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Preparation and Characterization of $W(OR)_4Cl_2$ Complexes (R = Pentafluorophenyl, 2,6-Dichlorophenyl) and Some of Their Reduction Products, Including an X-ray Study of $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_4Cl(Et_2O)$

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WCl_6 reacts with 4 equiv of pentafluorophenol in carbon tetrachloride to give $W(OC_6F_5)_4Cl_2$ in ~90% yield. $W(OC_6F_5)_4Cl_2$ can be reduced with 2 equiv of sodium amalgam in ether to give paramagnetic $[Na(ether)_x]_2[W(OC_6F_5)_4Cl_2]$ in ~65% yield. Cation exchange with either tetraphenylarsonium chloride or tetra-*n*-butylammonium bromide yields $[AsPh_4]_2[W(OC_6F_5)_4Cl_2]$ or $[(n\text{-}Bu)_4N]_2[W(OC_6F_5)_4Cl_2]$, respectively. WCl_6 reacts with an excess of melted 2,6-dichlorophenol (HDCP) to give $W(DCP)_4Cl_2$ in ~65% yield. $W(DCP)_4Cl_2$ can be reduced with 1 equiv of sodium amalgam in ether to give paramagnetic W(DCP)$_4$Cl(ether) in ~75% yield. W(DCP)$_4$Cl(ether) belongs to the space group $P2/n$ with $a = 12.241$ (9) Å, $b = 8.643$ (2) Å, $c = 17.408$ (8) Å, $\beta = 102.25$ (5)°, $V = 1799.8$ Å^3, and $Z = 2$. Final $R_1 = 0.082$ and $R_2 = 0.090$. The complex is octahedral with the ether molecule trans to the chloride ligand. W(DCP)$_4$Cl(pyridine), which is prepared from W(DCP)$_4$Cl(ether) and 1 equiv of pyridine, and W(DCP)$_4$Cl(ether) do not react further with 0.5% sodium amalgam. W(DCP)$_4$Cl(PMe_3), which is prepared from W(DCP)$_4$Cl(ether) and 1 equiv of PMe_3, reacts with 1 equiv of sodium amalgam to yield paramagnetic W(DCP)$_4$(PMe_3) in ~65% yield. Cyclic voltammograms of $W(OC_6F_5)_4Cl_2$ and $W(DCP)_4Cl_2$ in dichloromethane consist of two reduction waves, the first of which is at best only quasi-reversible. The cyclic voltammogram of W(DCP)$_4$Cl(pyridine) in dichloromethane consists of one oxidation and one reduction wave, which appear to be reversible at scan speeds of 10–200 mV s^{-1}.

Introduction

Monomeric complexes with the formula MX_4 (M = Mo, W; X = alkyl,[1] amide,[2] thiolate,[3] alkoxide,[4] phenoxide[5]) are relatively rare. In all cases X is bulky, probably in order to stabilize such species. MX_4 complexes formally have only 10 electrons (not counting π electrons donated to M) and therefore often react readily with small donor molecules or form dimers if X is small enough to bridge. Such complexes may be relevant to the fixation and subsequent reduction of dinitrogen by molybdenum nitrogenase, since it is believed that a Mo(IV) center is responsible for the initial binding of nitrogen in the enzyme.[6] However, no MX_4 species has yet been reported to activate dinitrogen. One type of complex that we believe should be isolable would have the form $X_4M(\mu\text{-}N_2)MX_4$ on the basis of the existence of $[W(\eta^5\text{-}C_5Me_5)Me_3]_2(\mu\text{-}N_2)$[7a] and its preparation by reducing $W(\eta^5\text{-}C_5Me_5)Me_3$(triflate) with sodium amalgam in ether under dinitrogen.[7b]

W(DMP)$_4$ and W(DIPP)$_4$ (DMP = 2,6-dimethylphenoxide and DIPP = 2,6-diisopropylphenoxide) are the only well-characterized examples of $M(OR)_4$ complexes of molybdenum or tungsten.[5] They are essentially square planar and diamagnetic as a result of the strong π bonding of the phenoxides above and below the molecular plane, which raises the level of the e_g orbitals so that a_{1g} (d_{z^2}) or a ligand-based b_{2u} orbital becomes the HOMO. W(DMP)$_4$ reacts with substrates such as 3-hexyne, (trimethylsilyl)diazomethane, trimethylsilyl azide, and cyclohexene oxide to form W(DMP)$_4$(L) species (L = 3-hexyne, $NNCHSiMe_3$, $NSiMe_3$, O), while W(DIPP)$_4$ is relatively unreactive, presumably because the DIPP ligands are too bulky. Adding electron-withdrawing groups to the phenoxide ligands while maintaining the appropriate steric bulk around the metal center would address the question as to whether more electron deficient d^2 complexes can be prepared and what the structure of such species might be in view of what is likely to be sharply reduced π bonding.

