stretching coordinates are then

$$F_{ii} = K + \sum_{j}^{j \neq i} (t_{ij}^2 F' + s_{ij}^2 F) \qquad (10)$$

$$F_{ij} = -t_{ij}^2 F' + s_{ij}^2 F \qquad (11)$$

where s_{ij}^2 and t_{ij}^2 can be written as functions of θ and b as in (12)-(16) and the summation runs over all neighboring M-S

$$s_{S_AS_B}^2 = s_{S_AS_C}^2 = \left(3 - \frac{3}{4}b^2\right) \Big/ 4\cos^2\theta \qquad (12)$$

$$s_{S_AS_D}^2 = b^2/4 \qquad (13)$$

$$s_{S_AS_F}^2 = [4\cos^2\theta - (4 - b^2)\cos^2(60° - \theta)]/4\cos^2\theta \qquad (14)$$

$$s_{S_AS_E}^2 = [4\cos^2\theta - (4 - b^2)\cos^2(60° + \theta)]/4\cos^2\theta \qquad (15)$$

$$t_{ij}^2 = 1 - s_{ij}^2 \qquad (16)$$

bonds. The second term of the diagonal elements (10) becomes a constant, and we write F_{ii} as K^0. When F' is taken as $-1/10F$,[20] the off-diagonal elements are functions of θ, b, and F. The **F** matrix may be transformed to symmetry coordinates leading to the form analogous to (7)-(9), from which, combined with (7)-(9), the eigenvalues of **GF** may be calculated.

Supplementary Material Available: Complete listings of thermal parameters and hydrogen atom parameters for **1a** (3 pages); a listing of observed and calculated structure factors for **1a** (23 pages). Ordering information is given on any current masthead page.

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(20) This approximation assumes that the repulsive energy between nonbonded sulfur atoms is proportional to $1/r^9$.

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Synthesis, Structure, and Spectroscopic Properties of Octahedral Complexes of Tungsten(VI), -(V), and -(IV) Containing 2,6-Diphenylphenoxide Ligation

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The tungsten(VI) complex *cis*-$WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**) ($OAr\text{-}2,6\text{-}Ph_2$ = 2,6-diphenylphenoxide) undergoes an overall one-electron reduction on treatment either with magnesium butadiene, $Mg(C_4H_6)$, in thf or with lithium borohydride, $LiBH_4$, in toluene. In the former case the octahedral thf adduct $WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(thf)$ (**2**) is formed in high yield, while the $LiBH_4$ reduction takes place in the presence of 1 equiv of PMe_2Ph to yield $WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)$ (**3**). Both **2** and **3** are deep red, paramagnetic compounds shown by single-crystal X-ray diffraction analyses to contain trans-aryloxide oxygen atoms and a *mer* arrangement of chloride groups about the octahedral tungsten metal center. Reduction of toluene solutions of $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ with sodium amalgam (2 Na/W) in the presence of monodentate phosphines leads to the formation of the bright orange W(IV) derivatives $WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)_2$ (**4a**) and $WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PMePh_2)_2$ (**4b**) in high yields. A structural study of **4a** shows the molecule to possess a crystallographic inversion center with a *trans*-,*trans*-,*trans*-$WCl_2O_2P_2$ core. Spectroscopically, well-resolved but contact-shifted ^1H NMR spectra can be obtained for the d^2 molecules (**4**). The bonding and electronic structure of these molecules are discussed, particularly with relevance to the importance of aryloxide oxygen-p to metal-d π-bonding. In this regard, the solid-state structure of $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**) has also been obtained. Although reported previously, the structure of **1** in the present study does not suffer from some of the solvent loss and decay problems evident in the earlier attempt. Crystal data are as follows. For $WCl_4O_2C_{36}H_{26}$ (**1**) at 22 °C: a = 11.051 (1) Å, b = 16.693 (3) Å, c = 17.515 (3) Å, β = 95.72 (1)°, Z = 4, d_{calcd} = 1.686 g cm^{-3} in space group $P2_1/c$. For $WCl_3O_3C_{40}H_{34}$ (**2**) at 19 °C: a = 11.582 (2) Å, b = 12.099 (1) Å, c = 24.828 (4) Å, Z = 4, d_{calcd} = 1.628 g cm^{-3} in space group $P2_12_12_1$. For $WCl_3PO_2C_{44}H_{37}$ (**3**) at 22 °C: a = 10.8028 (8) Å, b = 18.430 (2) Å, c = 21.746 (6) Å, β = 100.80 (1)°, Z = 4, d_{calcd} = 1.435 g cm^{-3} in space group $P2_1/c$. For $WCl_2P_2O_2C_{52}H_{48}$ (**4a**): a = 10.687 (3) Å, b = 11.335 (3) Å, c = 10.289 (2) Å, α = 92.30 (1)°, β = 110.95 (1)°, γ = 108.21 (1)°, Z = 1, d_{calcd} = 1.557 g cm^{-3} in space group $P\bar{1}$.

Introduction

There has been considerable recent research interest focused on the transition-metal chemistry supported by and directly involved with 2,6-dialkylphenoxide[2-4] and 2,6-dialkylthiophenoxide[5,6] ligation. In the case of the related derivatives 2,6-diphenylphenoxide ($OAr\text{-}2,6\text{-}Ph_2$)[7,8] and 2,6-diphenylthiophenoxide ($SAr\text{-}2,6\text{-}Ph_2$),[5] interactions between the aryl substituents and the metal center to which the ligand is bound have been characterized. Hence, chelation to the metal center through a σ-aryl bond or via an η^6-arene interaction has been shown to be possible.[8,9] In the aryloxide case, activation and cleavage of the arene C-H bond can take place either by oxidative addition or by a heterolytic pathway.[8,9] Both types of coordination and even the cyclometalation of an initially chelated η^6-arene ring have been shown possible at low-valent tungsten metal centers.[9] An important substrate used for these and other studies, *cis*-$WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$[10] undergoes reduction in the presence of phosphine ligands to yield a number of products. We wish to report here the nature of some of the midvalent tungsten derivatives of 2,6-diphenyl-

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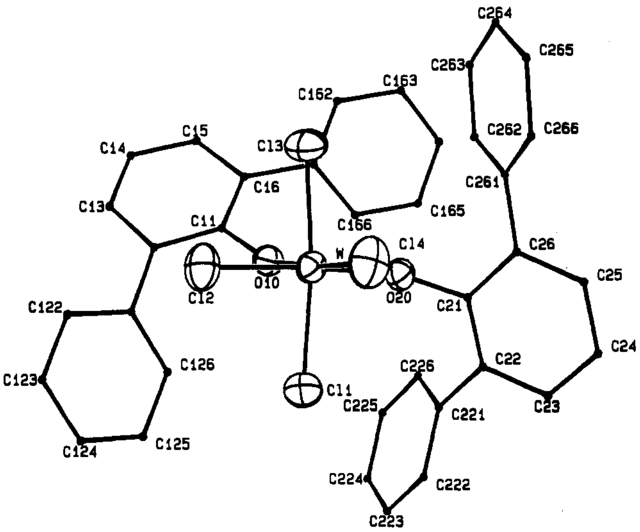

Figure 1. ORTEP view of $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**), emphasizing the central coordination sphere.

