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Contribution from the Institut de Recherches sur la Catalyse (IRSC), Laboratoire Propre du CNRS,
conventionnê a l'Universitê Claude Bernard—Lyon I, 2, Avenue Albert Einstein, 69626 Villeurbanne Cêdex, France,
and Department of Chemistry, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio 43210

Aryloxide Ligands in the Metathesis of Olefins: Syntheses of $W(OAr)_xCl_{6-x}$ Complexes with $x = 2$, 3, and 4. Crystal Structures of $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3Cl_3$ and $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$

Francoise Quignard,[†] Michel Leconte,[†] Jean-Marie Basset,*[†] Leh-Yeh Hsu,[‡] John J. Alexander,[‡]
and Sheldon G. Shore*[‡]

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Syntheses and characterization of three families of aryloxide complexes of W(VI), which are useful precursors for metathesis of olefins, are reported: $W(OAr)_x(Cl)_{6-x}$ ($x = 2, 3, 4$). The structures of $Cl_3W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$ and $Cl_4W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2$ are described. Both complexes have slightly distorted octahedral coordination spheres. For the structure of $Cl_3W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$, the chlorines occupy the meridional sites, while in the case of $Cl_4W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2$, the $OC_6H_3Ph_2$ groups are cis to each other. Crystal data for $Cl_3W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$: space group $P2_1/n$, monoclinic, $a = 13.446$ (2) Å, $b = 17.824$ (4) Å, $c = 16.289$ (3) Å, $\beta = 99.55$ (1)°, $V = 3851$ Å^3, mol wt 882.02, $\rho_{calcd} = 1.418$ g cm^{-3} for $Z = 4$. For Mo Kα 7164 unique reflections were collected at 298 K over the range $4° \leq 2\theta \leq 50°$ with 5582 reflections $>3\sigma(I)$ used in the final refinement. $R_F = 0.023$ and $R_{wF} = 0.031$. Crystal data for $Cl_4W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2\cdot{}^1/_2C_7H_8$: space group $P\bar{1}$, triclinic, $a = 10.547$ (3) Å, $b = 13.669$ (1) Å, $c = 14.632$ (1) Å, $\alpha = 84.89$ (2)°, $\beta = 78.34$ (1)°, $\gamma = 83.48$ (2)°, $V = 2062$ Å^3, mol wt 816.26, $\rho_{calcd} = 1.317$ g cm^{-3} for $Z = 2$. For Mo Kα 2915 reflections were collected at 298 K over the range $4° \leq 2\theta \leq 40°$ with 2588 reflections $\geq 3\sigma(I)$ used in the final refinement. $R_F = 0.058$ and $R_{wF} = 0.094$.

Introduction

The origin of both the activity and the stereoselectivity of metathesis catalysts is a subject of considerable research.[1] A theory has been proposed that has been deduced from experiments carried out with a large variety of olefins and catalytic systems.[2-4] Its main features are based on the relative energy levels of the metallacyclobutane intermediate compared with that of the metallacarbene–olefin complex. It has been suggested that the parameters that govern these energy levels are the cyclic and acyclic nature of the olefin, the nature of the alkyl substituents on (or close to) the double bond, and the nature of the transition metal (Cr, Mo, W). Concerning the effect of ligands, it has been proposed, but without any real proof, that they will govern both activity and stereoselectivity by their electronic effect rather than their steric effect.[5]

As a first step in testing this hypothesis, we have carried out the synthesis of variously substituted aryloxide complexes of W(VI) that can be used as precursor complexes in two-component catalytic systems. The general advantage of such ligands, especially when compared with alkoxide ligands, is that their electron-withdrawing properties can be easily varied by changing the substituents on the ring and their steric effect in close proximity to tungsten can also be modified by changing the bulkiness of the substituents in ortho and ortho' positions on the ring. Such versatile properties of aryloxides might be one of the reasons why phenoxide ligands have been very widely used recently in the field of organometallic chemistry related to metathesis[6] or C–H activation.[7]

A few tungsten complexes with phenoxide ligands have been tested as metathesis catalyst precursors, namely $W(OPh)_6$,[8,9] $WO(OPh)_4$,[10] $W(OPh)_4Cl_2$, and related complexes.[9,11-13] We report here the synthesis and characterization of three families of aryloxide complexes of W(VI): $W(OAr)_xCl_{6-x}$ with $x = 2$, 3, and 4. The structures of complexes having $x = 2$ and 3 were established by X-ray crystallography in the present report. The catalytic properties derived from these precursors have been recently described.[14]

Results and Discussion

1. Synthesis of $W(OAr)_xCl_{6-x}$ Complexes ($x = 4, 3, 2$). Treatment of WCl_6 with various substituted phenols ArOH in toluene or carbon tetrachloride solvents leads to chloro aryloxide complexes of tungsten $W(OAr)_xCl_{6-x}$.

The procedure used for these syntheses was adapted from the method described by Funk and Baumann[15] for the synthesis of $W(OPh)_4Cl_2$. An extensive series of substituted phenols was used, and it has been found that the number of chlorine atoms that may be substituted in WCl_6 is strongly dependent on the nature, the number, and the position of the substituents on the aromatic ring of the phenol. Similar results have been recently observed by Chamberlain et al.[16] with chloro aryloxides of tantalum. Depending on the nature of the substituted phenol, three series of chloro aryloxides of tungsten were synthesized: $W(OAr)_4Cl_2$, $W(OAr)_3Cl_3$, and $W(OAr)_2Cl_4$.

[†] IRSC.

[‡] The Ohio State University.

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Table I. Crystallographic Data and Refinement Results for $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3Cl_3$ (**12**) and $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$ (**15**)

	12	15
chem formula	$WCl_3O_3C_{36}H_{51}$	$WCl_4O_2C_{36}H_{26}\cdot{}^1/_2C_7H_8$
mol wt	882.02	816.26
cryst color	black	black
space group	$P2_1/n$	$P\bar{1}$
molecules/unit cell	4	2
temp, °C	25	25
a, Å	13.446 (2)	10.547 (3)
b, Å	17.824 (4)	13.669 (1)
c, Å	16.289 (3)	14.632 (1)
α, deg	90.00	84.89 (2)
β, deg	99.55 (1)	78.34 (1)
γ, deg	90.00	83.48 (2)
vol unit cell, Å^3	3851	2062
cryst dimens, mm	0.30 × 0.45 × 0.55	0.83 × 0.10 × 0.02
d(calcd), g cm^{-3}	1.418	1.317
radiation (λ, Å)	Mo K_α (0.71030)	Mo K_α (0.710730)
abs coeff, cm^{-1}	33.0	31.5
scan mode	ω–2θ	ω–2θ
data collcn limits, deg	4–50	4–40
no. of unique reflcs	7164	2915
no. of reflcns used in structure refinement ($>3\sigma(I)$)	5582	2588
$R_F = \sum\|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.023	0.058
$R_{wF} = (\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2)^{1/2}$	0.031	0.094
$w = [\sigma(\|F_o\|)^2 + (k\|F_o\|)^2]^{-1}$	0.02	0.04

1.1. $W(OAr)_4Cl_2$ Complexes. These complexes are obtained according to the reaction (eq 1), in toluene or carbon tetrachloride

$$WCl_6 + 4ArOH \rightarrow W(OAr)_4Cl_2 + 4HCl \qquad (1)$$

(at reflux temperature) of 1 equiv of WCl_6 with 4 equiv of various unsubstituted, monosubstituted, or disubstituted phenols (except 2,6-disubstituted phenols). The following compounds were synthesized: $W(OC_6H_5)_4Cl_2$ (**1**), $W(O\text{-}3\text{-}C_6H_4Me)_4Cl_2$ (**2**), $W(O\text{-}4\text{-}C_6H_4Me)_4Cl_2$ (**3**), $W(O\text{-}3,5\text{-}C_6H_3Me_2)_4Cl_2$ (**4**), $W(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4Cl_2$ (**5**), $W(O\text{-}4\text{-}C_6H_4Ph)_4Cl_2$ (**6**), $W(O\text{-}4\text{-}C_6H_4OMe)_4Cl_2$ (**7**), $W(O\text{-}2\text{-}C_6H_4Cl)_4Cl_2$ (**8**), and $W(O\text{-}4\text{-}C_6H_4Cl)_4Cl_2$ (**9**).