Here we describe the preparation and characterization of $W(OR)_4Cl_2$ complexes, where OR = OC_6F_5 and 2,6-dichlorophenoxide (DCP), and their subsequent reduction products. The X-ray structure of one of the reduced species, W(DCP)$_4$Cl(Et_2O) (as a dichloromethane solvate), is also reported.

Results and Discussion

Preparation of $W(DCP)_4Cl_2$ and $W(OC_6F_5)_4Cl_2$. $W(DCP)_4Cl_2$ and $W(OC_6F_5)_4Cl_2$ can both be prepared from WCl_6 and the corresponding phenol. $W(OC_6F_5)_4Cl_2$ is prepared by treating WCl_6 with 4 equiv of pentafluorophenol in refluxing carbon tetrachloride for 12 h (eq 1). After the solvent is removed,

$$WCl_6 + 4C_6F_5OH \xrightarrow[-4HCl]{CCl_4,\ 12\ h} W(OC_6F_5)_4Cl_2 \qquad (1)$$

$W(OC_6F_5)_4Cl_2$ can be recrystallized from a mixture of methylene chloride and pentane in ~90% yield as large green blocks. The ^{19}F NMR spectrum of $W(OC_6F_5)_4Cl_2$ consists of three multiplets in a 2:2:1 ratio between −148 and −160 ppm (relative to CCl_3F), a result that implies that the chloride ligands are trans. This geometry is the same as that for the related W(OPh)$_4$Cl$_2$ complex,[8] which was prepared in a fashion similar to that shown in eq 1. In contrast, $W(DCP)_4Cl_2$ must be prepared from WCl_6 and a large excess (~16 equiv) of melted 2,6-dichlorophenol (eq 2). W(D-

$$WCl_6 + 2,6\text{-}C_6H_3Cl_2OH\ (\text{neat}) \xrightarrow[-4HCl]{130\ °C,\ 12\ h} W(DCP)_4Cl_2 \qquad (2)$$

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CP)$_4$Cl$_2$ can be isolated in ~65% yield as a black microcrystalline solid after removing the excess phenol by extraction with pentane. The ^{1}H NMR spectrum consists of one triplet and one doublet in the aromatic region, as expected if the chloride ligands are mutually trans.

The much milder conditions required to prepare W(OC$_6$F$_5$)$_4$Cl$_2$ compared to those for W(DCP)$_4$Cl$_2$ must be attributed to the steric bulk of 2,6-dichlorophenol. For comparison it should be noted that W(DMP)$_4$Cl$_2$ also must be prepared in melted phenol (10 min),[5] even though 2,6-dimethylphenol is the most basic of the three phenols considered here. The conditions required to prepare W(DCP)$_4$Cl$_2$ are the harshest of all, most likely because 2,6-dichlorophenol is significantly less basic than 2,6-dimethylphenol.

Reduction of W(DCP)$_4$Cl$_2$. W(DCP)$_4$Cl$_2$ can be reduced by 1 equiv of sodium amalgam in ether to give W(DCP)$_4$Cl(Et$_2$O) (eq 3). W(DCP)$_4$Cl(Et$_2$O) can be isolated in ~75% yield and

$$\mathrm{W(DCP)_4Cl_2 + Na/Hg \xrightarrow[-NaCl]{Et_2O} W(DCP)_4Cl(Et_2O)} \quad (3)$$

recrystallized from methylene chloride as red cubes that contain one molecule of methylene chloride per tungsten. W(DCP)$_4$Cl(Et$_2$O) is extremely air sensitive in solution and decomposes in the solid state under N$_2$ at room temperature over a period of ~24 h. W(DCP)$_4$Cl(Et$_2$O) is paramagnetic but has no EPR spectrum down to 77 K; μ_{eff} was determined to be 1.70 μ_B at 25 °C by the Evans NMR technique.[9] The ^{1}H NMR spectrum displays two broad resonances at 9.7 and 2.7 ppm (2:1 ratio) that can be ascribed to the meta and para phenyl protons, respectively, while resonances for the ether are sharp and appear at the same position as those for free ether. Therefore, if ether is bound to tungsten in the solid state, and we assume it is on the basis of the fact that other adducts can be isolated (see below), it must be lost readily in solution. The lability of ether in W(DCP)$_4$Cl(Et$_2$O) could help explain the instability of this compound in both solution and the solid state.