phenoxide that are intermediates in the formation of some of the more interesting low-valent tungsten compounds.[9]

Results and Discussion

The bis(aryloxide) $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**) can be obtained in almost quantitative yield by simple treatment of WCl_6 with $HOAr\text{-}2,6\text{-}Ph_2$ (2 equiv) in refluxing toluene.[10a] A previous structural study by Bassett and Shore on compound **1** was fraught with many problems due to excessive decay of the crystals during analysis caused by severe loss of solvent.[10a] Completely independently we had also examined a sample of solvent-free **1** by X-ray diffraction methods and had managed to obtain a complete data set. Due to the importance of the structural parameters of molecule **1** to this particular study, our structural results are reported here. An ORTEP view of **1** is given in Figure 1, while Table I contains the fractional coordinates and isotropic thermal parameters. Some selected bond distances and angles are given in Table II. Although the overall coordination geometry shown in Figure 1 is the same as that reported by Bassett and Shore, the lack of solvent molecules in our sample means that there are considerable differences in the crystallographic data between the two studies (Table X). It can be seen that despite steric demands, a mutually cis arrangement of aryloxide oxygens is found for **1**, while there is a slight lengthening of the W-Cl bonds trans to the oxygen atoms (vide infra). The ease of reduction of $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**) is hinted at by its cyclic voltammogram in a thf solution with TBAH ($Bu^n{}_4N^+PF_6^-$; 0.2 M) as the supporting electrolyte. A one-electron-reduction wave is shown at the very accessible potential of +0.43 V ($CpFe^{0/+}$ couple at +0.47 V).

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
W	0.24156 (2)	−0.00297 (1)	0.25042 (1)	2.660 (5)
Cl(1)	0.0528 (1)	−0.06199 (9)	0.24057 (8)	4.08 (3)
Cl(2)	0.3070 (1)	−0.12040 (9)	0.31311 (9)	4.41 (3)
Cl(3)	0.4404 (1)	0.0409 (1)	0.26711 (9)	4.62 (4)
Cl(4)	0.2879 (1)	−0.0556 (1)	0.13731 (8)	4.80 (4)
O(10)	0.2227 (3)	0.0485 (2)	0.3413 (2)	2.80 (7)
O(20)	0.1817 (3)	0.0801 (2)	0.1877 (2)	2.87 (7)
C(11)	0.2727 (5)	0.0684 (3)	0.4145 (3)	3.3 (1)
C(12)	0.2655 (6)	0.0123 (3)	0.4732 (3)	4.3 (1)
C(13)	0.3352 (7)	0.0296 (4)	0.5427 (3)	5.9 (2)
C(14)	0.4011 (7)	0.0976 (5)	0.5524 (4)	6.4 (2)
C(15)	0.3997 (6)	0.1547 (7)	0.4948 (3)	5.0 (2)
C(16)	0.3329 (5)	0.1421 (3)	0.4241 (3)	3.7 (1)
C(21)	0.1296 (5)	0.0993 (3)	0.1146 (3)	2.8 (1)
C(22)	0.0026 (5)	0.0978 (3)	0.1018 (3)	3.3 (1)
C(23)	−0.0481 (6)	0.1015 (4)	0.0250 (3)	4.4 (1)
C(24)	0.0259 (6)	0.1123 (4)	−0.0334 (3)	4.9 (2)
C(25)	0.1492 (6)	0.1213 (3)	−0.0177 (3)	4.3 (1)
C(26)	0.2064 (5)	0.1150 (3)	0.0573 (3)	3.3 (1)
C(121)	0.1829 (6)	−0.0569 (4)	0.4660 (3)	4.6 (1)
C(122)	0.2208 (8)	−0.1311 (4)	0.4992 (4)	6.4 (2)
C(123)	0.1390 (9)	−0.1947 (4)	0.4968 (4)	8.1 (2)
C(124)	0.0212 (8)	−0.1845 (5)	0.4635 (5)	8.0 (2)
C(125)	−0.0154 (7)	−0.1127 (4)	0.4308 (4)	6.6 (2)
C(126)	0.0643 (6)	−0.0485 (4)	0.4323 (3)	5.0 (1)
C(161)	0.3238 (5)	0.2073 (3)	0.3664 (3)	3.8 (1)
C(162)	0.4237 (6)	0.2525 (4)	0.3528 (4)	5.2 (2)
C(163)	0.4111 (8)	0.3183 (4)	0.3024 (4)	7.3 (2)
C(164)	0.3001 (8)	0.3379 (4)	0.2666 (4)	7.1 (2)
C(165)	0.1996 (7)	0.2937 (4)	0.2793 (4)	6.0 (2)
C(166)	0.2120 (6)	0.2282 (3)	0.3291 (3)	4.4 (1)
C(221)	−0.0783 (5)	0.0992 (3)	0.1638 (3)	3.7 (1)
C(222)	−0.1781 (6)	0.0485 (4)	0.1628 (4)	5.7 (2)
C(223)	−0.2569 (6)	0.0549 (5)	0.2195 (5)	7.4 (2)
C(224)	−0.2376 (6)	0.1097 (6)	0.2760 (5)	8.1 (2)
C(225)	−0.1398 (7)	0.1599 (6)	0.2778 (4)	8.4 (2)
C(226)	−0.0605 (6)	0.1557 (5)	0.2211 (4)	6.1 (2)
C(261)	0.3383 (5)	0.1315 (3)	0.0728 (3)	3.5 (1)
C(262)	0.3833 (5)	0.1797 (3)	0.1324 (3)	3.9 (1)
C(263)	0.5039 (5)	0.2007 (4)	0.1426 (3)	4.6 (1)
C(264)	0.5848 (6)	0.1740 (4)	0.0926 (4)	5.3 (2)
C(265)	0.5425 (6)	0.1262 (4)	0.0341 (4)	5.7 (2)
C(266)	0.4192 (6)	0.1028 (4)	0.0229 (3)	4.7 (1)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table II. Selected Bond Distances (Å) and Angles (deg) for $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**)[a]

W-Cl(1)	2.297 (1)	W-Cl(4)	2.34 (1)
W-Cl(2)	2.326 (1)	W-O(10)	1.840 (3)
W-Cl(3)	2.307 (1)	W-O(20)	1.851 (3)
Cl(1)-W-Cl(2)	84.90 (5)	Cl(3)-W-Cl(4)	87.89 (5)
Cl(1)-W-Cl(3)	172.61 (5)	Cl(3)-W-O(10)	86.02 (9)
Cl(1)-W-Cl(4)	91.05 (5)	Cl(3)-W-O(20)	96.72 (9)
Cl(1)-W-O(10)	94.87 (9)	Cl(4)-W-O(10)	173.86 (9)
Cl(1)-W-O(20)	90.50 (9)	Cl(4)-W-O(20)	85.85 (9)
Cl(2)-W-Cl(3)	87.74 (5)	O(10)-W-O(20)	95.7 (1)
Cl(2)-W-Cl(4)	86.52 (5)	W-O(10)-C(11)	147.6 (3)
Cl(2)-W-O(10)	92.4 (1)	W-O(20)-C(21)	144.2 (3)
Cl(2)-W-O(20)	171.01 (9)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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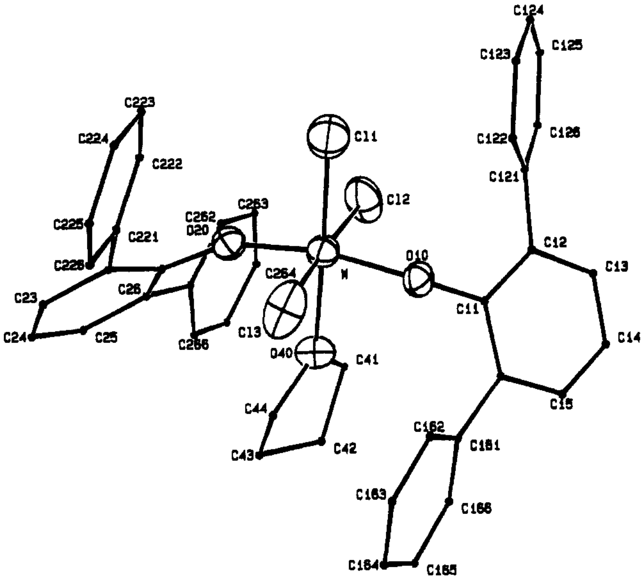

