[May, 1992] *Bull. Chem. Soc. Jpn.*, ***65***, *1197—1201 (1992)* 1197

Unique Molecular Structures of Tungsten Phenoxides

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(Received November 11, 1991)

As a series of structural chemistry of early transition metal-phenoxides, the molecular structures of $WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$ (**1**) and $WCl_4[2,6\text{-}(CH_3)_2C_6H_3O]_2$ (**2**)have been determined by an X-ray diffraction method. Crystal data: **1**; orthorhombic, space group *Cmcm*, a=7.979 (3), b=17.094 (4), c=12.536 (2) Å, V=1709.7 (8) Å^3, Z=4, D_c=2.412 g cm^{-3}, **2**; monoclinic, space group $C2/m$, a=17.615 (4), b=7.188 (2), c=8.396 (2) Å, β=119.93 (2)°, V=921.3 (4) Å^3, Z=2, D_c=2.047 g cm^{-3}. Complexes **1**and **2** have a molecular symmetry of C_{2v} (mm) and C_{2h} ($2/m$), respectively; the W–O–C(phenoxy) angles are 180° in **1** and 179° in **2**. These are the first examples with a straight W–O–C(phenoxy) bond. By retrieval from the Cambridge Crystallographic Database the W–O–C(phenoxy) angles have been revealed to cover a wide range of 117—180°, which correlated with the W–O distance in the hyperbolic mode.

During the past decade the chemistry of early transition metal organometallics has attained rapid progress, trebling the publication of the papers concerning the chemistry of group 3—5 organometallics. Such a pronounced advance is greatly indebted to success in the isolation of an unprecedented series of highly reactive metal complexes utilizing sensible auxiliary ligands, such as Cp, OR, bulky neopentyl, or silyl groups. The most striking feature emerging from the chemistry of early transition metal complexes lies in its high reactivity towards both electrophiles and unsaturated hydrocarbons. In some favorable cases, they can proceed highly regio- and stereo-selective catalytic or stoichiometric hydrocarbon conversion. Crystallographic analysis of this class of complexes is a fundamental requirement to penetrate into the origin of their unique behavior, reaction pathways and to reveal their own structural characteristics.

The use of bulky aryloxy or alkoxy metal compounds of group 4—6 as an alternative to the cyclopentadienyl compounds is of current interest in organometallic chemistry.[1-3] We have reported a facile method for synthesizing a new series of pure mono- and bis(phenoxy)metal halides as well as two crystal structures of bis(phenoxy)titanium and niobium complexes.[4] Mono- and bis(phenoxy)tungsten complexes have recently been synthesized using WCl_6 and 2,6-dimethylphenoxy(trimethyl)silan in a THF solution, which is a method used to produce mono- or bis(phenoxy)tungsten as the sole product, different from the reported method.[5] Here, we report on the crystal structures of $WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$ (**1**) and $WCl_4[2,6\text{-}(CH_3)_2C_6H_3O]_2$ (**2**), together with the unique bonding character of W–O regarding the hitherto reported crystal structures of tungsten-phenoxides.

Experimental

General. All manipulations involving air- and moisture-sensitive compounds were carried out using the standard Schlenk technique under an argon atmosphere. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl.

The nuclear magnetic resonance (^{1}H NMR) spectra were measured on a JEOL JNM-FX90Q and JEOL GX-270 spectrometers. The mass spectra were recorded on a JEOL SX-102 spectrometer. Elemental analyses were performed at Elemental Analysis Center of Osaka University. All of the melting points were measured in sealed tubes and were not corrected.