Compounds **1**–**9** are all black solids (dark red-purple in solution), stable in air at room temperature, and insoluble in pentane, hexane, and alcohols but are soluble in aromatic and chlorinated solvents.

The reaction with WCl_6 in the presence of less than 4 equiv of phenols with no 2,6-disubstitution (2 or 3 equiv) does not lead to the corresponding $W(OAr)_2Cl_4$ or $W(OAr)_3Cl_3$ complexes but gives $W(OAr)_4Cl_2$ and unreacted WCl_6. Under our experimental conditions, an excess of phenol (6 equiv) does not lead to $W(OAr)_6$ but to $W(OAr)_4Cl_2$ and unreacted ArOH.

1.2. $W(OAr)_3Cl_3$ Complexes. The reaction of WCl_6 with 3 equiv of 2,6-dimethyl or 2,6-diisopropyl disubstituted phenol gave a mixture of $W(OAr)_3Cl_3$ and $W(OAr)_2Cl_4$ compounds, which may be separated due to the large difference in their solubilities in the reaction medium. (The trisubstituted complexes are soluble in carbon tetrachloride whereas the disubstituted complexes are not.) Three $W(OAr)_3Cl_3$ compounds were synthesized: $W(O\text{-}2,6\text{-}C_6H_3Me_2)_3Cl_3$ (**10**), $W(O\text{-}2,4,6\text{-}C_6H_2Me_3)_3Cl_3$ (**11**), and $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3Cl_3$ (**12**). They are black solids (dark red-purple in solution), stable in air at room temperature, insoluble in pentane, hexane, and alcohols but are soluble in aromatic and chlorinated solvents.

If an excess of these disubstituted phenols (>3 equiv) is used, one does not obtain $W(OAr)_4Cl_2$ compounds but again a mixture of $W(OAr)_3Cl_3$ and $W(OAr)_2Cl_4$. The same result is also obtained by employing 2 equiv of these phenols.

1.3. $W(OAr)_2Cl_4$ Complexes. These complexes are obtained by reaction of WCl_6 with 2 equiv of phenols disubstituted in the 2,6-positions by methyl groups, phenyl groups, or halogen atoms. The following compounds were synthesized: $W(O\text{-}2,6\text{-}C_6H_3Me_2)_2Cl_4$ (**13**), $W(O\text{-}2,4,6\text{-}C_6H_2Me_3)_2Cl_4$ (**14**), $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$ (**15**), $W(O\text{-}2,6\text{-}C_6H_3Br_2)_2Cl_4$ (**16**), $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ (**17**), and $W(O\text{-}2,6\text{-}C_6H_3F_2)_2Cl_4$ (**18**). These compounds are slightly soluble in the reaction medium (CCl_4) and may be isolated by filtration of the reaction mixture. These are black solids (dark red-purple in solution), which are stable in air at room temperature except for complexes **16** and **18**, which slowly decompose in air. Complexes **13**–**18** are insoluble in pentane, hexane, and alcohols and are slightly soluble in chlorinated or aromatic solvents.

Table II. Atomic Coordinates, Esd's, and Equivalent Isotropic Thermal Parameters for $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3Cl_3$

atom	x	y	z	B,[a] Å^2
W	0.35733 (1)	0.19751 (1)	0.15068 (1)	2.589 (3)
Cl(1)	0.37767 (8)	0.11651 (6)	0.26500 (6)	4.02 (2)
Cl(2)	0.31797 (8)	0.26691 (7)	0.02821 (6)	4.22 (2)
Cl(3)	0.28009 (8)	0.09428 (6)	0.07471 (7)	4.54 (2)
O(1)	0.4773 (2)	0.1664 (2)	0.1228 (1)	3.07 (5)
O(2)	0.2349 (2)	0.2261 (1)	0.1763 (2)	3.11 (5)
O(3)	0.4224 (2)	0.2752 (2)	0.2129 (2)	3.09 (5)
C(11)	0.5632 (3)	0.1342 (2)	0.1032 (2)	2.86 (7)
C(12)	0.5682 (3)	0.1207 (2)	0.0189 (2)	3.14 (8)
C(13)	0.6560 (3)	0.0884 (3)	0.0018 (2)	4.03 (9)
C(14)	0.7339 (3)	0.0696 (3)	0.0636 (3)	4.4 (1)
C(15)	0.7266 (3)	0.0840 (3)	0.1452 (3)	3.96 (9)
C(16)	0.6422 (3)	0.1172 (2)	0.1678 (2)	3.02 (8)
C(21)	0.1372 (3)	0.2470 (2)	0.1759 (2)	3.04 (8)
C(22)	0.0677 (3)	0.1923 (2)	0.1885 (3)	3.47 (8)
C(23)	−0.0323 (3)	0.2156 (3)	0.1836 (3)	4.5 (1)
C(24)	−0.0590 (3)	0.2888 (3)	0.1698 (3)	5.1 (1)
C(25)	0.0118 (3)	0.3424 (3)	0.1611 (3)	4.4 (1)
C(26)	0.1125 (3)	0.3229 (2)	0.1635 (2)	3.48 (8)
C(31)	0.5040 (3)	0.3135 (2)	0.2561 (2)	3.25 (8)
C(32)	0.5121 (3)	0.3149 (2)	0.3432 (3)	4.02 (9)
C(33)	0.5965 (4)	0.3517 (3)	0.3862 (3)	5.7 (1)
C(34)	0.6648 (4)	0.3848 (3)	0.3455 (3)	6.6 (1)
C(35)	0.6529 (4)	0.3841 (3)	0.2597 (3)	5.7 (1)
C(36)	0.5726 (3)	0.3478 (2)	0.2125 (3)	4.1 (1)
C(120)	0.4842 (3)	0.1411 (3)	−0.0512 (2)	4.02 (9)
C(121)	0.4616 (4)	0.0795 (3)	−0.1149 (3)	5.4 (1)
C(122)	0.5107 (5)	0.2136 (3)	−0.0931 (3)	6.5 (1)
C(160)	0.6372 (3)	0.1301 (3)	0.2589 (2)	3.74 (9)
C(161)	0.7270 (4)	0.1768 (3)	0.3010 (3)	6.4 (1)
C(162)	0.6303 (4)	0.0558 (3)	0.3042 (3)	6.1 (1)
C(220)	0.0977 (3)	0.1127 (3)	0.2137 (3)	4.5 (1)
C(221)	0.0326 (5)	0.0540 (3)	0.1657 (5)	9.8 (2)
C(222)	0.1003 (6)	0.1042 (4)	0.3061 (4)	9.1 (2)
C(260)	0.1911 (3)	0.3826 (2)	0.1598 (3)	4.7 (1)
C(261)	0.2192 (5)	0.4192 (3)	0.2447 (4)	7.3 (2)
C(262)	0.1617 (5)	0.4396 (4)	0.0931 (4)	7.9 (2)
C(320)	0.4377 (4)	0.2785 (3)	0.3894 (3)	4.7 (1)
C(321)	0.4841 (5)	0.2143 (3)	0.4442 (3)	7.0 (2)
C(322)	0.3917 (5)	0.3354 (4)	0.4444 (3)	8.0 (2)
C(360)	0.5574 (3)	0.3503 (3)	0.1191 (3)	4.9 (1)
C(361)	0.4966 (6)	0.4192 (4)	0.0869 (4)	9.1 (2)
C(362)	0.6555 (4)	0.3452 (5)	0.0843 (4)	9.4 (2)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as ${}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\alpha)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\gamma)\beta_{13}]$.