Figure 2. ORTEP view of $WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(thf)$ (**2**).

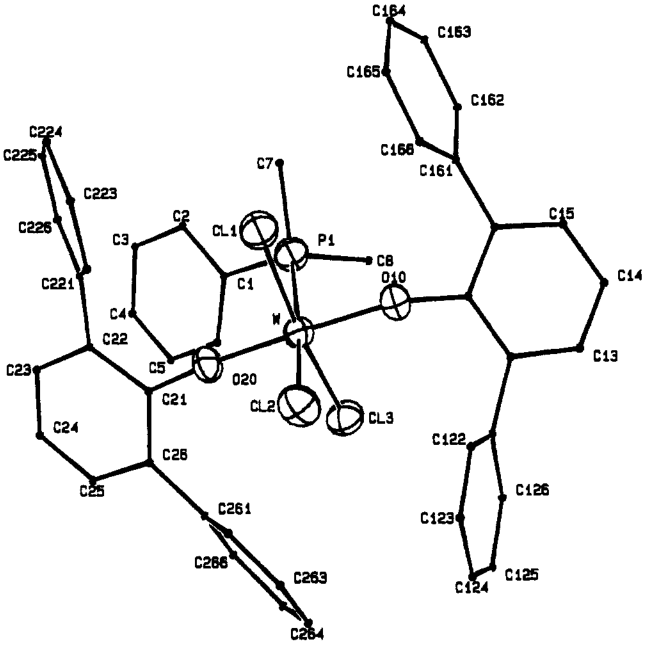

Figure 3. ORTEP view of $WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)$ (**3**).

Electrochemical studies show the reduction to be reversible, with $I_a/I_p = 1$ at all scan speeds. This ease of reduction is reflected in the fact that many attempted metathetic exchange reactions of the tetrachloride (**1**) lead to d^1, tungsten(V) compounds. Hence, treatment of deep purple $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**) with magnesium butadiene in thf leads rapidly to the formation of deep red solutions from which the complex $WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(thf)$ (**2**) can be isolated. Similarly, attempts to prepare a tungsten phosphine hydride compound from **1** by treatment with excess $LiBH_4$ in the presence of PMe_2Ph led only to the formation of $WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)$ (**3**). Compound **3** is also obtained by sodium amalgam (1 Na/W) reduction of toluene solutions of the tetrachloride with an added 1 equiv of PMe_2Ph.

Both of the tungsten(V) derivatives **2** and **3** have been subjected to single-crystal X-ray diffraction analysis. A representation of the two molecules is given in Figures 2 and 3, respectively, while Tables III and V contain the fractional coordinates and isotropic thermal parameters. Some selected bond distances and angles for **2** and **3** are also given in Tables IV and VI. It can be seen that both molecules adopt closely related coordination geometries about the metal center. The two aryloxide ligands, which were initially mutually cis in $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**), are now found to be mutually trans. The rest of the coordination environment then consists of three chloride ligands (in a *mer* arrangement) and either the oxygen atom of the thf molecule in **2** or phosphorus

Table III. Fractional Coordinates and Isotropic Thermal Parameters for $W(OAr\text{-}2,6\text{-}Ph_2)_2Cl_3(thf)$ (**2**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
W	0.81177 (2)	0.94204 (2)	0.87579 (1)	2.984 (5)
Cl(1)	0.6910 (2)	1.0938 (2)	0.8755 (1)	7.28 (6)
Cl(2)	0.9574 (2)	1.0506 (2)	0.9135 (1)	5.55 (5)
Cl(3)	0.6638 (2)	0.8293 (2)	0.8424 (1)	5.19 (5)
O(10)	0.7781 (4)	0.8942 (4)	0.9451 (2)	3.0 (1)
O(20)	0.8682 (4)	0.9636 (4)	0.8067 (2)	3.1 (1)
O(40)	0.9284 (4)	0.8037 (4)	0.8739 (2)	3.2 (1)
C(11)	0.8105 (6)	0.8667 (6)	0.9933 (3)	3.0 (1)
C(12)	0.8257 (5)	0.9491 (7)	1.0341 (3)	3.2 (2)
C(13)	0.8732 (6)	0.9204 (7)	1.0846 (3)	3.3 (2)
C(14)	0.9062 (6)	0.8145 (8)	1.0959 (4)	4.0 (2)
C(15)	0.8820 (8)	0.7334 (7)	1.0596 (4)	4.2 (2)
C(16)	0.8349 (6)	0.7546 (7)	1.0092 (3)	3.1 (2)
C(21)	0.9047 (6)	0.9288 (6)	0.7567 (3)	2.9 (1)
C(22)	0.8161 (7)	0.9134 (6)	0.7169 (3)	3.6 (2)
C(23)	0.8475 (8)	0.8634 (7)	0.6679 (4)	4.3 (2)
C(24)	0.9644 (9)	0.8309 (7)	0.6586 (4)	4.7 (2)
C(25)	1.0464 (8)	0.8535 (7)	0.6972 (4)	4.3 (2)
C(26)	1.0183 (7)	0.9051 (6)	0.7465 (4)	3.4 (2)
C(41)	1.0408 (8)	0.7964 (9)	0.9005 (4)	5.1 (2)
C(42)	1.0861 (7)	0.6820 (8)	0.8844 (5)	6.8 (3)
C(43)	1.0267 (9)	0.6542 (8)	0.8340(6)	6.6 (3)
C(44)	0.9100 (7)	0.7028 (7)	0.8410 (4)	4.2 (2)
C(121)	0.7880 (6)	1.0674 (6)	1.0271 (3)	3.2 (2)
C(122)	0.6764 (7)	1.0910 (7)	1.0098 (4)	4.1 (2)
C(123)	0.6390 (8)	1.2008 (8)	1.0109 (4)	5.5 (2)
C(124)	0.710 (1)	1.2835 (7)	1.0272 (5)	6.1 (2)
C(125)	0.819 (1)	1.2603 (8)	1.0431 (5)	6.0 (2)
C(126)	0.8603 (7)	1.1523 (7)	1.0432 (4)	4.1 (2)
C(161)	0.8060 (6)	0.6571 (6)	0.9742 (3)	3.2 (2)
C(162)	0.7014 (7)	0.6476 (7)	0.9474 (4)	3.9 (2)
C(163)	0.6772 (8)	0.5528 (8)	0.9183 (4)	4.9 (2)
C(164)	0.754 (1)	0.4678 (7)	0.9161 (4)	5.3 (2)
C(165)	0.8558 (9)	0.4761 (8)	0.9435 (4)	5.4 (2)
C(166)	0.8830 (8)	0.5704 (7)	0.9719 (4)	4.3 (2)
C(221)	0.6968 (7)	0.9513 (7)	0.7218 (3)	4.1 (2)
C(222)	0.6717 (7)	1.0560 (7)	0.7384 (4)	4.4 (2)
C(223)	0.559 (1)	1.098 (1)	0.7383 (5)	6.9 (3)
C(224)	0.470 (1)	1.029 (1)	0.7196 (4)	8.0 (3)
C(225)	0.495 (1)	0.922 (1)	0.7031 (4)	6.9 (3)
C(226)	0.6068 (8)	0.8837 (9)	0.7034 (4)	5.2 (2)
C(261)	1.1166 (7)	0.9384 (7)	0.7815 (3)	3.6 (2)
C(262)	1.1173 (7)	1.0412 (7)	0.8063 (4)	3.7 (2)
C(263)	1.2142 (8)	1.0767 (8)	0.8356 (4)	5.0 (2)
C(264)	1.3093 (8)	1.0082 (9)	0.8396 (4)	5.1 (2)
C(265)	1.3090 (8)	0.9071 (8)	0.8148 (4)	4.9 (2)
C(266)	1.2139 (7)	0.8721 (7)	0.7866 (4)	4.0 (2)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $W(OAr\text{-}2,6\text{-}Ph_2)_2Cl_3(thf)$ (**2**)[a]