Preparation of $Me_3Si[2,6\text{-}(CH_3)_2C_6H_3O]$. A solution of *n*-BuLi (210 mmol) in hexane (130 mL) was dropwise added to a solution of 2,6-dimethylphenol (25.1 g, 206 mmol) in THF (100 mL) at 0 °C. The reaction mixture was warmed up to ambient temperature and stirred for 1 h. To the resulting solution of 2,6-dimethylphenoxolithium was dropwise added Me_3SiCl (27.4 g, 252 mmol) at 0 °C. After stirring the reaction mixture for 1 h at ambient temperature, the precipitated salt was removed by filtration. Distillation under reduced pressure (110 °C, 24 mmHg, 1 mmHg=133.322 Pa) afforded $Me_3Si[2,6\text{-}(CH_3)_2C_6H_3O]$ (36.6 g, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 30 °C): δ=6.8—7.0 (3H, aromatic protons), 2.20 (6H, CH_3), 0.40 (9H, $SiMe_3$). Mass spectrum m/z, 194(M^+). Spectral data was superimposable to that of literature.[6]

Synthesis of $WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$. To a solution of WCl_6 (3.49 g, 8.80 mmol) in toluene (100 mL) at −78 °C was added $Me_3Si[2,6\text{-}(CH_3)_2C_6H_3O]$ (1.75 g, 8.99 mmol). The reaction mixture was allowed to warm to ambient temperature. During this period, a deep-purple powdery product was precipitated. The powder was dissolved in toluene by heating to 80 °C. Deep-purple crystals of $WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$ (3.12 g, 73%), which contained a small amount of bisphenoxo complex as an impurity (ca. 6%), were obtained upon cooling the solution to −20 °C. Repeated recrystallization afforded an analytically pure complex. Mp 244—248 °C. Anal. Calcd for $C_8H_9Cl_5OW$: C, 19.92; H: 1.88%. Found: C, 20.13; H, 1.99%. ^{1}H NMR ($CDCl_3$, 30 °C): δ=7.38 (d, 2H, *m*-H), 6.28 (t, 1H, *p*-H), 3.58 (s, 6H, CH_3). Mass spectrum for ^{184}W *m*/*z*, 307 ($M^+-C_6H_3Me_2Cl$).

Synthesis of $WCl_4[2,6\text{-}(CH_3)_2C_6H_3O]_2$. After a reaction mixture of WCl_6 (2.25 g, 5.67 mmol) and $Me_3Si[2,6\text{-}(CH_3)_2C_6H_3O]$ (2.41 g, 12.41 mmol) in toluene (100 mL) was refluxed with stirring for 2 h, the solution was cooled to 0 °C so as to afford the titled complex as dark blue crystals (1.08 g, 39%). Concentration of the supernatant solution gave 2nd and 3rd crops. Total yield was 60%. Mp 162—170 °C. Anal. Calcd for $C_{16}H_{18}Cl_4O_2W$: C, 33.84; H: 3.19%. Found: C, 34.00; H, 3.25%. ^{1}H NMR ($CDCl_3$, 30 °C): δ=7.21 (d, 4H, *m*-H), 6.76 (t, 2H, *p*-H), 2.91 (s, 12H, CH_3). Mass spectrum for ^{184}W *m*/*z*, 566 (M^+).

Crystal Data. Crystals of **1** and **2** are deep-purple and dark-blue in color with a regular prismatic shape, respectively. The unit-cell parameters were determined at room temperature by a least-squares fit of the 2θ values of 25 strong higher-angle reflections observed on a four-circle diffractometer. Crystal data are summarized in Table 1.

Table 1. Crystal Data, Data Collection, and Parameters for Structure Refinement of $WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$ (**1**) and $WCl_4[2,6\text{-}(CH_3)_2C_6H_3O]_2$ (**2**)

Complex	1	2
Formula	$WCl_5OC_8H_9$	$WCl_4O_2C_{16}H_{18}$
Formula weight	482.3	568.0
Crystal system	Orthorhombic	Monoclinic
Space group	*Cmcm*	*C*2/*m*
Temp/°C	23	20
$a^{a)}$/Å	12.952(5)	17.615(4)
b/Å	12.386(3)	7.188(2)
c/Å	8.279(3)	8.396(2)
β/deg		119.93(2)
V/Å^3	1328.0(10)	921.3(4)
Z	4	4
D_{calcd}/g cm^{-3}	2.412	2.047
F(000)/e	896	544
μ(Mo *K*α)/cm^{-1}	98.7	72.2
Crystal size/mm	0.20×0.25×0.40	0.20×0.70×0.13
2θ range$^{b)}$/deg	$6<2\theta<55$	$4<2\theta<60$.
Scan width/deg in 2θ	1.0+0.30 tan θ	1.0+0.35 tan θ
Scan speed/deg min^{-1}	8.0-16.0	4.0
Background count on each side/s	25% of peak scan	5
Reflections measured	895	912
Reflections observed$^{c)}$	576	908
Radiation damage	no	no
No. of variables	48	101
GOF$^{d)}$	1.84	1.969
$R^{e)}$	0.046	0.032
$R_w^{f)}$	0.036	0.061