When more than 2-equiv amounts of these 2,6-disubstituted phenols are used, one does not obtain the $W(OAr)_4Cl_2$ derivatives but always the disubstituted ones and unreacted phenol (and in some cases $W(OAr)_3Cl_3$ compounds **10**–**12**).

It has been of interest to determine the X-ray structure of two typical derivatives with sterically crowded aryloxide ligands. The disubstituted aryloxide complexes were found to be active in metathesis of functionalized olefins when they are associated with SnR_4 or PbR_4 cocatalysts.[14]

2. Structures of $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3Cl_3$ (12) and $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$ (15). Table I gives a summary of crystal data and refinement results obtained for compound **12**. Positional parameters and equivalent isotropic thermal parameters are given in Table II.. Figure 1 shows an ORTEP drawing of **12**, and Tables III and IV give selected bond distances and bond angles for this compound.

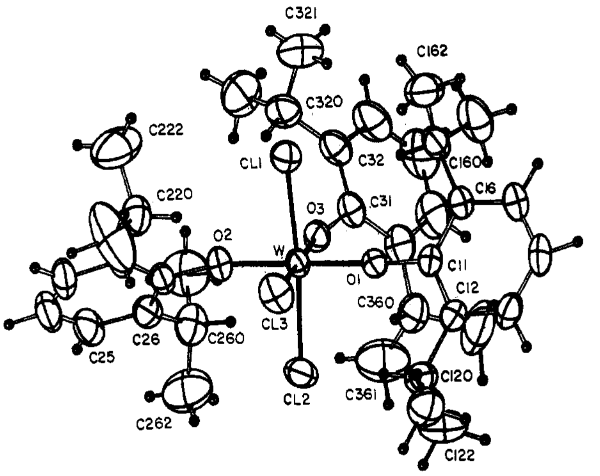

Figure 1. ORTEP plot of W(O-2,6-C_6H_3-*i*-Pr_2)$_3$$Cl_3$ with 50% probability ellipsoids.

Table III. Bond Distances (Å) and Their Estimated Standard Deviations for W(O-2,6-C_6H_3-*i*-Pr_2)$_3$$Cl_3$

(A) W–Cl and W–O Distances			
W–Cl(1)	2.337 (1)	W–O(1)	1.832 (2)
W–Cl(2)	2.333 (1)	W–O(2)	1.836 (2)
W–Cl(3)	2.360 (1)	W–O(3)	1.848 (2)
(B) O–C Distances			
O(1)–C(11)	1.375 (3)	O(3)–C(31)	1.383 (3)
O(2)–C(21)	1.365 (3)		
(C) C–C Distances			
C(11)–C(12)	1.406 (4)	C(12)–C(120)	1.512 (4)
C(12)–C(13)	1.383 (4)	C(120–C(121)	1.506 (5)
C(13)–C(14)	1.369 (4)	C(120)–C(122)	1.532 (5)
C(14)–C(15)	1.374 (4)	C(16)–C(160)	1.513 (4)
C(15)–C(16)	1.384 (4)	C(160)–C(161)	1.532 (5)
C(16)–C(11)	1.400 (4)	C(160)–C(162)	1.526 (5)
C(21)–C(22)	1.389 (4)	C(22)–C(220)	1.514 (4)
C(22)–C(23)	1.397 (4)	C(220)–C(221)	1.497 (5)
C(23)–C(24)	1.362 (5)	C(220)–C(222)	1.508 (5)
C(24)–C(25)	1.372 (5)	C(26)–C(260)	1.508 (4)
C(25)–C(26)	1.393 (4)	C(260)–C(261)	1.520 (5)
C(26)–C(21)	1.400 (4)	C(260)–C(262)	1.491 (5)
C(31)–C(32)	1.407 (4)	C(32)–C(320)	1.496 (5)
C(32)–C(33)	1.394 (4)	C(320–C(321)	1.521 (5)
C(33)–C(34)	1.353 (6)	C(320)–C(322)	1.548 (5)
C(34)–C(35)	1.380 (5)	C(36)–C(360)	1.501 (5)
C(35)–C(36)	1.378 (4)	C(360)–C(361)	1.519 (6)
C(36)–C(31)	1.395 (3)	C(360)–C(362)	1.522 (5)

Table IV. Bond Angles (deg) and Their Estimated Standard Deviations for W(O-2,6-C_6H_3-*i*-Pr_2)$_3$$Cl_3$

(A) Cl–W–Cl, Cl–W–O, and O–W–O Angles			
Cl(1)–W–Cl(2)	171.69 (3)	O(1)–W–O(2)	178.02 (8)
Cl(1)–W–Cl(3)	85.38 (3)	O(1)–W–O(3)	90.37 (8)
Cl(2)–W–Cl(3)	86.97 (3)	O(2)–W–O(3)	91.61 (8)
Cl(1)–W–O(1)	91.11 (6)	Cl(2)–W–O–(3)	95.24 (6)
Cl(1)–W–O(2)	88.93 (6)	Cl(3)–W–O(1)	87.90 (6)
Cl(1)–W–O(3)	92.50 (6)	Cl(3)–W–O(2)	90.13 (6)
Cl(2)–W–O(1)	91.86 (6)	Cl(3)–W–O(3)	177.23 (6)
Cl(2)–W–O(2)	87.84 (6)		
(B) W–O–C Angles			
W–O(1)–C(11)	172.9 (2)	W–O(3)–C(3)	156.0 (2)
W–O(2)–C(21)	166.8 (2)		
(C) O–C–C Angles			
O(1)–C(11)–C(12)	118.5 (2)	O(1)–C(11)–C(16)	118.5 (2)
O(2)–C(21)–C(22)	118.6 (3)	O(2)–C(21)–C(26)	118.0 (3)
O(3)–C(31)–C(32)	116.4 (3)	O(3)–C(31)–C(36)	119.6 (3)
(D) C–C–C Angles			
C(12)–C(11)–C(16)	123.0 (3)	C(11)–C(12)–C(120)	123.1 (3)
C(11)–C(12)–C(13)	116.7 (3)	C(13)–C(12)–C(120)	120.2 (3)
C(12)–C(13)–C(14)	121.9 (3)	C(12)–C(120)–C(121)	112.7 (3)
C(13)–C(14)–C(15)	119.8 (3)	C(12)–C(20)–C(122)	109.9 (3)
C(14)–C(15)–C(16)	122.1 (3)	C(121)–C(120)–C(122)	110.1 (3)
C(15)–C(16)–C(11)	116.5 (3)		
C(22)–C(21)–C(26)	123.4 (3)	C(21)–C(22)–C(220)	122.9 (3)
C(21)–C(22)–C(23)	116.6 (3)	C(23)–C(22)–C(220)	120.4 (3)
C(22)–C(23)–C(24	121.3 (3)	C(22)–C(220)–C(221)	114.0 (3)
C(23)–C(24)–C(25)	121.1 (3)	C(22)–C(220)–C(222)	109.0 (3)
C(24)–C(25)–C(26)	120.8 (3)	C(221)–C(220)–C(222)	111.5 (4)
C(25)–C(26)–C(21)	116.8 (3)		
C(32)–C(31)–C(36)	124.0 (3)	C(31)–C(32)–C(320)	123.6 (3)
C(31)–C(32)–C(33)	115.8 (3)	C(33)–C(32)–C(320)	120.6 (3)
C(32)–C(33)–C(34)	121.4 (4)	C(32)–C(320)–C(321)	112.2 (3)
C(33)–C(34)–C(35)	121.2 (3)	C(32)–C(320)–C(322)	111.8 (3)
C(34)–C(35)–C(36)	121.2 (4)	C(32)–C(320)–C(322)	108.5 (3)
C(35)–C(36)–C(31)	116.4 (3)		