W–Cl(1)	2.308 (3)	W–O(10)	1.857 (5)
W–Cl(2)	2.335 (2)	W–O(20)	1.855 (5)
W–Cl(3)	2.342 (2)	W–O(40)	2.151 (4)
Cl(1)–W–Cl(2)	89.5 (1)	Cl(3)–W–O(20)	90.7 (2)
Cl(1)–W–Cl(3)	91.1 (1)	Cl(3)–W–O(40)	89.9 (1)
Cl(1)–W–O(10)	97.1 (2)	O(10)–W–O(20)	167.2 (2)
Cl(1)–W–O(20)	95.7 (2)	O(10)–W–O(40)	84.8 (2)
Cl(1)–W–O(40)	177.9 (2)	O(10)–W–O(40)	82.4 (2)
Cl(2)–W–Cl(3)	177.03 (9)	W–O(10)–Cl(11)	151.7 (4)
Cl(2)–W–O(10)	87.4 (2)	W–O(20)–C(21)	154.1 (4)
Cl(2)–W–O(20)	92.2 (2)	W–O(40)–C(41)	126.6 (5)
Cl(2)–W–O(40)	89.6 (1)	W–O(40)–C(44)	124.2 (4)
Cl(3)–W–O(10)	89.6 (2)	C(41)–O(40)–C(44)	109.0 (6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Fractional Coordinates and Isotropic Thermal Parameters for W(OAr-2,6-Ph_2)$_2$$Cl_3$($PMe_2Ph$) (**3**)

atom	x	y	z	B,[a] Å^2
W	0.25231 (3)	−0.21247 (2)	0.22810 (1)	2.488 (7)
Cl(1)	0.3566 (2)	−0.3029 (1)	0.2946 (1)	3.97 (5)
Cl(2)	0.3815 (2)	−0.2448 (1)	0.1543 (1)	4.01 (5)
Cl(3)	0.1450 (2)	−0.1128 (1)	0.1750 (1)	3.61 (5)
P(1)	0.1144 (2)	−0.1870 (1)	0.3105 (1)	3.27 (5)
O(10)	0.3674 (5)	−0.1433 (3)	0.2682 (2)	2.9 (1)
O(20)	0.1259 (5)	−0.2735 (3)	0.1885 (3)	3.0 (1)
C(1)	−0.0495 (9)	−0.2135 (5)	0.2895 (4)	3.8 (2)
C(2)	−0.1060 (9)	−0.2544 (6)	0.3301 (5)	4.8 (2)
C(3)	−0.239 (1)	−0.2703 (7)	0.3114 (7)	7.5 (3)
C(4)	−0.300 (1)	−0.2466 (9)	0.2531 (8)	8.2 (4)
C(5)	−0.245 (1)	−0.2083 (8)	0.2152 (6)	6.6 (3)
C(6)	−0.122 (1)	−0.1910 (7)	0.2332 (5)	4.9 (3)
C(7)	0.174 (1)	−0.2318 (7)	0.3830 (5)	4.9 (3)
C(8)	0.1072 (9)	−0.0910 (6)	0.3279 (5)	4.4 (2)
C(11)	0.4127 (8)	−0.0750 (5)	0.2880 (4)	3.4 (2)
C(12)	0.4233 (8)	−0.0211 (5)	0.2451 (4)	3.8 (2)
C(13)	0.457 (1)	0.0488 (6)	0.2681 (5)	5.3 (3)
C(14)	0.483 (1)	0.0622 (6)	0.3301 (6)	6.5 (3)
C(15)	0.477 (1)	0.0083 (6)	0.3715 (5)	5.1 (3)
C(16)	0.4450 (8)	−0.0622 (5)	0.3527 (4)	3.7 (2)
C(21)	0.0147 (8)	−0.3040 (5)	0.1595 (4)	3.4 (2)
C(22)	−0.0318 (8)	−0.3642 (5)	0.1879 (5)	3.9 (2)
C(23)	−0.153 (1)	−0.3884 (6)	0.1638 (6)	5.2 (3)
C(24)	−0.223 (1)	−0.3567 (7)	0.1114 (6)	6.2 (3)
C(25)	−0.173 (1)	−0.3018 (7)	0.0812 (6)	5.7 (3)
C(26)	−0.0532 (9)	−0.2735 (5)	0.1027 (5)	4.0 (2)
C(121)	0.4147 (9)	−0.0328 (6)	0.1744 (5)	4.8 (2)
C(122)	0.488 (1)	−0.0832 (6)	0.1524 (5)	5.3 (3)
C(123)	0.490 (1)	−0.0897 (9)	0.0914 (6)	9.5 (4)
C(124)	0.420 (1)	−0.043 (1)	0.0512 (6)	14.5 (5)
C(125)	0.346 (2)	0.007 (1)	0.0678 (6)	12.1 (5)
C(126)	0.343 (1)	0.0139 (8)	0.1290 (7)	8.4 (4)
C(161)	0.4523 (9)	−0.1187 (6)	0.4003 (4)	4.1 (2)
C(162)	0.404 (1)	−0.1048 (7)	0.4553 (5)	5.2 (3)
C(163)	0.421 (1)	−0.1587 (8)	0.5034 (5)	7.1 (3)
C(164)	0.482 (1)	−0.2216 (7)	0.4984 (6)	6.8 (3)
C(165)	0.527 (1)	−0.2355 (8)	0.4451 (6)	6.0 (3)
C(166)	0.513 (1)	−0.1838 (6)	0.3965 (5)	4.4 (2)
C(221)	0.0433 (9)	−0.4047 (5)	0.2413 (5)	3.7 (2)
C(222)	0.164 (1)	−0.4299 (6)	0.2369 (5)	4.9 (3)
C(223)	0.228 (1)	−0.4744 (7)	0.2839 (7)	7.3 (4)
C(224)	0.172 (1)	−0.4943 (7)	0.3345 (6)	6.5 (3)
C(225)	0.058 (1)	−0.4686 (7)	0.3360 (5)	5.9 (3)
C(226)	−0.008 (1)	−0.4254 (6)	0.2901 (5)	4.5 (2)
C(261)	−0.002 (1)	−0.2172 (6)	0.0658 (4)	4.4 (2)
C(262)	0.118 (1)	−0.2250 (6)	0.0497 (4)	4.4 (2)
C(263)	0.164 (1)	−0.1739 (7)	0.0152 (5)	5.7 (3)
C(264)	0.095 (1)	−0.1144 (8)	−0.0071 (5)	7.3 (4)
C(265)	−0.062 (2)	−0.1056 (7)	0.0067 (6)	7.9 (4)
C(266)	−0.075 (1)	−0.1565 (7)	0.0429 (6)	5.9 (3)