a) Least-squares refinement of the θ values for 25 reflections with $2\theta>25°$. b)Intensity data were collected on a Rigaku four-circle diffractometer using graphite-monochromatized Mo*K*α radiation by the θ-2θ scan method. c) non-zero reflections. d) $[\Sigma w(|F_o|-|F_c|)^2/(n-m)]^{1/2}$, where *n* and *m* are the No. of reflections used and variables refined, respectively. e) $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. f) $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w=4F_o^2/\sigma^2(F_o^2)$ for **1**, and $w=[\sigma^2(F_o)+g(F_o)^2]^{-1}$, and g=0.003 for **2**, respectively.

Collection and Reduction of Intensity Data. The integrated intensity data were measured on a Rigaku four-circle diffractometer with graphite monochromatized Mo*K*α (λ=0.71069 Å) radiation. Two types of rotating anodes and sealed-off tube diffractometers were used for **1** and **2**, respectively. The data measurements for **1** were proceeded by a MSC/AFC software.[7] The experimental conditions were as follows:

1) a θ-2θ scan technique, with a variable scan rate of 8—16° min^{-1} in θ, depending on the peak intensity of each reflection; weak reflections were repeated up to three times, with a scan width of $\Delta\theta$=1.0+0.30 tan θ, total background countings of 50% of the peak scan times.

2) a θ-2θ scan technique, with a fixed scan rate of 2° min^{-1} in θ, a scan width of $\Delta\theta$=1.0+0.35 tan θ, and a fixed background count of 5 s on each end of scan. Three standard reflections were measured after every 150 (**1**) or 61 (**2**) reflections in order to monitor the radiation damage and any change in the crystal orientation. No significant intensity decay of the standard reflections was observed for either crystal. The number of reflection intensities collected up to 2θ=55° for **1** ($\sin\theta_{max}/\lambda$=0.650) and 2θ=60° for **2** ($\sin\theta_{max}/\lambda$=0.704) were 895 and 912, among which the observed reflections $[|F_o|>3\sigma(F_o)]$ were 576 and 908, respectively. The usual Lorentz and polarization effects were corrected for the intensity data, together with an absorption correction for **1**.

Determination and Refinement of the Structure. The determination and refinement of the crystal structure of **1** were carried out by using the TEXSAN software system.[8] The crystal structures of **1** and **2** were solved by a heavy-atom

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for Nonhydrogen Atoms in $WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$ (**1**) and $WCl_4[2,6\text{-}(CH_3)_2C_6H_3O]_2$ (**2**) with Estimated Standard Deviations in Parentheses

$WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$ (**1**)

Atom	*x*	*y*	*z*	B_{eq}
W	0	0.1828(1)	1/4	2.82
Cl(1)	0	−0.0028(7)	1/4	5.4
Cl(2)	0.1264(2)	0.1777(4)	0.0538(4)	5.0
O	0	0.329(2)	1/4	4
C(1)	0	0.443(3)	1/4	7
C(2)	−0.100(1)	0.495(2)	1/4	4
C(3)	−0.096(1)	0.607(2)	1/4	4
C(4)	0	0.659(2)	1/4	4
C(5)	−0.199(1)	0.432(2)	1/4	7

$WCl_4[2,6\text{-}(CH_3)_2C_6H_3O]_2$ (**2**)