The molecule is slightly distorted from octahedral geometry, with the chlorines occupying meridional positions. Largest deviations from ideal geometry occur for the coordination geometry of the chlorine atoms around the tungsten atom. Bond angles are Cl(1)–W–Cl(2) = 171.69 (3)°, Cl(1)–W–Cl(3) = 85.38 (3)°, and Cl(2)–W–Cl(3) = 86.97 (3)°. The W–Cl bond distances are shorter for the trans chlorines (W–Cl(1) = 2.337 (1) Å and W–Cl(2) = 2.333 (1) Å) than that for the cis chlorine (W–Cl(3) = 2.360 (1) Å). On the other hand the coordination geometry around the tungsten atom is more regular for the oxygen atoms, showing little deviation from a regular octahedral arrangement. Bond angles are O(1)–W–O(2) = 178.02 (8)°, O(1)–W–O(3) = 90.37 (8)°, and O(2)–W–O(3) = 91.61 (8)°. Only small differences are observed among the W–O bond lengths: W–O(1) = 1.832 (2) Å, W–O(2) = 1.836 (2) Å, and W–O(3) = 1.848 (2) Å. All of the Cl–W–O angles are less than 3° from the angles expected for an ideal octahedral arrangement with the exception of the angle Cl(2)–W–O(3) = 95.23 (6)°.

W–O bond lengths are comparable to those found in *trans*-W(OC_6H_5)$_4$$Cl_2$[17] (average W–O = 1.82 Å[13]) and to Ta–O bond lengths found by Chamberlain et al.[16] for Ta(O-2,6-C_6H_3-*t*-Bu_2)$_2$$Cl_3$ (1.872 and 1.836 Å); these W–O distances are shorter than those recently observed by Churchill and Schrock[6d] in the W(C_3Et_3)(O-2,6-C_6H_3-*i*-Pr_2)$_3$ complex (W–O = 1.885 (6), 2.008 (6), and 1.979 (6) Å). Concerning W–O–C angles, it appears that there are significant differences among the three aryloxide ligands (W–O(1)–C(11) = 172.9 (2)°, W–O(2)–C(21) = 166.8 (2)°, and W–O(3)–C(31) = 156.0 (2)°). Such differences in metal–O–Ar angles, depending on the position of aryloxide ligands in the molecule, were observed in the five-coordinate complexes Ta(O-2,6-C_6H_3-*t*-Bu_2)$_2$$Cl_3$ (Ta–O–C = 157.3 and 171.6°)[16] and W(C_3Et_3)(O-2,6-C_6H_3-*i*-Pr_2)$_3$ (W–O–C = 151.5, 131.4, and 135.1°).[6d] Figure 1 shows that the trans aryloxide ligands tend to have their aryl planes roughly perpendicular while the aryl ring planes of the cis ligands have a dihedral angle of 56°, probably to minimize the isopropyl–isopropyl and isopropyl–chlorine repulsions.

Table I also gives a summary of crystal data and refinement results obtained for compound **15**. This compound crystallizes with toluene solvent. Only 50% of the solvent site is occupied in the asymmetric unit. The only suitable crystal that could be obtained decomposed before a full set of data up to 40° 2*θ* could be collected, and an absorption correction could not be made because of the decomposition. Table V gives positional parameters and equivalent isotropic thermal parameters. Figure 2 shows an ORTEP drawing of Cl_4W(O-2,6-$C_6H_3Ph_2$)$_2$ (**15**) and Tables VI and VII give selected bond distances and bond angles. The two phenoxide ligands are in a cis orientation.

Because of the limited amount of data available for **15**, the structural results are intended primarily to show the configuration of the ligands around the central atom. However, because of the conformity of molecular parameters in **15** to those of similar complexes, it is still of interest to make some comparisons between **12** and **15**. Compound **12** shows deviation from an ideal octahedral arrangement around W to about the same extent as compound **15**. Distances in **15** are comparable to the corresponding bonds in **12**. As in the structure of **12**, the W–Cl distances for the trans

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Table V. Atomic Coordinates, Esd's, and Equivalent Isotropic Thermal Parameters for $W[O\text{-}2,6\text{-}C_6H_3(C_6H_5)_2]_2Cl_4$

atom	*x*	*y*	*z*	B,[a] Å^2
W	−0.90110 (7)	0.17727 (5)	0.16246 (4)	2.51 (2)
Cl(1)	−0.9686 (5)	0.0671 (4)	0.0759 (3)	4.4 (1)
Cl(2)	−0.9199 (6)	0.3006 (4)	0.0455 (3)	5.1 (1)
Cl(3)	−0.6915 (5)	0.1462 (4)	0.0785 (3)	4.3 (1)
Cl(4)	−0.8074 (5)	0.2924 (3)	0.2332 (3)	4.2 (1)
O(1)	−0.876 (1)	0.0866 (7)	0.2566 (7)	2.9 (2)*
O(2)	−1.071 (1)	0.2033 (7)	0.2185 (7)	3.0 (2)*
C(11)	−0.781 (2)	0.050 (1)	0.306 (1)	3.0 (4)*
C(12)	−0.697 (2)	−0.024 (1)	0.270 (1)	3.6 (4)*
C(13)	−0.586 (2)	−0.044 (1)	0.315 (1)	4.6 (5)*
C(14)	−0.575 (2)	0.003 (1)	0.390 (1)	5.1 (5)*
C(15)	−0.666 (2)	0.070 (1)	0.427 (1)	4.4 (4)*
C(16)	−0.776 (2)	0.092 (1)	0.389 (1)	3.3 (4)*
C(21)	−0.882 (2)	0.152 (1)	0.437 (1)	3.1 (4)*
C(22)	−0.851 (2)	0.238 (1)	0.475 (1)	4.6 (5)*
C(23)	−0.956 (2)	0.290 (2)	0.527 (1)	5.7 (5)*
C(24)	−1.081 (2)	0.254 (2)	0.543 (1)	5.7 (5)*
C(25)	−1.102 (2)	0.172 (1)	0.505 (1)	5.2 (5)*
C(26)	−1.008 (2)	0.121 (1)	0.452 (1)	3.5 (4)*
C(31)	−0.721 (2)	−0.082 (1)	0.196 (1)	3.8 (4)*
C(32)	−0.845 (2)	−0.117 (1)	0.198 (1)	3.9 (4)*
C(33)	−0.864 (2)	−0.176 (1)	0.130 (1)	4.8 (5)*
C(34)	−0.760 (2)	−0.202 (1)	0.059 (1)	5.4 (5)*
C(35)	−0.639 (2)	−0.171 (1)	0.059 (1)	5.4 (5)*
C(36)	−0.615 (2)	−0.112 (1)	0.125 (1)	5.2 (5)*
C(41)	−1.195 (2)	0.232 (1)	0.210 (1)	3.8 (4)*
C(42)	−1.282 (2)	0.157 (1)	0.207 (1)	3.0 (4)*
C(43)	−1.401 (2)	0.189 (1)	0.184 (1)	4.4 (4)*
C(44)	−1.431 (2)	0.285 (1)	0.173 (1)	5.2 (5)*
C(45)	−1.343 (2)	0.356 (1)	0.181 (1)	4.7 (5)*
C(46)	−1.219 (2)	0.334 (1)	0.201 (1)	4.0 (4)*
C(51)	−0.136 (2)	0.407 (1)	0.218 (1)	3.4 (4)*
C(52)	−0.110 (2)	0.489 (1)	0.156 (1)	5.4 (5)*
C(53)	−0.037 (2)	0.564 (2)	0.173 (1)	5.9 (5)*
C(54)	0.016 (2)	0.556 (2)	0.254 (1)	6.1 (5)*
C(55)	−0.007 (2)	0.477 (1)	0.316 (1)	4.6 (5)*
C(56)	−0.084 (2)	0.404 (1)	0.298 (1)	3.8 (4)*
C(61)	−1.253 (2)	0.053 (1)	0.219 (1)	3.5 (4)*
C(62)	−1.207 (2)	0.012 (1)	0.300 (1)	3.9 (4)*
C(63)	−1.182 (2)	−0.085 (1)	0.312 (1)	5.6 (5)*
C(64)	−1.208 (2)	−0.145 (2)	0.245 (1)	5.8 (5)*
C(65)	−1.249 (2)	−0.113 (1)	0.170 (1)	4.5 (4)*
C(66)	−1.273 (2)	−0.013 (1)	0.154 (1)	4.0 (4)*
C(713)	−0.362	0.570	3.508	7 (1)*
C(723)	−0.365	0.599	0.414	5 (1)*
C(733)	−0.448	0.675	0.393	7 (1)*
C(743)	−0.527	0.722	0.464	6 (1)*
C(753)	−0.519	0.690	0.549	6 (1)*
C(763)	−0.440	0.618	0.579	7 (1)*
C(773)	−0.277	0.493	0.530	12 (2)*