W(DCP)$_4$Cl(py) (py = pyridine) can be prepared in ~60% yield by adding 1 equiv of pyridine to W(DCP)$_4$Cl(Et$_2$O). W(DCP)$_4$Cl(py) can be recrystallized from methylene chloride as red cubes. It is paramagnetic but has no EPR spectrum down to 77 K. Its ^{1}H NMR spectrum consists of five broad resonances in the region -11 to +17 ppm with the expected intensity ratios if it is assumed that the phenoxide ligands are equivalent. Probably because pyridine is relatively tightly bound to tungsten in solution, W(DCP)$_4$Cl(py) is fairly robust, stable to oxygen in solution, and stable indefinitely in the solid state.

W(DCP)$_4$Cl(PMe$_3$) can be prepared in ~80% yield by treating W(DCP)$_4$Cl(Et$_2$O) with 1 equiv of PMe$_3$. It too has no EPR spectrum down to 77 K. Its ^{1}H NMR spectrum exhibits six broad peaks in the region -6 to +19 ppm. If W(DCP)$_4$Cl(PMe$_3$) were to contain equivalent phenoxide ligands, the ^{1}H NMR spectrum should contain only three broad peaks at most (two for the phenoxide ligands and one for the PMe$_3$ ligand). Since six resonances are observed, W(DCP)$_4$Cl(PMe$_3$) must be a less symmetric isomer, or a mixture of isomers. If the structure of W(DCP)$_4$Cl(PMe$_3$) were to consist of a cis arrangement of chloride and PMe$_3$, six resonances would be expected in the ^{1}H NMR spectrum corresponding to three types of phenoxide ligands in a 4:2:2:2:1:1 intensity ratio, plus one resonance for the PMe$_3$ ligand with intensity 9. It is possible that this is in fact the structure and that either two resonances overlap or the PMe$_3$ resonance (most likely) is so broad as to be unobservable.

We were surprised to find that neither W(DCP)$_4$Cl(Et$_2$O) nor W(DCP)$_4$Cl(py) can be reduced further by 0.5% sodium amalgam in ether, while W(DCP)$_4$Cl(PMe$_3$) can be reduced to W(DCP)$_4$(PMe$_3$) (brown cubes in ~65% yield after recrystallization). This paramagnetic d^2 complex has no EPR spectrum down to 77 K, while the ^{1}H NMR spectrum displays three relatively sharp resonances in the region -24 to +18 ppm with intensity ratios consistent with equivalent phenoxide ligands on the ^{1}H NMR time scale. The fact that W(DCP)$_4$(PMe$_3$) is paramagnetic is consistent with the paramagnetism of a variety of other MX$_4$L and MX$_4$L$_2$ (M = Mo, W) complexes (see references in ref 5b).

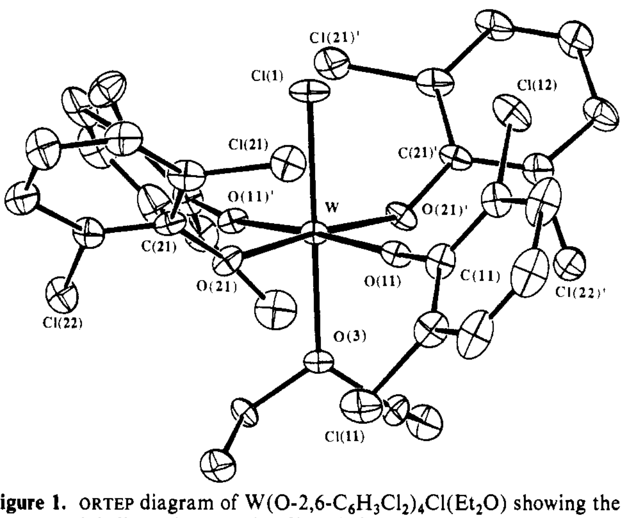

Figure 1. ORTEP diagram of W(O-2,6-C$_6$H$_3$Cl$_2$)$_4$Cl(Et$_2$O) showing the core atom labeling scheme and 30% probability thermal ellipsoids. Hydrogen atoms have been omitted.