[a] B values anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\gamma)B(2,3)]$.

Table VI. Selected Bond Distances (Å) and Angles (deg) for W(OAr-2,6-Ph_2)$_2$$Cl_3$($PMe_2Ph$) (**3**)

W–Cl(1)	2.351 (2)	W–O(10)	1.877 (4)
W–Cl(2)	2.392 (2)	W–O(20)	1.853 (4)
W–Cl(3)	2.356 (2)	W–P(1)	2.579 (2)
Cl(1)–W–Cl(2)	87.89 (6)	Cl(3)–W–P(1)	84.47 (6)
Cl(1)–W–Cl(3)	171.67 (6)	Cl(3)–W–O(10)	85.5 (1)
Cl(1)–W–P(1)	88.55 (6)	Cl(3)–W–O(20)	89.6 (1)
Cl(1)–W–O(10)	89.8 (1)	P(1)–W–O(10)	88.4 (1)
Cl(1)–W–O(20)	94.7 (1)	P(1)–W–O(20)	87.8 (1)
Cl(2)–W–Cl(3)	99.22 (6)	O(10)–W–O(20)	174.1 (2)
Cl(2)–W–P(1)	175.94 (6)	W–P(1)–C(1)	116.1 (2)
Cl(2)–W–O(10)	93.5 (1)	W–P(1)–C(7)	111.7 (3)
Cl(2)–W–O(20)	90.5 (1)	W–P(1)–C(8)	112.1 (2)

Table VII. Fractional Coordinates and Isotropic Thermal Parameters for W(OAr-2,6-Ph_2)$_2$$Cl_2$($PMe_2Ph$)$_2$ (**4a**)[a]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	10000*	0*	0*	12
Cl(2)	9517 (2)	−2053 (1)	538 (1)	17
P(3)	12489 (2)	17 (1)	335 (2)	17
C(4)	13218 (7)	0872 (6)	1646 (8)	25
C(5)	12505 (7)	747 (7)	−1238 (8)	28
C(6)	13904 (6)	1538 (5)	743 (6)	18
C(7)	15038 (7)	2012 (6)	2040 (7)	24
C(8)	16125 (7)	3148 (6)	2276 (8)	29
C(9)	16053 (8)	3847 (7)	1194 (9)	34
C(10)	14902 (7)	3409 (7)	−93 (8)	31
C(11)	13839 (7)	2274 (6)	−331 (7)	26
O(12)	10606 (4)	689 (3)	2000 (4)	15
C(13)	11812 (6)	1129 (6)	3211 (6)	19
C(14)	12167 (6)	296 (6)	4158 (6)	19
C(15)	13498 (7)	749 (6)	5295 (7)	24
C(16)	14413 (7)	1966 (6)	5546 (7)	23
C(17)	14001 (7)	2807 (6)	4714 (6)	19
C(18)	12672 (6)	2406 (6)	3537 (6)	17
C(19)	11184 (6)	995 (5)	4043 (6)	18
C(20)	11679 (7)	−1988 (6)	4296 (6)	21
C(21)	10744 (8)	−3186 (6)	4293 (7)	27
C(22)	9369 (9)	−3367 (6)	4068 (7)	30
C(23)	8861 (8)	−2383 (6)	3827 (6)	25
C(24)	9757 (7)	−1208 (6)	3800 (6)	20
C(25)	12172 (6)	3376 (5)	2805 (6)	17
C(26)	13042 (7)	4334 (6)	2380 (6)	20
C(27)	12564 (7)	5272 (6)	1793 (7)	24
C(28)	11238 (7)	5269 (6)	1626 (7)	24
C(29)	10378 (7)	4342 (6)	2067 (6)	20
C(30)	10838 (7)	3393 (6)	2661 (6)	19

[a] Asterisks indicate fixed coordinates.

atom of the PMe_2Ph ligand in **3**. Although the W–OAr-2,6-Ph_2 distances in **2** and **3** are comparable, there is a significant difference in W–Cl distances between the two complexes. Specifically, it can be seen that the W–Cl distances are definitely shorter in the thf adduct (**2**) than in the phosphine derivative (**3**). This is most noticeable for the chloride atoms located trans to the neutral donor atoms. In **2** the W–Cl(1) distance trans to the thf molecule is 2.308 (2) Å, while in **3** the stereochemically related chlorine atom distance, W–Cl(2), is 2.392 (2) Å. The greater trans influence of the phosphine over the thf ligand is hence evident in these systems.

An interesting feature of the formation of **2** and **3** from WCl_4(OAr-2,6-Ph_2)$_2$ (**1**) concerns the rearrangement of the aryloxide ligands from mutually cis to mutually trans. Two important points about the rearrangement concern its driving force and the pathway whereby it takes place. The formation of *cis*-WCl_4(OAr-2,6-Ph_2)$_2$ (**1**) from WCl_6/HOAr-2,6-Ph_2 mixtures may itself be a kinetic process although one would predict that a cis arrangment does lead to a maximization of oxygen-p to metal-d π-bonding, which is an important aspect of high-valent metal alkoxide and aryloxide chemistry[11] (vide infra). The rearrangement of the aryloxides on reduction to a trans configuration could have as its driving force a combination of steric and electronic components. The trans configuration means that the metal-based electron can occupy an orbital (d_{xy} assuming the z axis lies along the OWO vector) that is not being raised in energy by the π-donor aryloxides. However, the pathway for isomerization is obscure. Although an intermediate, five-coordinate species WCl_3(OAr-2,6-Ph_2)$_2$ is reasonable, it has also been shown possible for octahedral compounds of the group 6 metals to undergo facile isomerization via a trigonal-twist mechanism.[12]

The reduction of toluene solutions of WCl_4(OAr-2,6-Ph_2)$_2$ (**1**) with sodium amalgam (2 Na/W) in the presence of PMe_2Ph or $PMePh_2$ (≥2 equiv) leads to the formation of the orange W(IV) compounds WCl_2(OAr-2,6-Ph_2)$_2$(PMe_2Ph)$_2$ (**4a**) and WCl_2(OAr-2,6-Ph_2)$_2$($PMePh_2$)$_2$ (**4b**). A solid-state structural study of **4a** was performed (Figure 4) in order to accurately characterize

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(11) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R., *McCleverty*, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, Chapter 15.3.