[a] *B* values marked with an asterisk were for atoms refined isotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\alpha)\beta_{13} + ac(\cos\beta)\beta_{13} + bc(\cos\gamma)\beta_{13}]$

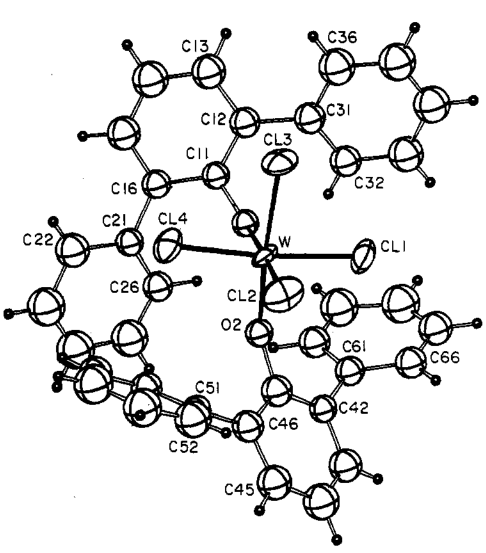

Figure 2. ORTEP plot of $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$ with 50% probability ellipsoids.

Table VI. Bond Distances (Å) and Their Estimated Standard Deviations for $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$

	(A) W–Cl and W–O Distances		
W–Cl(1)	2.267 (2)	W–Cl(4)	2.304 (3)
W–Cl(2)	2.327 (2)	W–O(1)	1.824 (6)
W–Cl(3)	2.350 (3)	W–O(2)	1.855 (7)
	(B) O–C Distances		
O(1)–C(11)	1.41 (1)	O(2)–C(41)	1.38 (1)
	(C) C–C Distances		
C(11)–C(12)	1.39 (1)	C(41)–C(42)	1.41 (1)
C(12)–C(13)	1.45 (1)	C(42)–C(43)	1.40 (1)
C(13)–C(14)	1.35 (1)	C(43)–C(44)	1.35 (1)
C(14)–C(15)	1.37 (1)	C(44)–C(45)	1.38 (1)
C(15)–C(16)	1.41 (1)	C(45)–C(46)	1.42 (1)
C(16)–C(11)	1.41 (1)	C(46)–C(41)	1.42 (1)
C(12)–C(31)	1.48 (1)	C(42)–C(61)	1.45 (1)
C(16)–C(21)	1.46 (1)	C(46)–C(51)	1.42 (1)
C(21)–C(22)	1.42 (1)	C(51)–C(52)	1.36 (1)
C(22)–C(23)	1.43 (2)	C(52)–C(53)	1.36 (2)
C(23)–C(24)	1.39 (2)	C(53)–C(54)	1.41 (2)
C(24)–C(25)	1.34 (2)	C(54)–C(55)	1.34 (1)
C(25)–C(26)	1.35 (1)	C(55)–C(56)	1.38 (1)
C(26)–C(21)	1.38 (1)	C(56)–C(51)	1.39 (1)
C(31)–C(32)	1.40 (1)	C(61)–C(62)	1.43 (1)
C(32)–C(33)	1.38 (1)	C(62)–C(63)	1.36 (1)
C(33)–C(34)	1.41 (2)	C(63)–C(64)	1.40 (2)
C(34)–C(35)	1.36 (2)	C(64)–C(65)	1.30 (1)
C(35)–C(36)	1.38 (2)	C(65)–C(66)	1.39 (1)
C(36)–C(31)	1.44 (1)	C(66)–C(61)	1.41 (1)

chlorines in **15** are a little shorter than the distances observed for the cis chlorines.

The angles W–O(1)–C(11) = 141.8 (6)° and W–O(2)–C(41) = 149.3 (6)° are significantly less (7–30°) than those in **12**, suggesting that steric crowding on account of the 2,6-phenyl groups as compared to isopropyl groups in **12** is less important that the relief of steric strain provided by the replacement of a bulky alkoxide by chloride in going from compound **12** to compound **15**.

All of the phenyl rings are planar within ±0.06 Å. Some apparent distortion of possible significance is observed in the aryloxide ligands. There is a slight opening of the angles involving the ring C's bonded to O's: C(12)–C(11)–C(16) = 124 (1)° and C(42)–C(41)–C(46) = 126 (1)° compared to the ideal value of 120°. Concomitantly the adjacent ring angles are somewhat closed up: C(11)–C(12)–C(13) = 116.1 (9)°, C(11)–C(16)–C(15) = 115.5 (9)°, C(41)–C(42)–C(43) = 115.2 (9)°, C(41)–C(46)–C(45) = 112 (1)°. A similar situation is observed in $W(C_3Et_3)(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$.[6d] The dihedral angles between the planes of the O-bonded rings in **12** and **15** are about 50°.

A pertinent question is whether steric or electronic effects control the gometry of **12** and **15**. Because these are 12-electron W(VI) complexes, it might be expected that ligand-to-metal π-donation would be of importance.[18-20] Consistent with the presence of pπ–dπ bonding is the fact that in both **12** and **15** W–Cl bond lengths are longer for Cl atoms trans to O than for Cl atoms trans to Cl. This behavior can be rationalized on the assumption that π-donation to W is possible for both O and Cl but O is a slightly superior π-donor thereby tying up the greater fraction of the W π-acceptor orbital shared with a trans Cl.