Table I. Relevant Bond Distances (Å) and Angles (deg) in W(O-2,6-C$_6$H$_3$Cl$_2$)$_4$Cl(Et$_2$O)[a]

W-Cl(1)	2.298 (5)	W-O(3)	2.104 (13)
W-O(11)	1.853 (9)	Cl(21)···Cl(1)	3.422
W-O(21)	1.964 (10)	Cl(12)···Cl(1)	3.475
O(11)-W-Cl(1)	92.4 (3)	O(3)-W-O(11)	87.6 (3)
O(21)-W-Cl(1)	92.7 (3)	O(3)-W-O(21)	87.3 (3)
O(21)-W-O(11)	90.1 (4)	W-O(11)-C(11)	165.5 (10)
O(3)-W-Cl(1)	180.0	W-O(21)-C(21)	139.9 (10)

[a] Atoms are labeled as shown in Figure 1.

X-ray Structure of W(DCP)$_4$Cl(Et$_2$O). A drawing of the structure of W(DCP)$_4$Cl(Et$_2$O) is shown in Figure 1. Selected bond distances and angles can be found in Table I. Final atomic positions are listed in Table II. A complete description of the structure solution can be found in the Experimental Section.

W(DCP)$_4$Cl(Et$_2$O) has a nearly perfect octahedral arrangement of the four phenoxide oxygen atoms, the chloride, and the ether oxygen atom. The O(11)-W-O(21) angle is 90.1°, the O(11)-W-Cl(1) and O(21)-W-Cl(1) angles are 92.4 and 92.7°, respectively, and the O(3)-W-O(11) and O(3)-W-O(21) angles are 87.6 and 87.3°, respectively. The O(3)-W-Cl(1) angle is 180°. The slight bending of the phenoxide oxygens away from the chloride might be ascribed to steric interactions between the ortho chlorides of the phenoxide rings and Cl(1), although the fact that all phenyl rings are tipped away from the ether ligand could be taken as evidence for steric interaction between the phenyl rings and the ether ligand. The plane that contains the α-carbon atoms and the oxygen of the bound ether molecule bisects the O(11)'-W-O(21) and O(11)-W-O(21)' angles. The W-O(3) bond distance is 2.104 Å, normal for a bound ether. The fact that W-O(11)-C(11) is 165.5° while W-O(21)-C(21) is 139.9° suggests that one phenoxide is a stronger π donor than the other. This interpretation is consistent with a W-O(21) distance of 1.964 Å compared to a W-O(11) distance of 1.853 Å. According to Figure 1 it appears that Cl(1) is in a protective pocket formed by the ortho chlorides of the phenoxide ligands. The distance from Cl(21) to Cl(1) is 3.422 Å while the distance from Cl(12) to Cl(1) is 3.475 Å. All other bond distances are normal.

Reduction of W(OC$_6$F$_5$)$_4$Cl$_2$. W(OC$_6$F$_5$)$_4$Cl$_2$ is reduced by 2 equiv of sodium amalgam in ether to give [Na(Et$_2$O)$_x$]$_2$[W(OC$_6$F$_5$)$_4$Cl$_2$] as a light green powder in ~65% yield (eq 4). The

$$\mathrm{W(OC_6F_5)_4Cl_2 + 2Na/Hg \xrightarrow{Et_2O} [Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]} \quad (4)$$

amount of ether present in this compound varies from sample to sample and cannot be removed completely in vacuo without some

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Table II. Final Positional Parameters for the Atoms of $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_4Cl(Et_2O)$[a]