Atom	*x*	*y*	*z*	B_{eq}
W	0.0	0.0	0.0	2.77
Cl(1)	−0.04868(13)	0.2303(3)	0.1237(4)	3.63
O	0.1090(5)	0.0	0.2132(14)	2.9
C(1)	0.1878(7)	0.0	0.366(3)	3.2
C(2)	0.1915(7)	0.0	0.537(3)	3.1
C(3)	0.2746(8)	0.0	0.687(4)	3.9
C(4)	0.3509(8)	0.0	0.675(4)	4.6
C(5)	0.3441(7)	0.0	0.502(4)	3.5
C(6)	0.2638(7)	0.0	0.347(3)	3.5
C(7)	0.1122(9)	0.0	0.547(3)	3.7
C(8)	0.2600(9)	0.0	0.160(4)	5.0

method. Successive Fourier syntheses phased by the tungsten atoms found in Patterson maps clearly revealed the remaining nonhydrogen atoms. The structures were refined anisotropically by a full-matrix least-squares method (XRAY-76[9] for **2**), the function minimized being $\Sigma w(\Delta F)^2$. All of the hydrogen atoms were located on difference Fourier maps and were included in the refinement with isotropic temperature factors. The applied weighting schemes were $w=4(F_o)^2/\sigma^2(F_o^2)$ for **1** and $w=[\sigma_{cs}^2(F_o)+0.003(F_o)^2]^{-1}$ for **2**, respectively. The final discrepancy factors, $R(R_w)$, are 0.046 (0.036) for **1** and 0.032 (0.061) for **2**, respectively. The refinement parameters are summarized in Table 1.

The final atomic coordinates of complexes **1** and **2**, together with the equivalent isotropic temperature factors (B_{eq}) for nonhydrogen atoms, are listed in Table 2.[#] The computations for **1** were proceeded on a VAXstation 3100 in Rigaku AFC-5R system in the Department of Applied Chemistry, Faculty of Engineering, while those for **1** were carried out on ACOS-850 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Results and Discussion

Molecular Structures. The molecular structures of **1** and **2** are shown in Fig. 1 by ORTEP drawings,[10] together with the atomic numberings. X-Ray structure analyses of **1** and **2** revealed that the crystallographic molecular symmetry is C_{2v} (*mm*) for **1**and C_{2h} (2/*m*) for **2**, respectively. Therefore, two phenoxy ligands in **2** are *trans* to each other, in contrast to the *cis* configuration in an analogous complex, $WCl_4[2,6\text{-}(C_6H_5)_2C_6H_3O]_2$.[11] In complex **1**, one of two crystallographic mirror planes passes through all of the non-hydrogen atoms except Cl (2), to which another mirror plane is perpendicular and including Cl (1), W, C (1), and C (4) atoms. In molecule **2**, two phenoxy ligands and a tungsten atom are located on the mirror plane, perpendicular to which a 2-fold axis passes through penetrating the tungsten atom. Therefore, the bond angle of the W–O–C(phenoxy) in **1** is

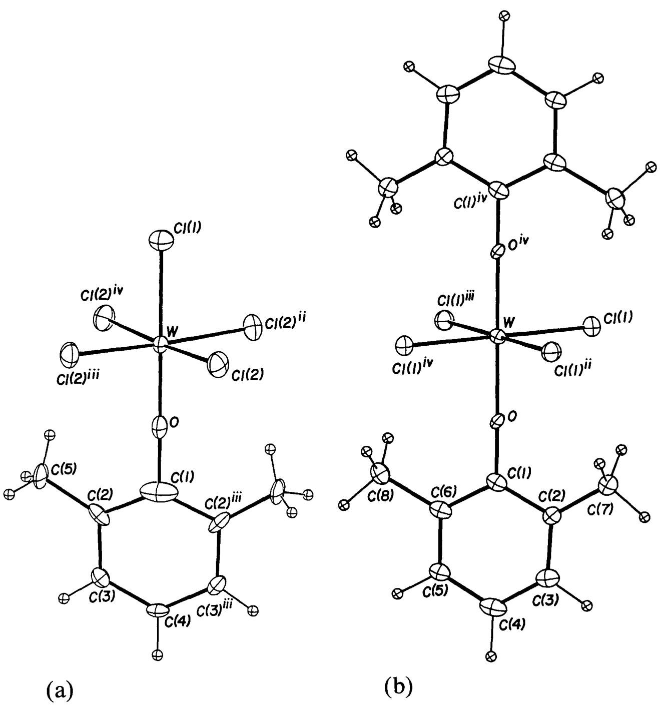

Fig. 1. Molecular structures of (a) $WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$ (**1**) and (b) $WCl_4[2,6\text{-}(CH_3)_2C_6H_3O]_2$ (**2**) by the ORTEP drawings with the thermal ellipsoids at 20% probablity level.