(12) Conner, K. A.; Walton, R. A. *Organometallics* **1983**, *2*, 169.

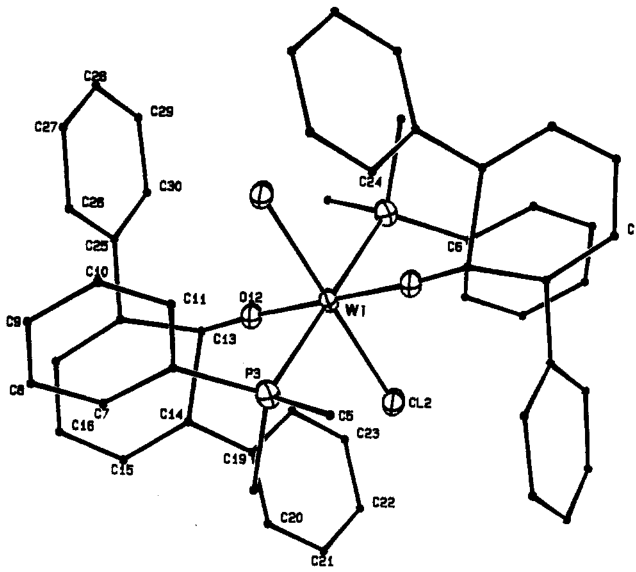

Figure 4. ORTEP view of $WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)_2$ (**4a**).

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $W(OAr\text{-}2,6\text{-}Ph_2)_2Cl_2(PMe_2Ph)_2$ (**4a**)

W-Cl(2)	2.354 (2)	W-O(12)	1.966 (4)
W-P(3)	2.551 (2)		
O(12)-W-Cl(2)	89.9 (1)	O(12)-W-P(3)′	87.1 (1)
O(12)-W-Cl(2)′	90.1 (1)	Cl(2)-W-P(3)′	92.66 (5)
O(12)-W-P(3)	92.9 (1)	W-O(12)-C(13)	140.0 (4)

its molecular structure. Fractional coordinates and isotropic thermal parameters for **4a** are contained in Table VII, while Table VIII contains some selected bond distances and angles. The molecule is found to contain a crystallographically imposed inversion center, with an all *trans*-$WO_2P_2Cl_2$ core. The molecular geometry in **4a** can be seen to be formed by replacement of the chloride atom in **3** that is trans to the PMe_2Ph group by another phosphine ligand. This implies that the trans influence observed in **3** might carry over as a trans effect in the substitution in the presumed intermediate anion $[WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)]^-$ (3^-) formed by the reduction. The relevance of the bond distances in **4a** are discussed below. The d^2 compounds (**4**) exhibit sharp but contact-shifted ^1H NMR spectra (Figure 5). In this respect they behave similarly to the related tetrachlorides $WCl_4(L)_2$.[13] The methyl groups of the PMe_2Ph or $PMePh_2$ ligands resonate to high field at δ −21.5 ppm, while the aryl groups attached to phosphorus are less shifted, appearing in the δ 5–10 ppm ranges. The protons attached to the central, phenolic ring of the aryloxide ligands can be assigned by using spin-decoupling experiments and are more dramatically shifted. The protons in the meta position are shifted downfield, appearing as a sharp doublet at $\delta \sim$13–14 ppm, while the central para hydrogen is shifted upfield to $\delta \sim$−8 ppm (Figure 5). This oscillation of shifts up and downfield on moving around the aromatic ring is indicative of the spin denisty from the metal being transferred through the aromatic ring of the phenoxide by a hyperconjugative mechanism.[14] The shifts imply that a positive spin density is present at the 4-position and a negative one at the 3- and 5-positions. All other aromatic protons are found in the δ 5–10 ppm region and are difficult to assign.

The octahedral compounds obtained in this study allow some analysis of the structural impact of oxygen-p to metal-d π-bonding and its dependence on the metal electron configuration. In Table IX are collected the bond distances for a number of mixed chloro aryloxides of tungsten, ranging from the d^0 W(VI) complex (**1**) to the 18-electron compound $W(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)(Cl)(dmpe)$, which contains a 2,6-diphenylphenoxide group chelated to the metal by an η^6-interaction with one of the aryl side chains. It can be seen from Table IX that both the W–OAr and W–Cl distances increase as the metal center becomes more electronically saturated and simultaneously drops in formal oxidation state. However, the increase in the W–OAr distances from 1.84 to 2.14 Å (0.3 Å or 15%) is much more significant than the increase in W–Cl distances, which represents an elongation of only 9%. This is shown graphically in Figures 6 and 7 for the variation in the W–O distances. Although the tungsten–oxygen distance appears to be an excellent probe of the electronic demands of the metal center, even a cursory analysis of the W–O–Ar angles shows the latter parameter to be totally unreliable in these systems. Similar conclusions based on a series of niobium aryloxide compounds were reached.[15]

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in vacuo either in a Vacuum Atmospheres Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone. $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (**1**)[10a] was obtained by previously reported procedures, and crystals totally lacking in trapped solvent were obtained upon slow cooling of a hot benzene solution. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian Associates XL-200 and Gemini 200 spectrometers and are referenced to Me_4Si by using protio impurities of commercial benzene-d_6 or toluene-d_8 as internal standards (^1H and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). The ESR spectra were obtained by using the nonaqueous cavity of a Varian E-Drive Century Series spectrometer. Microanalyses were obtained from the Purdue Microanalytical Laboratory.

Cyclic voltammograms and coulometric experiments were performed by using a BioAnalytical Systems, Inc., Model CV-27 instrument. A three-compartment (H) cell was used with a Pt-disk or Pt-gauze working electrode, Pt-wire auxiliary electrode, and Ag/AgCl pseudoreference electrode to which all potentials refer. Scan rates were 25 mV/s. Under these conditions the Cp_2Fe/Cp_2Fe^+ couple was measured at +0.47 V consistent to ±10 mV, with a separation between the anodic and cathodic waves of 90 mV.

$W(OAr\text{-}2,6\text{-}Ph_2)_2(thf)Cl_3$ (2). To a solution of $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (1.00 g, 1.23 mmol) in benzene (50 mL) was added $MgC_4H_6(thf)$ (0.20 g, 1.37 mmol). The solution was stirred under N_2 for 24 h. The solution was filtered to remove excess magnesium salts, and red crystals were grown from a concentrated toluene/hexane (1:1) solution. Typical yield: 30%. Anal. Calcd for $WC_{40}H_{34}O_3Cl_3$: C, 56.53; H, 3.68; Cl, 12.51. Found: C, 56.21; H, 3.60; Cl, 12.76. EPR (toluene): g = 1.671, very broad with no resolvable structure.