atom	*x*	*y*	*z*
W	0.2500	0.13335 (11)	0.2500
Cl(1)	0.2500	0.3993 (6)	0.2500
O(11)	0.0956 (8)	0.1244 (12)	0.2206 (5)
C(11)	−0.0117 (12)	0.139 (2)	0.1837 (8)
C(12)	−0.0611 (14)	0.041 (2)	0.1225 (9)
C(13)	−0.1712 (17)	0.061 (3)	0.0822 (11)
C(14)	−0.2317 (17)	0.177 (3)	0.1054 (13)
C(15)	−0.1889 (16)	0.280 (3)	0.1664 (11)
C(16)	−0.0759 (14)	0.2548 (19)	0.2055 (9)
Cl(11)	0.0185 (4)	−0.1033 (6)	0.0952 (3)
Cl(12)	−0.0209 (4)	0.3801 (6)	0.2811 (3)
O(21)	0.2605 (8)	0.1225 (13)	0.1391 (6)
C(21)	0.2847 (14)	0.2127 (17)	0.0830 (8)
C(22)	0.3798 (15)	0.1925 (19)	0.0572 (9)
C(23)	0.4136 (18)	0.277 (2)	−0.0017 (10)
C(24)	0.3391 (17)	0.393 (2)	−0.0387 (10)
C(25)	0.2413 (18)	0.416 (2)	−0.0168 (10)
C(26)	0.2121 (15)	0.3279 (18)	0.0419 (9)
Cl(21)	0.0844 (4)	0.3571 (5)	0.0663 (2)
Cl(22)	0.4720 (4)	0.0446 (6)	0.1021 (3)
O(3)	0.2500	−0.1101 (15)	0.2500
C(31)	0.3298 (13)	−0.2044 (19)	0.2187 (9)
C(32)	0.2818 (17)	−0.266 (2)	0.1360 (10)
C(41)	0.7500	0.870 (4)	0.2500
Cl(41)	0.8707 (5)	0.7585 (9)	0.2566 (5)

[a] Numbers in parentheses are errors in the last significant digits. C(41) and Cl(41) refer to the dichloromethane molecule present in the crystal.

decomposition of the sample. $[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]$ is only soluble in coordinating solvents, in which it decomposes. For example it decomposes in minutes when dissolved in tetrahydrofuran or acetonitrile. It is very sensitive to oxygen. Attempts to isolate products in the reaction between $W(OC_6F_5)_4Cl_2$ and 1 equiv of Na/Hg have repeatedly failed.

Treating $[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]$ with 2 equiv of either $AsPh_4Cl$ or $N(n\text{-}Bu)_4Br$ yields $[AsPh_4]_2[W(OC_6F_5)_4Cl_2]$ or $[N(n\text{-}Bu)_4]_2[W(OC_6F_5)_4Cl_2]$, respectively. $[AsPh_4]_2[W(OC_6F_5)_4Cl_2]$ can be recrystallized from methylene chloride to give light green needles of a dichloromethane solvate or from acetonitrile to give yellow plates of an acetonitrile solvate. Likewise $[N(n\text{-}Bu)_4]_2[W(OC_6F_5)_4Cl_2]$ can be recrystallized from methylene chloride layered with toluene to give light green cubes that contain 1.5 equiv of toluene of crystallization. Both $[AsPh_4]_2[W(OC_6F_5)_4Cl_2]$ and $[N(n\text{-}Bu)_4]_2[W(OC_6F_5)_4Cl_2]$ are significantly more robust than $[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]$, both being stable in coordinating solvents and methylene chloride in the presence of oxygen.

The $[W(OC_6F_5)_4Cl_2]^{2-}$ complexes are paramagnetic, but no EPR spectrum was observed down to 77 K. The effective magnetic moment for $[AsPh_4]_2[W(OC_6F_5)_4Cl_2]$ (acetonitrile solvate) was determined to be 1.62 μ_B by using the Evans NMR method.[9] Nevertheless, ^{19}F NMR spectra for these complexes can be observed; three broadened resonances at ~−120 ppm, −145 to −150 ppm, and −160 to −165 ppm in a 2:2:1 ratio are indicative of equivalent phenoxide ligands and trans chlorides. The resonance at ~−120 ppm is somewhat broader than that at −145 to −150 ppm and therefore is assigned to the two ortho fluorides of the phenoxide ligands.

$[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]$ reacts with excess 3-hexyne (3-hxy) to give $W(OC_6F_5)_4(3\text{-hxy})(Et_2O)$ as large red crystals, after recrystallization from ether (eq 5). On the basis of the ^{19}F

$$[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2] + \text{3-hexyne} \xrightarrow[-2NaCl]{Et_2O} W(OC_6F_5)_4(\text{3-hxy})(Et_2O) \quad (5)$$