Table 3. Interatomic Bond Distances (Å) and Angles (°) in $WCl_5[2,6\text{-}(CH_3)_2C_6H_3O]$ (**1**) with Estimated Standard Deviations in Parentheses

(a) Bond distances/Å			
W-Cl(1)	2.299(9)	W-C1(2)	2.307(3)
W-O	1.82(2)	O-C(1)	1.41(4)
C(1)-C(2)	1.45(2)	C(2)-C(3)	1.38(2)
C(2)-C(5)	1.49(2)	C(3)-C(4)	1.41(2)
(b) Bond angles/°			
C1(1)-W-Cl(2)	88.4(1)	Cl(2)-W-Cl(2)^{ii}	89.5(3)
Cl(2)-W-Cl(2)^{iii}	90.4(3)	Cl(2)-W-Cl(2)^{iv}	176.9(3)
Cl(1)-W-O	180.0	Cl(2)-W-O	91.6(1)
W-O-C(1)	180.0	O-C(1)-C(2)	116(2)
C(2)-C(1)-C(2)^{iii}	132(3)	C(1)-C(2)-C(3)	114(2)
C(1)-C(2)-C(5)	125(2)	C(3)-C(2)-C(5)	123(2)
C(2)-C(3)-C(4)	118(1)	C(3)-C(4)-C(3)^{iii}	125(2)

Code for superscript.

i	*x*,	*y*,	*z*
ii	*x*,	*y*,	1/2−*z*
iii	−*x*,	*y*,	*z*
iv	−*x*,	*y*,	1/2−*z*

Table 4. Interatomic Bond Distances (Å) and Angles (°) in $WCl_4[2,6\text{-}(CH_3)_2C_6H_3O]_2$ (**2**) with Estimated Standard Deviations in Parentheses

(a) Bond distances/Å			
W-Cl(1)	2.333(3)	W-O	1.860(7)
O-C(1)	1.34(1)	C(1)-C(2)	1.41(3)
C(1)-C(6)	1.42(2)	C(2)-C(3)	1.38(2)
C(2)-C(7)	1.44(3)	C(3)-C(4)	1.40(3)
C(4)-C(5)	1.40(4)	C(5)-C(6)	1.36(2)
C(6)-C(8)	1.54(4)		
(b) Bond angles/°			
C1(1)-W-O	90.2(3)	W-O-C(1)	179(1)
O-C(1)-C(2)	118(1)	O-C(1)-C(6)	119(2)
C(2)-C(1)-C(6)	123(1)	C(1)-C2-C(3)	115(2)
C(1)-C(2)-C(7)	121(1)	C(3)-C(2)-C(7)	124(2)
C(2)-C(3)-C(4)	124(2)	C(3)-C(4)-C(5)	119(1)
C(4)-C(5)-C(6)	120(2)	C(1)-C(6)-C(5)	119(2)
C(1)-C(6)-C(8)	123(1)	C(5)-C(6)-C(8)	118(2)
Cl(1)^{iii}-W-O	89.8(1)	Cl(1)-W-Cl(1)^{ii}	90.4(1)
Cl(1)-W-Cl(1)^{iii}	89.6(1)	Cl(1)-W-Cl(1)^{iv}	180.0

Code for superscript.

i	*x*,	*y*,	*z*
ii	*x*,	−*y*,	*z*
iii	−*x*,	*y*,	−*z*
iv	−*x*,	−*y*,	−*z*

[#] Tables of anisotropic thermal parameters for nonhydrogen atoms, atomic coordinates for hydrogen atoms with isotropic temperature factors, and observed and calculated structure factors are kept as Document No. 8988 at the Office of the Editor of Bull. Chem. Soc. Jpn.