If Cl and O were very different in terms of their π-donating ability toward W(VI), the expectation would be that Cl and

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Table VII. Bond Angles (deg) and Their Estimated Standard Deviations for $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$

(A) Cl–W–Cl, Cl–W–O, and O–W–O Angles			
Cl(1)–W–Cl(2)	89.1 (1)	Cl(2)–W–O(2)	88.3 (2)
Cl(1)–W–Cl(3)	86.1 (1)	Cl(3)–W–Cl(4)	86.5 (1)
Cl(1)–W–Cl(4)	171.84 (9)	Cl(3)–W–O(1)	90.3 (2)
Cl(1)–W–O(1)	95.1 (2)	Cl(3)–W–O(2)	174.9 (2)
Cl(1)–W–O(2)	90.6 (2)	Cl(4)–W–O(1)	88.3 (2)
Cl(2)–W–Cl(3)	87.7 (1)	Cl(4)–W–O(2)	96.6 (2)
Cl(2)–W–Cl(4)	87.3 (1)	O(1)–W–O(2)	93.9 (3)
Cl(2)–W–O(1)	175.3 (2)		
(B) W–O–C Angles			
W–O(1)–C(11)	141.8 (6)	W–O(2)–C(41)	149.3 (6)
(C) O–C–C Angles			
O(1)–C(11)–C(12)	119.7 (8)	O(2)–C(41)–C(42)	117.2 (8)
O(1)–C(11)–C(16)	116.6 (8)	O(2)–C(41)–C(46)	116 (1)
(D) C–C–C Angles			
C(12)–C(11)–C(16)	124 (1)	C(62)–C(61)–C(66)	116.8 (8)
C(11)–C(12)–C(13)	116.1 (9)	C(61)–C(62)–C(63)	121.2 (9)
C(12)–C(13)–C(14)	120 (1)	C(62)–C(63)–C(64)	117 (1)
C(13)–C(14)–C(15)	122 (1)	C(63)–C(64)–C(65)	125 (1)
C(14)–C(15)–C(16)	122 (1)	C(64)–C(65)–C(66)	119 (1)
C(15)–C(16)–C(11)	115.6 (9)	C(65)–C(66)–C(61)	121.1 (9)
C(22)–C(21)–C(26)	120.9 (9)		
C(21)–C(22)–C(23)	117 (1)	C(12)–C(13)–C(32)	120.5 (9)
C(22)–C(23)–C(24)	120 (1)	C(12)–C(31)–C(36)	120 (1)
C(23)–C(24)–C(25)	119 (1)	C(16)–C(21)–C(22)	119 (1)
C(24)–C(25)–C(26)	124 (1)	C(16)–C(21)–C(26)	120.3 (8)
C(25)–C(26)–C(21)	118.8 (9)	C(21)–C(16)–C(11)	123 (1)
C(32)–C(31)–C(36)	119.3 (9)	C(31)–C(12)–C(13)	121.6 (9)
C(31)–C(32)–C(33)	119 (1)	C(21)–C(16)–C(15)	121.6 (9)
C(32)–C(33)–C(34)	121 (1)	C(31)–C(12)–C(11)	122 (1)
C(33)–C(34)–C(35)	120 (1)	C(42)–C(61)–C(62)	121.0 (8)
C(34)–C(35)–C(36)	121 (1)	C(42)–C(61)–C(66)	122.2 (9)
C(35)–C(36)–C(31)	119 (1)	C(46)–C(51)–C(52)	120 (1)
C(42)–C(41)–C(46)	126 (1)	C(46)–C(51)–C(56)	122.9 (9)
C(41)–C(42)–C(43)	115.2 (8)	C(51)–C(46)–C(41)	125 (1)
C(42)–C(43)–C(44)	122 (1)	C(51)–C(46)–C(45)	122.8 (9)
C(43)–C(44)–C(45)	120 (1)	C(61)–C(42)–C(41)	124 (1)
C(44)–C(45)–C(46)	124 (1)	C(61)–C(42)–C(43)	120.6 (9)
C(45)–C(46)–C(41)	112 (1)		
C(52)–C(51)–C(56)	117 (1)		
C(51)–C(52)–C(53)	122 (1)		
C(52)–C(53)–C(54)	120 (1)		
C(53)–C(54)–C(55)	121 (1)		
C(54)–C(55)–C(56)	118 (1)		
C(55)–C(56)–C(51)	123.5 (9)		

aryloxy ligands should be in the cis orientation, thereby avoiding competition between two molecules of the better π-donor ligand. On the other hand, bulky groups attached to the coordinating ligand favor the trans orientation of similar ligands.[21]

The simplest interpretation of the structures of **15** and **12** is that Cl and O aryl ligands are not greatly different in π-bonding capacity so that the balance between electronic and steric control is easy to tip. Thus, in **15**, the two $O\text{-}2,6\text{-}C_6H_3Ph_2$ ligands are in the electronically dictated cis orientation. In **12** the $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$ ligands adopt meridional (cis, cis, trans) instead of the facial (all cis) geometry because of the bulkiness of the isopropyl groups.

Therefore, simple steric effects could account for the fact that tetrasubstitution of WCl_6 by $HO\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$ is not observed.

On the other hand, steric effects alone do not account for the fact that only two chlorides of WCl_6 can be substituted by $HO\text{-}2,6\text{-}C_6H_3X_2$ (X = Br, Cl, F) ligands (complexes **16**–**18**). Possibly further displacement of chloride after disubstitution could be more difficult due to the stabilization of W–Cl bonds by the presence of the electron-withdrawing $O\text{-}2,6\text{-}C_6H_3X_2$ ligands on the metal.

Concerning complex **12**, two types of aryloxide ligands appear in solution. The ^1H NMR spectrum of **12** at room temperature (Experimental Section) shows clearly two types of isopropyl resonances for $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$ groups in a 2:1 ratio. They correspond to (i) the two ligands in trans position to each other (O_1Ar and O_2Ar) and (ii) the ligand in a trans position to a chlorine atom (O_3Ar).

Experimental Section

All reactions and manipulations were carried out under Ar by using Schlenk techniques. Solvents were dried by distillation over P_2O_5 under Ar and stored under Ar over 5-Å molecular sieves. WCl_6 was purchased in resublimed form from Alfa. All phenols were commercial products and were distilled or sublimed before use.

$W(O\text{-}C_6H_5)_4Cl_2$ (1). To WCl_6 (3.5 g, 8.8 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of C_6H_5OH (3.5 g, 37 mmol) in carbon tetrachloride (30 mL). The reaction mixture was stirred under reflux over 1 h. Evaporation followed by recrystallization from toluene/ethanol (1/2) at −5 °C gave the pure product as black needles (3.9 g, 70% yield). Anal. Calcd for $WC_{24}H_{20}O_4Cl_2$: W, 29.3; C, 45.9; H, 3.2; Cl, 11.3. Found: W, 29.3; C, 45.6; H, 3.1; Cl, 11.3.

$W(O\text{-}3\text{-}C_6H_4Me)_4Cl_2$ (2). To WCl_6 (2.10 g, 5.28 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of $HO\text{-}3\text{-}C_6H_4Me$ (2.31 g, 21.4 mmol) in carbon tetrachloride (10 mL). The reaction mixture was stirred under reflux for 2 h. Evaporation followed by chromatography on a silica gel column (toluene/hexane, 50/50) and crystallization at −5 °C gave the pure product as black needles (1.4 g, 40% yield). Anal. Calcd for $WC_{28}H_{28}O_4Cl_2$: W, 26.94; C, 49.20; H, 4.10; Cl, 10.39. Found: W, 27.10; C, 49.03; H, 4.13; Cl, 10.13.

$W(O\text{-}4\text{-}C_6H_4Me)_4Cl_2$ (3). To WCl_6 (1.74 g, 4.36 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of $HO\text{-}4\text{-}C_6H_4Me$ (1.89 g, 17.5 mmol) in carbon tetrachloride (10 mL).

The reaction mixture was stirred under reflux for 1 h. Evaporation followed by chromatography on a silica gel column (toluene/hexane, 50/50) and crystallization at −5 °C gave the pure product as black needles (1.8 g, 60% yield). Anal. Calcd for $WC_{28}H_{28}O_4Cl_2$: W, 26.94; C, 49.20; H, 4.10; Cl, 10.39. Found: W, 26.17; C, 49.48; H, 4.33; Cl, 9.68. IR spectrum (Nujol mull) between 1100 and 200 cm^{-1}: 1000 (m), 950 (m), 781 (m), 680 (s), 655 (s), 460 (s), 438 (m), 330–356 (s), 300 (s), 288 (m), 276 (m), 244 (m), 222 (m).