NMR spectrum, this compound has equivalent phenoxide ligands on the NMR time scale at 25 °C. The ^1H NMR chemical shifts for ether (primarily) and 3-hexyne are concentration and temperature dependent. All spectra are fully consistent with rapid loss of ether from $W(OC_6F_5)_4(3\text{-hxy})(Et_2O)$ to give a significant amount of $W(OC_6F_5)_4(3\text{-hxy})$ (see Experimental Section for details). In contrast, the related $Mo(DIPP)_4$(diphenylacetylene) complex is a trigonal bipyramid (with the alkyne ligand occupying an equatorial position)[10] that does not bind ether. These results are fully understandable in terms of the smaller size and greater electron-withdrawing ability of the OC_6F_5 ligand relative to those of the $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$ ligand. At low temperatures where ether exchange is slow the NMR spectra are consistent with a square arrangement of equivalent perfluorophenoxide ligands. $W(OC_6F_5)_4(3\text{-hxy})(Et_2O)$ also can be prepared in ~50% yield from $WCl_4(3\text{-hxy})(Et_2O)$[11] and potassium pentafluorophenoxide in ether (eq 6).

$$WCl_4(\text{3-hxy})(Et_2O) + 4KOC_6F_5 \xrightarrow[-4KCl]{Et_2O} W(OC_6F_5)_4(\text{3-hxy})(Et_2O) \quad (6)$$

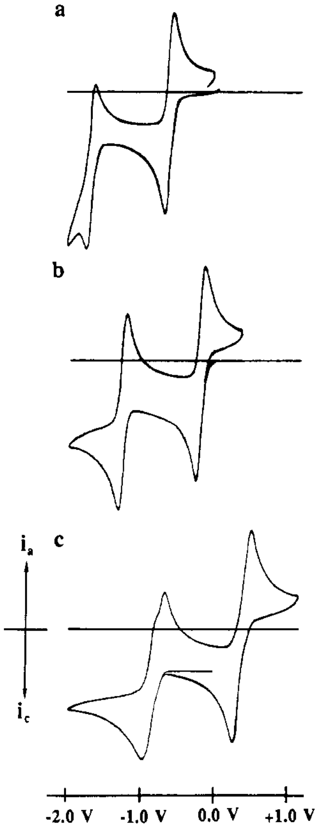

Figure 2. Cyclic voltammograms of (a) $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4Cl_2$, (b) $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_4Cl_2$, and (c) $W(OC_6F_5)_4Cl_2$ in methylene chloride containing ~0.1 M $[N(n\text{-}Bu)_4][PF_6]$ at 298 K. All potentials are in volts vs Ag/Ag^+ in CH_3CN; the scan rate is 200 mV s^{-1}.

Electrochemistry. Cyclic voltammetric data for the compounds reported here are summarized in Table III, and cyclic voltammograms in methylene chloride for $W(OC_6F_5)_4Cl_2$, $W(DCP)_4Cl_2$, and $W(DMP)_4Cl_2$[5] are displayed in Figure 2. Two reduction waves are observed for each of the W(VI) complexes. The first reduction waves have i_{p_a}/i_{p_c} values ~0.80–1.00 for scan speeds of 10–1000 mV s^{-1}. Plots of i_{p_c} vs $\nu^{1/2}$ gave straight lines in the scan speed range 10–200 mV s^{-1}. Peak separations ($E_{p_c} - E_{p_a}$) are ~100–185 mV in the range 10–1000 mV s^{-1} for $W(DCP)_4Cl_2$ and $W(DMP)_4Cl_2$ and somewhat larger for $W(OC_6F_5)_4Cl_2$ (165–335 mV) in the same range. The second reduction waves have $i_{p_c}/i_{p_a} \approx 0.60$–0.90, significantly lower than i_{p_c}/i_{p_a} for the first reduction waves, although plots of i_{p_c} vs $\nu^{1/2}$ are linear in the range 10–200 mV s^{-1} and peak separations are comparable to those for the first reductions. Clearly the first reductions are more reversible than the second reductions under the conditions we employed. At

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Table III. Electrochemical Data in Methylene Chloride at 298 K for Selected Compounds[a]

compd	$E_{1/2}$(redn), V	$E_{1/2}$(oxidn), V
$W(OC_6F_5)_4Cl_2$[b]	+0.40 (235), −0.81 (255)	
$W(DCP)_4Cl_2$[b]	−0.18 (110), −1.25 (100)	
$W(DMP)_4Cl_2$[b]	−0.62 (105), −1.68 (100)	
$[AsPh_4]_2$-$[W(OC_6F_5)_4Cl_2]$[c]		+0.46 (190), −0.73 (210)
$W(DCP)_4Cl(py)$[d]	−0.91 (135)	+0.36 (140)