exactly 180°, while that in **2** [179°] is essentially, but not exactly, 180°. These are the first examples of a tungsten phenoxy complex with a straight W–O–C bond. The interatomic bond distances and angles in **1** and **2** are summarized in Tables 3 and 4, respectively. In complex **1**, the W–Cl (1) bond *trans* to the phenoxy ligand is 2.299 (9) Å, which is equal to the W–Cl (2) bond [2.307 (3) Å] *cis* to the phenoxy ligand. These W–Cl bonds are rather longer than that found in an inorganic complex, such as $WClF_5$ [2.251 Å]. The W–O bond distance of 1.82 (2) Å is the shortest in the tungsten-phenoxides hitherto reported, though the many comparable W–O distances were reported in $WCl_3[2,6\text{-}(i\text{-}Pr)_2C_6H_3O]_3$;[5] 1.832 (2), 1.836 (2), and 1.848 (2) Å, in $W[2,6\text{-}(i\text{-}Pr)_2C_6H_3O]_4$;[12] 1.849 (5), 1.851 (6), 1.851 (5), and 1.866 (5) Å, and in $W[2,6\text{-}(CH_3)_2C_6H_3O]_4$;[12] 1.843 (4) Å, etc. The $W[2,6\text{-}(i\text{-}Pr)_2C_6H_3O]_4$ and $W[2,6\text{-}(CH_3)_2C_6H_3O]_4$ complexes include the phenoxy ligand as the sole ligand, and are suitable as a standard value for the W–O (phenoxy) distance. They distribute over the range from 1.843 to 1.866 Å. The W–O distance in **2** [1.860(7) Å] is comparable with these values, though a little longer than that in **1**. Very long W–O distances were also reported in $WCl_3[2,6\text{-}(C_6H_5)_2C_6H_3O]_2[P(CH_3)_2C_6H_5]$ [1.877 (5) and 1.853 (4) Å] and $WCl_2[2,6\text{-}(C_6H_5)_2C_6H_3O]_2[P(CH_3)_2C_6H_5]$ [1.966 (4) Å],[11] in which two phenoxy ligands are *trans* to each other.

