kappa CCD area-detector diffractometer using graphite monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å). The data collection was performed using φ and ω scans. The data were processed using DENZO-SMN v0.93.0 [12]. SHELXA [13] absorption correction was applied for the data of all compounds

The structures were solved by direct methods using the SIR-92 program [14] and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97 program [15]. All heavy atoms were refined anisotropically. The CH hydrogen atoms were included at the fixed distances with fixed displacement parameters from their host atoms. Figures were drawn with ORTEP-3 for Windows [16].

Table 3
Crystal data and experimental details of the structure determination of **2a**–**3b**

	2a	**2b**	**3a**·(1/2)C_7H_8	**3b**
Formula	$Cr_{16}H_{22}O_6W$	$C_{23}H_{36}O_6W$	$C_{35.5}H_{36}O_6W$	$C_{40}H_{48}O_6W$
M_r	530.22	586.32	742.49	808.63
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group (no.)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$C2/c$	$C2/c$
a (Å)	8.3697(3)	9.2680(2)	25.4847(4)	12.8773(4)
b (Å)	25.2663(9)	13.1542(2)	13.5182(2)	14.5047(5)
c (Å)	9.0952(3)	18.4518(5)	19.5823(4)	18.9984(6)
α (°)	90	100.2491(6)	90	90
β (°)	110.781(2)	91.5157(7)	104.6210(10)	101.067(2)
δ (°)	90	91.2994(9)	90	90
U (Å^3)	1798.25(11)	2211.99(8)	6527.78(19)	3482.6(2)
Z	4	4	8	4
D_{calc} (g cm^{-1})	1.958	1.761	1.511	1.542
μ(MO Kα) (cm^{-1})	64.57	52.58	35.82	33.64
Observed reflections	3109	7733	6534	4286
R_{int}	0.0443	0.0510	0.0597	0.0561
Parameters	235	541	389	219
R_1	0.046 (0.030) [a]	0.060 (0.040)	0.061 (0.039)	0.063 (0.043)
wR_2	0.066 (0.061)	0.090 (0.063)	0.100 (0.092)	0.074 (0.068)

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP)]$, where $P = (2F_c^2+F_o^2)/3$.

[a] Values in parentheses for reflections with $I > 2.0\sigma(I)$.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-198063-4 for **2b** and **3b** along with CCDC-205480-1 for **2a** and **3a**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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