[a] All measurements were recorded under N_2 with ~0.1 M $[N(n\text{-}Bu)_4][PF_6]$ as supporting electrolyte. All potentials are referenced to Ag/Ag^+ in CH_3CN; the scan range was −2.0 to +2.0 V. Anodic and cathodic peak separations at a scan rate of 100 mV s^{-1} are shown in parentheses. [b] For the first reductions $i_{p_a}/i_{p_c} \approx 0.80-1.00$ for scans of 10–1000 mV s^{-1}; second reductions have $i_{p_a}/i_{p_c} \approx 0.60-0.90$ in the same scan range. [c] For the first oxidation $i_{p_c}/i_{p_a} \approx 0.65-0.80$ for scans of 10–1000 mV s^{-1}; the second oxidation has $i_{p_a}/i_{p_c} \approx 0.60-0.70$ in the same range. [d] Ratios of peak currents are ~1 for the reduction and oxidation in the scan range 10–1000 mV s^{-1}.

best the first reductions can be said to be approaching reversibility, while the second reductions are better described as irreversible.[12]

A cyclic voltammogram of $[AsPh_4]_2[W(OC_6F_5)_4Cl_2]$ in methylene chloride displays two oxidation waves at +0.46 and −0.73 V in the sweep range −2.0 to +2.0 V. These oxidation waves should correspond to the reduction waves of $W(OC_6F_5)_4Cl_2$, and therefore it is not surprising that the $E_{1/2}$ values for the two complexes are similar. Although plots of i_{p_a} vs $\nu^{1/2}$ are linear in the range 10–200 mV s^{-1} and peak separations are 140–300 mV in the range 10–1000 mV s^{-1}, $i_{p_c}/i_{p_a} \approx 0.65-0.80$ for the first oxidation and $i_{p_c}/i_{p_a} \approx 0.60-0.70$ for the second oxidation. Therefore, these oxidations appear to be irreversible under the conditions we have employed. Most likely the lack of reversibility of the reduction waves starting with $W(OC_6F_5)_4Cl_2$ and the two oxidation waves starting with $[AsPh_4]_2[W(OC_6F_5)_4Cl_2]$ can be ascribed to some significant instability of intermediate "$[W(OC_6F_5)_4Cl_2]^-$".

The reduction potentials for the three W(VI) complexes follow the trend one would expect on the basis of electron-withdrawing ability of the phenoxide ligands. $W(DMP)_4Cl_2$ is the most difficult to reduce electrochemically ($E_{1/2}$ = −0.62, −1.68 V), while $W(OC_6F_5)_4Cl_2$ is the easiest to reduce ($E_{1/2}$ = +0.40, −0.81 V). The reduction potentials for $W(DCP)_4Cl_2$ are intermediate ($E_{1/2}$ = −0.18, −1.25 V). Therefore, it is interesting to note that $W(DMP)_4Cl_2$ can be reduced chemically in ether by 2 equiv of sodium amalgam to give $W(DMP)_4$,[5] while reduction of $W(DCP)_4Cl_2$ in ether yields only $W(DCP)_4Cl(Et_2O)$. A cyclic voltammogram of $W(DCP)_4Cl(Et_2O)$ in dichloromethane shows no cathodic or anodic wave in the sweep range −2.0 to +2.0 V. Evidently intermediate $W(DMP)_4Cl$ in ether behaves quite differently from $W(DCP)_4Cl$ in ether, while $W(DCP)_4Cl$ generated electrochemically in dichloromethane behaves quite differently from isolated $W(DCP)_4Cl(Et_2O)$ in dichloromethane.

The resistance of $W(DCP)_4Cl(Et_2O)$ to further reduction by sodium amalgam in ether or by electrochemical means in dichloromethane is even more puzzling because of the fact that other $W(DCP)_4Cl(L)$ complexes, one of which (L = pyridine) appears to have a structure analogous to that found for $W(DCP)_4Cl(Et_2O)$ in the solid state, can be reduced further electrochemically. A cyclic voltammogram of $W(DCP)_4Cl(py)$ in the sweep range −2.0 to +2.0 V displays two apparently electrochemically reversible waves, an oxidation wave at +0.36 V and a reduction wave at −0.91 V. Both have i_{p_c}/i_{p_a} and $i_{p_a}/i_{p_c} \approx 1$ in the range 10–1000 mV s^{-1}. Plots of $i_{p_{c,a}}$ vs $\nu^{1/2}$ are linear in the range 10–200 mV s^{-1}, and $E_{p_c} - E_{p_a} \approx 100-220$ mV for scan speeds of 10–1000 mV s^{-1}. $W(DCP)_4Cl(PMe_3)$ has multiple anodic and cathodic features in the −2.0 V to +2.0 V range, none of which appears to be well-behaved.