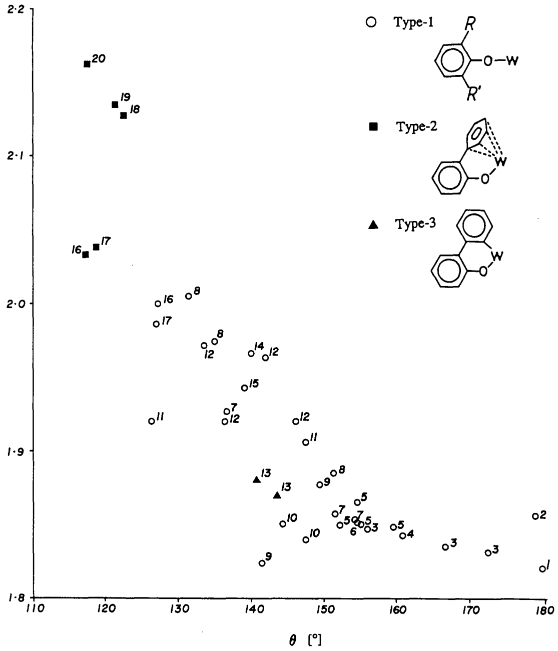

Fig. 2. Coordination geometry of phenoxy ligand in the molecular structures of tungsten-phenoxides by the W–O bond distance vs. W–O–C bond angle plotting.[13] **1**: $W(2,6\text{-}Me_2C_6H_3O)_2Cl_4$; **2**: $W(2,6\text{-}Me_2C_6H_3O)Cl_5$; **3**: $W(2,6\text{-}i\text{-}Pr_2C_6H_3O)_3Cl_3$; **4**: $W(2,6\text{-}Me_2C_6H_3O)_4$; **5**: $W(2,6\text{-}i\text{-}Pr_2C_6H_3O)_4$; **6**: $W(2,6\text{-}Ph_2C_6H_3O)_2(C_4Et_4)$; **7**: $W(2,6\text{-}Ph_2C_6H_3O)_2Cl_3(THF)$; **8**: $W(2,6\text{-}i\text{-}Pr_2C_6H_3O)_3(C_3Et_3)$; **9**: $W(2,6\text{-}Ph_2C_6H_3O)_2Cl_4$; **10**: $W(2,6\text{-}Ph_2C_6H_3O)_2Cl_4$; **11**: $W(2,6\text{-}Ph_2C_6H_3O)_2(NBu^t)_2$; **12**: $W(2\text{-}PhC_6H_4O)_4(NBu^t)(NH_2Bu^t)$; **13**: $W(PhC_6H_4C_6H_3O)_2(PMePh_2)_2$; **14**: $W(2,6\text{-}Ph_2C_6H_3O)_2Cl_2(PMe_2Ph)_2$; **15** $W(C_6H_5O)_6$; **16**: $W(2\text{-}Ph\text{-}6\text{-}\eta^6\text{-}C_6H_5C_6H_3O)(2,6\text{-}Ph_2C_6H_3O)(PMePh_2)_2$; **17**: $W(2\text{-}Ph\text{-}6\text{-}\eta^6\text{-}C_6H_5C_6H_3O)(2,6\text{-}Ph_2C_6H_3O)(Dppm)$; **18**: $W(2\text{-}Ph\text{-}6\text{-}\eta^6\text{-}C_6H_5C_6H_3O)Cl(PMe_2Ph)_2$; **19**: $W(2\text{-}Ph\text{-}6\text{-}\eta^6\text{-}C_6H_5C_6H_3O)Cl(dppe)_2$; **20**: $W(2\text{-}Ph\text{-}6\text{-}\eta^6\text{-}C_6H_5C_6H_3O)(H)(PMe_2Ph)_2$.

Characteristics of W–O (phenoxy) Bond. From a comparison of the molecular structures of tungsten-phenoxides, the W–O (phenoxy) distances are found to be distributed over a wide range, depending on many structural and/or electronic parameters. In order to understand the bonding character of the phenoxy ligand to the metals more clearly, it is interesting to study the correlation between W–O (phenoxy) distances and M–O–C (phenoxy) angles. All of the tungsten-phenoxides were extracted from the Cambridge Crystallographic Database and were examined regarding their W–O distances and W–O–C angles. After excluding some structures with low accuracy, the correlation between these parameters were plotted (Fig. 2). The retrieved tungsten-phenoxides are grouped into three types. Type-1 has phenoxy ligand without any direct interaction between the phenoxy substituent and tungsten atom. In contrast to the type-1 structure, several structures were reported to have a direct interaction between the phenyl substituent on the 2 or 6 position of the phenoxy ligand and the central tungsten atom formed by C–H bond activation. Type-2 includes the η^6-phenyl substituent on the 6-position of the phenoxy ligand found in $W(2\text{-}Ph\text{-}6\text{-}\eta^6\text{-}C_6H_5C_6H_3O)(2,6\text{-}Ph_2C_6H_3O)(PMePh_2)_2$ (**16**), and other complexes.[13] Type-3 includes a tungsten-carbon σ-bond to the phenoxy substituent found in $W(PhC_6H_4C_6H_3O)_2(PMePh_2)_2$(**13**).[13] The constraint to the W–O–C bond angle for bending is largest in type-2, and next largest in type-3. This is easy to understand from the geometry illustrated in Fig. 2. Complexes **16**—**20** in Fig. 2 include the type-2 geometry, and have very long W–O bonds [2.033—2.163 Å] and very small W–O–C angles [117.5—122.5°]. Complex **13** in the figure, having the type-3 geometry, has W–O bonds of 1.87 and 1.88 Å and W–O–C angles of 140.7 and 143.5°, which are the middle values in the figure. The W–O bond distance and W–O–C bond angles determined in the present work are at another extreme in correlation plots; the shortest W–O bond (1.82 (2) Å) and largest W–O–C bond angle (180°) exist in **1**. The figure shows that the correlation between the W–O bond distances and W–O–C bond angles make a hyperbolic curve as a good approximation. The correlation plot between these parameters shows very flexible characteristics regarding the W-phenoxy bond, which depends on the degree of geometrical constraint for the ligand. The versatile parameters of W–O bond may be attained by controlling the pπ–dπ overlapping for the bond. The flexible W–O bond character may make possible C–H bond activation of a phenoxy substituent by tungsten atoms.

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