$W(OAr\text{-}2,6\text{-}Ph)_2(PMe_2Ph)Cl_3$ (3). To a solution of $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (2.00 g, 2.45 mmol) in toluene (100 mL) was added PMe_2Ph (0.71 g, 50 mmol) followed by the slow addition of an excess of $LiBH_4$ (0.22 g, 32.6 mmol). The mixture was stirred for 24 h in a drybox. The solution was filtered to remove excess lithium salts, and red crystalline blocks were produced from a toluene/hexane (1:1) solution. Typical yield: 60%. Anal. Calcd for $WCl_3C_{44}H_{37}O_2P$: C, 57.57; H, 4.06; Cl, 11.57; P, 3.37. Found: C, 57.54; H, 4.32; Cl, 11.20; P, 3.55. EPR (toluene): g = 1.713, very broad with no resolvable structure.

$WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)_2$ (4a). To a sodium amalgam containing Na metal (0.13 g, 5.60 mmol) below a toluene solution (100 mL) were added $WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (2.00 g, 2.45 mmol) and PMe_2Ph (0.71 g, 5.1 mmol). The mixture was vigorously stirred for 24 h at room temperature in a drybox, resulting in an orange suspension. The orange precipitate was filtered from the solution and recrystallized by slow cooling of a hot toluene solution. Typical yield: 60%. Anal. Calcd for $WC_{52}H_{48}Cl_2O_2P_2$: C, 61.13; H, 4.73; Cl, 6.94; P, 6.06. Found: C, 60.74; H, 4.56; Cl, 6.63; P, 6.65. ^1H NMR (C_7D_8, 30 °C): δ −21.50 (s, PMe_2Ph); δ −8.01 (t), 13.50 (d) (para and meta H's on the phenoxide); δ 6.79 (t), 9.40 (t), 9.66 (d) (aryl H's of PMe_2Ph).

$WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PPh_2Me)_2$ (4b). To a solution amalgam containing Na metal (0.13 g, 5.60 mmol) below a toluene solution (100 mL) were added $WCl_4(OAr\text{-}2,6\text{-}Ph)_2$ (2.00 g, 2.45 mmol) and PPh_2Me (1.08 g, 5.40 mmol). The mixture was stirred vigorously for 24 h at room temperature in a drybox, resulting in an orange suspension. The orange precipitate was filtered from the solution and recrystallized upon slow cooling of a hot toluene solution. Typical yield: 50%. Anal. Calcd for $WC_{62}H_{52}Cl_2O_2P_2$: C, 65.99; H, 4.57; Cl, 5.19; P, 5.41. Found: C, 64.66; H, 4.52; Cl, 5.81; P, 5.98. ^1H NMR (C_7D_8, 30 °C): δ −17.43 (s,

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Table IX. Selected Bond Distances for Various Aryloxide Chloride Derivatives of Tungsten

compd	electron confign	W–OAr, Å	W–Cl, Å
cis-$WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$	12	1.840 (3), 1.851 (3)	2.297 (1)–2.341 (1)
mer-$WCl_3(OAr\text{-}2,6\text{-}Pr^i{}_2)_3$[a]	12	1.832 (2)–1.848 (2)	2.333 (1)–2.360 (1)
cis-$WCl_2(OPh)_4$[b]	12	1.72 (1)–1.90 (1)	2.35 (1), 2.36 (1)
$WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(thf)$	13	1.855 (5), 1.857 (5)	2.308 (2)–2.342 (2)
$WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)$	13	1.853 (4), 1.877 (4)	2.351 (2)–2.392 (2)
$WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)_2$	14	1.966 (4)	2.354 (2)
$W(OC_6H_3Ph\text{–}\eta^6\text{-}C_6H_5)\text{-}(OAr\text{-}2,6\text{-}Ph_2)(PMePh_2)$	16	2.001 (6), 2.033 (6)	
$W(OC_6H_3Ph\text{–}\eta^6\text{-}C_6H_5)\text{-}(Cl)(dmpe)$	18	2.135 (8)	2.490 (3)

[a] Reference 10a. [b] Reference 17.

Table X. Crystallographic Data

	1	2	3	4
	$WCl_4O_2C_{36}H_{26}$	$WCl_3O_3C_{40}H_{34}$	$WCl_3PO_2C_{44}H_{37}$	$WCl_2P_2O_2C_{52}H_{48}$
fw	816.27	852.92	918.97	1021.65
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a, Å	11.051 (1)	11.582 (2)	10.8028 (8)	10.216 (5)
b, Å	16.693 (3)	12.099 (1)	18.430 (2)	11.335 (3)
c, Å	17.515 (3)	24.828 (4)	21.746 (6)	10.289 (2)
α, deg	90	90	90	92.30 (1)
β, deg	95.72 (1)	90	100.80 (1)	110.95 (1)
γ, deg	90	90	90	108.21 (1)
Z	4	4	4	1
V, Å^3	3215 (1)	3479	4253 (2)	1089.39
ρ_{calcd}, g cm^{-3}	1.686	1.628	1.435	1.557
T, °C	22	19	22	-151
μ, cm^{-1}	40.37	36.60	30.34	29.43
$R(F_o)$	0.029	0.025	0.034	0.034
$R_w(F_o)$	0.038	0.034	0.062	0.033

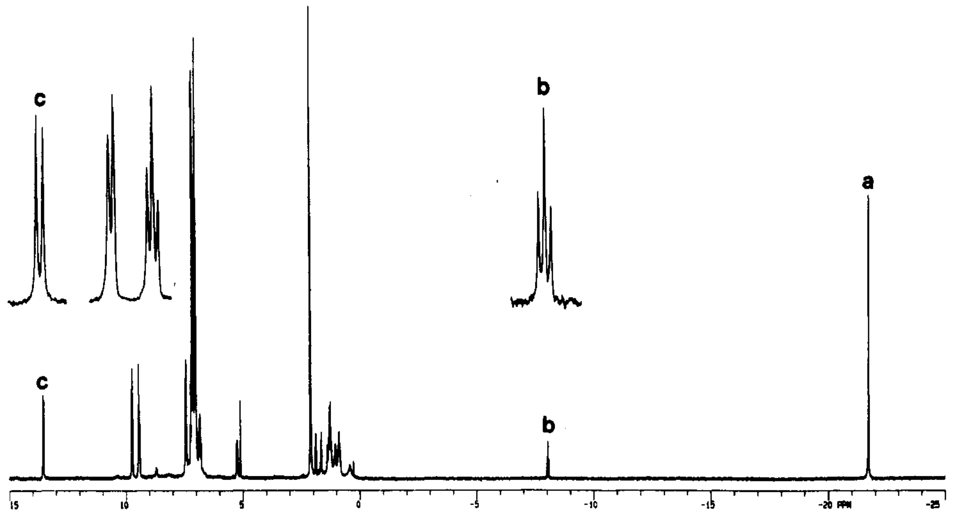

Figure 5. ^1H NMR spectrum of $WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)_2$ (**4a**): (a) P*Me*$_2$Ph; (b) para H and (c) meta H on phenolic ring.