$W(O\text{-}3,5\text{-}C_6H_3Me_2)_4Cl_2$ (4). To WCl_6 (1.60 g, 4.01 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of $HO\text{-}3,5\text{-}C_6H_3Me_2$ (2.10 g, 17.2 mmol) in carbon tetrachloride (10 mL). The reaction mixture was stirred under reflux for 3 h. Evaporation followed by chromatography on a silica gel column (toluene/hexane, 50/50) and crystallization at −5 °C gave the pure product as black needles (1.3 g, 45% yield). Anal. Calcd for $WC_{32}H_{36}O_4Cl_2$: W, 24.90; C, 51.96; H, 4.87; Cl, 9.61. Found: W, 25.0; C, 51.5; H, 4.84; Cl, 9.34.

$W(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4Cl_2$ (5). To WCl_6 (2.985 g, 7.5 mmol) suspended in toluene (20 mL) was added a solution of $HO\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu$ (4.5 g, 30 mmol) in toluene (30 mL). The reaction mixture was stirred under reflux for 6 h. Evaporation followed by recrystallization from toluene/ethanol (1/2) at −5 °C gave the pure product as a black powder (3.8 g, 60% yield). Anal. Calcd for $WC_{40}H_{52}O_4Cl_2$: W, 21.62; C, 56.40; H, 6.12; Cl, 8.34. Found: W, 21.4; C, 56.6; H, 6.2; Cl, 8.2.

$W(O\text{-}4\text{-}C_6H_4Ph)_4Cl_2$ (6). To WCl_6 (4.0 g, 10 mmol) suspended in carbon tetrachloride (30 mL) was added a suspension of $HO\text{-}4\text{-}C_6H_4Ph$ (6.8 g, 40 mmol) in carbon tetrachloride (30 mL). The reaction mixture was stirred under reflux for 6 h. Evaporation followed by washing with ethanol and extraction with toluene gave a black powder (3.5 g, 40% yield). Anal. Calcd for $WC_{48}H_{36}O_4Cl_2$: W, 19.76; C, 61.86; H, 3.86; Cl, 7.62. Found: W, 19.2; C, 61.3; H, 3.7; Cl, 7.7.

$W(O\text{-}4\text{-}C_6H_4OMe)_4Cl_2$ (7). To a solution of WCl_6 (3.30 g, 8.25 mmol) in toluene (30 mL) was added a solution of $HO\text{-}4\text{-}C_6H_4OMe$ (4.12 g, 33.5 mmol) in toluene (40 mL). The reaction mixture was stirred under reflux for 6 h. Evaporation followed by chromatography on a silica gel column (CH_2Cl_2/CCl_4, 90/10) gave the pure product as black crystals with golden-green luster (2.8 g, 45% yield). Anal. Calcd for $WC_{28}H_{28}O_8Cl_2$: W, 24.63; C, 45.00; H, 3.75; Cl, 9.50. Found: W, 24.63; C, 45.10; H, 3.76; Cl, 9.84.

$W(O\text{-}2\text{-}C_6H_4Cl)_4Cl_2$ (8). To WCl_6 (1.44 g, 3.6 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of $HO\text{-}2\text{-}C_6H_4Cl$ (1.5 mL) in carbon tetrachloride (10 mL). The reaction mixture was stirred under reflux for 5 h. Evaporation followed by recrystallization from toluene/ethanol (1/2) at −5 °C gave the product as a black powder (1.8 g, 60% yield). Anal. Calcd for $WC_{24}H_{16}O_4Cl_6$: W, 24.05; C, 37.60; H, 2.10; Cl, 27.84. Found: W, 24.1; C, 37.2; H, 2.05; Cl, 28.0.

$W(O\text{-}4\text{-}C_6H_4Cl)_4Cl_2$ (9). To WCl_6 (2.44 g, 6.13 mmol) suspended in carbon tetrachloride (10 mL) was added a solution of $HO\text{-}4\text{-}C_6H_4Cl$ (3.15 g, 24.5 mmol) in carbon tetrachloride (10 mL). The reaction mixture was stirred under reflux for 1 h. Evaporation followed by recrystallization from toluene/pentane (1/2) gave the pure product as black microcrystals with golden-green luster (3.5 g, 75% yield). Anal. Calcd for $WC_{24}H_{16}O_4Cl_6$: W, 24.05; C, 37.60; H, 2.10; Cl, 27.84. Found: W,

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[21] Zahrobsky, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 3313.

23.10; C, 37.33; H, 2.24; Cl, 27.80. IR spectrum (Nujol mull) between 1000 and 200 cm^{-1}: 892 (m), 827 (m), 716 (s), 632 (m), 511 (m), 448 (w), 432 (w), 427 (w), 368 (m), 348 (m), 332 (m), 296 (s), 270 (m), 243 (m), 222 (m).

$W(O-2,6-C_6H_3Me_2)_3Cl_3$ (10) and $W(O-2,6-C_6H_3Me_2)_2Cl_4$ (13). To WCl_6 (2.1 g, 5.3 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of $HO-2,6-C_6H_3Me_2$ (2.59 g, 21.2 mmol) in carbon tetrachloride (10 mL). The reaction mixture was stirred under reflux for 5 h. Filtration of the reaction mixture gave a black solid (**13**) and a deep red solution. Addition of ethanol to the solution gave black microcrystals of **10** (1.4 g, 57% yield). Anal. Calcd for $WC_{24}H_{27}O_3Cl_3$: W, 28.15; C, 44.0; H, 4.13; Cl, 16.29. Found: W, 28.34; C, 43.86; H, 4.09; Cl, 16.19. **13** was obtained as black microcrystals after the black solid insoluble in CCl_4 was washed with ethanol (0.9 g, 30% yield). Anal. Calcd for $WC_{16}H_{18}O_2Cl_4$: W, 32.39; C, 33.80; H, 3.16; Cl, 25.0. Found: W, 31.55; C, 33.40; H, 3.15; Cl, 24.4.

$W(O-2,4,6-C_6H_2Me_3)_3Cl_3$ (11) and $W(O-2,4,6-C_6H_2Me_3)_2Cl_4$ (14). To WCl_6 (3.18 g, 7.98 mmol) suspended in carbon tetrachloride (10 mL) was added a solution of $HO-2,4,6-C_6H_2Me_3$ (4.36 g, 32.0 mmol) in carbon tetrachloride (10 mL). The reaction mixture was stirred under reflux for 2 h. Filtration of the reaction mixture gave a black solid (**14**) and a deep red solution. Addition of ethanol to the solution gave black microcrystals of **11** (2.2 g, 40% yield). Anal. Calcd for $WC_{27}H_{33}O_3Cl_3$: W, 26.45; C, 46.58; H, 4.74; Cl, 15.30. Found: W, 26.77; C, 46.88; H, 4.76; Cl, 14.64. **14** was obtained as black microcrystals after the black solid insoluble in CCl_4 was washed with ethanol (1.4 g, 30% yield). Anal. Calcd for $WC_{18}H_{22}O_2Cl_4$: W, 30.87; C, 36.20; H, 3.70; Cl, 23.82. Found: W, 30.78; C, 36.26; H, 3.75; Cl, 23.35.