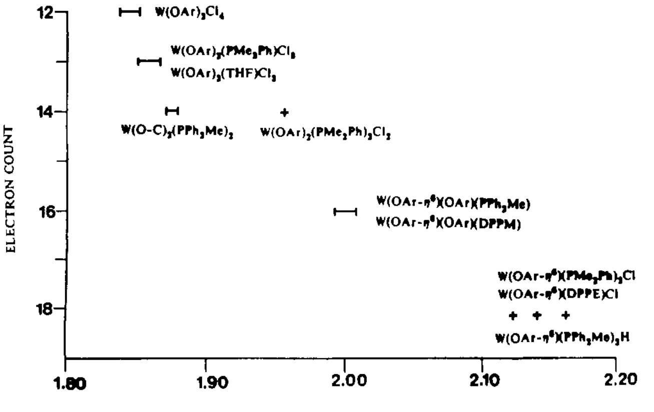

Figure 6. Plot of W–OAr bond distances vs metal electron configuration ($W(O\text{–}C)_2(PPh_2Me)_2 \equiv W(OC_6H_3Ph\text{–}C_6H_4)_2(PPh_2Me)_2$[9b]).

P*Me*Ph$_2$); δ −7.26 (t), 13.42 (d) (para and meta H's on the phenoxide); δ 10.81 (t), 11.60 (m) (aryl H's of PMePh$_2$).

Crystallographic Studies

Three of the X-ray diffraction studies were completed in-house at Purdue, while the fourth, that of **4a**, was obtained through the Indiana University Molecular Structure Center. General operating procedures have been reviewed.[16] Some selected crystallographic data are collected in Table X.

$WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2$ (1), $WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(thf)$ (2), and $WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)$ (3). A suitable sample of each of the three compounds was examined under deoxygenated Nujol and mounted in an appropriately sized glass capillary surrounded by epoxy resin. The positions for the hydrogen atoms were calculated by assuming idealized geometry and a carbon–hydrogen bond distance of 0.95 Å. For the

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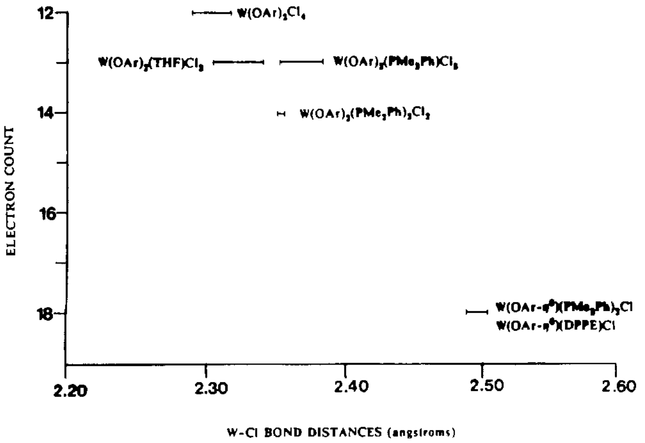

Figure 7. Plot of W–Cl bond distances vs metal electron configuration.

methyl groups, one hydrogen was located in a difference Fourier map, this position was idealized, and the remaining positions were calculated. No hydrogens were refined. No correction for extinction was applied, and there was no decay in the standards. For compound **2** another enantiomorph was resolved, but $R = 0.044$, $R_w = 0.061$, and GOF = 2.358, so the enantiomorph reported here is correct.

$WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)_2$ (4a). A small, orange crystal was selected and transferred to the goniostat, where it was cooled to −151 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited no symmetry or systematic extinctions. The reflections could be indexed on a triclinic lattice, and the choice of the centrosymmetric space group $P\bar{1}$ was confirmed by the subsequent solution and refinement of the structure. The data collection was carried out in the usual manner. A total of 3843 reflections were measured, standard data reduction and averaging resulted in a set of 2839 unique reflections, and 2754 were considered observed by the criterion $F > 3.0\sigma(F)$. The R for the averaging was 0.029 for 944 reflections observed more than once.

The structure was solved by using heavy-atom Fourier techniques. With only one molecule in the asymmetric unit, the molecule had to be situated with the W atom at the origin. All non-hydrogen atoms were located, and following initial refinement all hydrogen atoms were located in a difference map. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The final R was 0.034.

The final difference map was essentially featureless, except for a peak of about 1.5 e/Å^3 at the W position. The molecule possesses a crystallographic center of symmetry.

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Supplementary Material Available: Listings of crystal data and data collection parameters, hydrogen positional and thermal parameters, anisotropic thermal parameters, bond distances and angles, and torsion angles (35 pages); tables of observed and calculated structure factors (80 pages). Ordering information is given on any current masthead page.

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Photosubstitution Reactions of Terpyridine Complexes of Ruthenium(II)

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A series of ruthenium–terpyridine complexes, *trans*-Ru(trpy)LCl_2, *cis*-Ru(trpy)L_2Cl^+, Ru(trpy)L_3^{2+} (trpy = 2,2′:6′,2″-terpyridine; L = pyridine (py), acetonitrile, 4-methylpyridine, propionitrile), and *trans*-Ru(trpy)L_2Cl^+ (L = pyridine, 4-methylpyridine), were prepared and characterized by UV–visible and NMR spectroscopy and cyclic voltammetry. In acetone and dichloromethane, Ru(trpy)L_3^{2+} and Ru(trpy)L_2Cl^+ undergo efficient photosubstitution of L by solvent or chloride. For Ru(trpy)$(CH_3CN)_3^{2+}$, Ru(trpy)$(py)_3^{2+}$, *cis*-Ru(trpy)$(CH_3CN)_2Cl^+$, *cis*-Ru(trpy)$(py)_2Cl^+$, and *trans*-Ru(trpy)$(py)_2Cl^+$, Φ_{Cl^-} = 0.040, 0.037, 0.127, 0.049, and 0.0004, respectively; $\Phi_{solvent}$ = 0.020, 0.004, 0.053, 0.008, and 0.0002, respectively. Methyl-substituted complexes containing 4-methylpyridine and propionitrile were used to show that L sites were selectively photolabilized and most reactions occurred without rearrangement. The results are discussed in terms of current photosubstitution theories.

Introduction

In studies of photochemical substitution reactions of coordination complexes, it is desirable to be able to predict which ligand is likely to be photolabilized and what rearrangement processes are likely to occur during the substitution process. Models have been developed to predict each of these with varying degrees of success. For d^3 complexes, Adamson's rules have been used to predict ligand labilization.[1] More recently, Vanquickenborne and Ceulemans[2,3] and Wrighton[4] have expanded the concepts of Adamson with a semiempirical model based on the angular overlap model. Models have also been proposed[3,5-7] to explain the rearrangement that occurs following ligand labilization. In general, photolabilization is expected to occur on the axis with the weakest average ligand field to produce a square-pyramidal intermediate. Rearrangement through a trigonal-bipyramidal species may lead to a product with the incoming ligand in a position different from that of the leaving ligand. The occurrence of photosubstitution and isomerization depends on the thermodynamic and kinetic favorability of a number of fundamental steps.

Since (polypyridyl)ruthenium complexes are important as models for solar energy conversion schemes, their photochemical and photophysical properties are of great interest. Photosubstitution is generally undesirable in these schemes; however, an understanding of such reactions is needed to design photostable systems. Photosubstitution in Ru$(bpy)_3^{2+}$ [8-10] (bpy = 2,2′-bipyridine), Ru$(bpy)_2L_2^{n+}$,[11-13] and related systems have been studied, but often the bpy ligands place certain constraints on the lability of sites and modes of rearrangement. The ruthenium center in 2,2′;6′,2″-terpyridine (trpy) complexes of ruthenium is

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