$W(O-2,6-C_6H_3-i-Pr_2)_3Cl_3$ (12). To WCl_6 (4.53 g, 11.4 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of $HO-2,6-C_6H_3-i-Pr_2$ (8.44 mL, 45.6 mmol) in carbon tetrachloride (10 mL). The reaction mixture was stirred under reflux for 5 h. Evaporation of solvent gave a black oil, which was chromatographed on a silica gel column (toluene/cyclohexane, 25/75). Crystallization from ethanol at −5 °C gave the pure product as large, roughly rhombohedral black crystals (6.6 g, 70% yield). Anal. Calcd for $WC_{36}H_{51}O_3Cl_3$: W, 22.40; C, 52.50; H, 6.21; Cl, 12.96. Found: W, 22.62; C, 52.31; H, 6.50; Cl, 12.99. ^1H NMR (CD_2Cl_2): δ 7.29 (m, 6, $O-C_6H_3$), 6.98 (m, 3, $O-C_6H_3$), 4.06 (m, 4, $\mathit{CH}(CH_3)_2$), 3.64 (m, 2, $\mathit{CH}(CH_3)_2$), 1.12 (d, 24, $CH(\mathit{CH}_3)_2$), 1.02 (d, 12, $CH(\mathit{CH}_3)_2$). IR spectrum (Nujol mull) between 1000 and 200 cm^{-1}: 915 (s), 796 (m), 750 (s), 603 (w), 412 (w), 393 (w), 357 (w), 346 (w), 322 (s), 229 (m), 222 (w).

$W(O-2,6-C_6H_3Ph_2)_2Cl_4$ (15). To WCl_6 (3.44 g, 8.63 mmol) suspended in carbon tetrachloride (20 mL) was added a suspension of $HO-2,6-C_6H_3Ph_2$ (4.27 g, 17.3 mmol) in carbon tetrachloride (10 mL). The reaction mixture was stirred under reflux for 5 h. Filtration of the reaction mixture followed by recrystallization from CH_2Cl_2/EtOH gave **15** as black microcrystals (5.7 g, 80% yield). Anal. Calcd for $WC_{36}H_{26}O_2Cl_4$: W, 22.5; C, 52.9; H, 3.2; Cl, 17.37. Found: W, 23.0; C, 52.6; H, 3.2; Cl, 17.40.

$W(O-2,6-C_6H_3Br_2)_2Cl_4$ (16). To WCl_6 (2.39 g, 6.00 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of $HO-2,6-C_6H_3Br_2$ (3.045 g, 12.0 mmol) in carbon tetrachloride (20 mL). The reaction mixture was stirred under reflux for 4 h. Removal of solvent followed by washing with hexane gave **16** as a brown-black powder, which slowly decomposed in air (4.2 g, 85% yield). Anal. Calcd for $WC_{12}H_6O_2Br_4Cl_4$: W, 22.10; C, 17.30; H, 0.72; Br, 38.60; Cl, 17.12. Found: W, 22.0; C, 17.09; H, 0.72; Br, 36.99; Cl, 17.80.

$W(O-2,6-C_6H_3Cl_2)_2Cl_4$ (17). To WCl_6 (1.02 g, 2.56 mmol) suspended in carbon tetrachloride (20 mL) was added a solution of $HO-2,6-C_6H_3Cl_2$ (0.83 g, 5.1 mmol) in carbon tetrachloride (20 mL). The reaction mixture was stirred under reflux for 4 h. Removal of solvent followed by washing with ethanol gave **17** as black microcrystals with green luster (stable in air) (1.4 g, 85% yield). Anal. Calcd for $WC_{12}H_6O_2Cl_8$: W, 28.3; C, 22.2; H, 0.93; Cl, 43.6. Found: W, 28.0; C, 22.2; H, 1.2; Cl, 43.0. IR spectrum (Nujol mull) between 650 and 200 cm^{-1}: 559 (w), 529 (w), 440 (w), 415 (w), 346 (sh), 320 (s, br), 286 (m), 228 (m).

$W(O-2,6-C_6H_3F_2)_2Cl_4$ (18). To WCl_6 (3.22 g, 8.09 mmol) suspended in carbon tetrachloride (20 mL) was added a suspension of $HO-2,6-C_6H_3F_2$ (2.12 g, 16.3 mmol) in carbon tetrachloride (20 mL). The reaction mixture was stirred under reflux for 2 h. Removal of solvent followed by washing with hexane gave dark green microcrystals, which decomposed in air (2.6 g, 55% yield). Anal. Calcd for $WC_{12}H_6O_2F_4Cl_4$: W, 31.5; C, 24.6; H, 1.0; F, 13.0; Cl, 24.3. Found: W, 31.2; C, 24.55; H, 1.04; F, 12.2; Cl, 23.8.

Crystal Structure Determination of $W(O-2,6-C_6H_3-i-Pr_2)_3Cl_3$ (12) and $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ (15). Crystals of **12** were grown from CH_2Cl_2 (−15 °C). A crystal of **15** was obtained from CH_2Cl_2/toluene (−15 °C). All data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections well distributed in reciprocal space and lying in a 2θ range of 24–30°. Crystallographic parameters are given in Table I.

All data were corrected for Lorentz and polarization effects, and both structures were solved by a combination of Patterson and difference Fourier techniques with analytical atomic scattering factors used throughout the structure refinement with both real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms. Except where indicated below all the crystallographic computations were carried out on a PDP 11/44 computer using the Structure Determination Package (SDP).[22]

For $W(O-2,6-C_6H_3-i-Pr_2)_3Cl_3$ six standard reflections were monitored during data collection and showed no significant decay. An absorption correction was also applied on the basis of the Gaussian integration formula with grid $10 \times 4 \times 12$ points. Maximum and minimum transmission: 99.8%, 63.1%.

After all of the non-hydrogen atoms were located and refined, the hydrogen atoms of the phenyl groups were placed at calculated positions (CH = 0.95 Å, $B(H) = B(C) + 1$ Å^2) and all of the propyl hydrogens were located on a difference map. With all other atoms fixed, the positional parameters of the propyl hydrogens were refined with fixed thermal parameters ($B(H) = B(C) + 1$ Å^2). Then, with the positional and thermal parameters of all the hydrogens fixed, the non-hydrogen atoms were refined anisotropically for an additional three cycles.

In the case of $W(O-2,6-C_6H_3Ph_2)_2Cl_4$, monitoring of five standard reflections revealed that severe crystal decay occurred. An initial data set obtained in the range $4° \leq 2\theta \leq 30°$ contained 1662 observed, independent reflections with 1523 reflections $\leq 3\sigma(I)$. Crystal decay was 3%. An additional 1253 observed, independent reflections with 1065 reflections $I \geq 3\sigma(I)$ were collected in the range $30° \leq 2\theta \leq 40°$, but severe crystal decay (20% total) prevented collection of the full independent data set in this range of 2θ. Since we were unable to obtain another suitable crystal for data collection, decay correction was made on the available data, which was then used for the structure determination. No empirical absorption correction could be made because of the extensive decay. Crystalline faces were not sufficiently well-defined for a numerical absorption correction.

All of the non-hydrogen atoms in the molecule were located on Fourier difference maps. Refinements were full-matrix least squares with tungsten and chlorine atoms refined anisotropically. Because of the limited amount of reflection data available, all other non-hydrogen atoms were refined isotropically and the solvent molecule in the crystal, toluene, was fixed[23] with its ring C atoms in a regular hexagon. An occupancy of 0.5 assigned to the toluene gave the most reasonable thermal parameters. However, it is possible that the crystal decay observed occurred through loss of toluene and the occupancy of this molecule in a fresh crystal might be 1. Unfortunately, we were unable to obtain any better quality crystals even though numerous attempts were made. For the final three cycles of refinement, H atoms were added at calculated positions ($d(C-H) = 0.95$ Å), but their positional and thermal parameters were fixed ($B(H) = B(C) + 1$ Å^2).

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Supplementary Material Available: For the two structure determinations, listings of positional parameters of H atoms and anisotropic thermal parameters (7 pages); listings of calculated and observed structure factor amplitudes for both structures (64 pages). Ordering information is given on any current masthead page.

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[22] SDP (developed by B. A. Frenz and Associates, Inc., College Station, TX 77840) was used to process X-ray data, apply corrections, solve and refine the structures, produce drawings, and print tables.

[23] Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; University Chemical Laboratory: Cambridge, England, 1976.