Although $W(DCP)_4Cl(py)$ can be reduced electrochemically in dichloromethane, it *cannot* be reduced by sodium amalgam in ether. In contrast, $W(DCP)_4Cl(PMe_3)$, which has apparently messy electrochemistry in dichloromethane, can be reduced by sodium amalgam in ether to yield $W(DCP)_4(PMe_3)$. As mentioned above, $W(DCP)_4Cl(Et_2O)$, which is structurally similar to $W(DCP)_4Cl(py)$, also cannot be reduced by sodium amalgam in ether, and it has no electrochemistry in dichloromethane. The reason $W(DCP)_4Cl(Et_2O)$ and $W(DCP)_4Cl(py)$ cannot be reduced chemically, whereas $W(DCP)_4Cl(PMe_3)$ can be reduced chemically, is probably related to the structural difference between them (base trans to chloride in $W(DCP)_4Cl(Et_2O)$ and $W(DCP)_4Cl(py)$ or cis to chloride in $W(DCP)_4Cl(PMe_3)$).

Conclusion. These studies show that while the redox potentials of some W(VI) phenoxide species in dichloromethane follow trends that one would predict on the basis of the electron-withdrawing ability of the phenoxide ligands, these potentials cannot be relied upon as a measure of the ease of preparing W(phenoxide)$_4$ species. The reasons are varied and some of them difficult to explain satisfactorily in detail. The hypothesis that more electron-withdrawing bulky alkoxides will be needed in order to prevent formation of planar W(phenoxide)$_4$ complexes such as $W(DMP)_4$ instead of $\mu\text{-}N_2^{4-}$ complexes is going to be difficult to test because of the tendency for the metal in such circumstances to bind anions more strongly to form anionic (e.g., $[W(OC_6F_5)_4Cl_2]^{2-}$) rather than neutral complexes. To now adjust all parameters so that dinitrogen will competitively bind to form a stable $[WX_4]_2(\mu\text{-}N_2)$ complex, even though such a species may be prepared by other routes, would appear to be relatively difficult in homogeneous solution. For this reason we feel it is especially important to pursue more detailed studies of a system in which dinitrogen is known to be "fixed" in the form of a $\mu\text{-}N_2^{4-}$ species, $[W(\eta^5\text{-}C_5Me_5)Me_3]_2(\mu\text{-}N_2)$,[7] and to continue attempts to prepare the analogous molybdenum complex.

Experimental Section

General Details. All reactions were carried out in a Vacuum Atmospheres drybox or on a Schlenk line under dinitrogen. Tetrahydrofuran, ether, toluene, and pentane were distilled from sodium benzophenone ketyl and flushed with dinitrogen prior to use. Methylene chloride was distilled from calcium hydride. WCl_6 was purchased from Sylvania Chemical Co., and $WOCl_4$ was removed by sublimation. Phenols were used as purchased from Aldrich Chemical Co. All ^1H NMR spectra were obtained at 250 or 300 MHz, ^{19}F NMR spectra at 282.215 MHz (CCl_3F reference), and ^{13}C NMR spectra at 67.9 or 100.57 MHz. Analyses were performed by either Schwartzkopf Microanalytical Laboratory or Spang Microanalytical Laboratory. EPR spectra were obtained on a Bruker ESP 300 spectrometer or on a Varian E-Line spectrometer. Magnetic susceptibility measurements were determined by using the Evans NMR technique.[9] Diamagnetic corrections were calculated by using Pascal's constants.[13] The mass susceptibility of CD_2Cl_2 was approximated by using the measured value for dichloromethane of -0.682×10^{-6} cgsu g^{-1}.[14] Electrochemical data were obtained by using a Princeton Applied Research Model 173 potentiostat/galvanostat and Model 175 universal programmer, in conjunction with a Houston Instruments RE-0089 X-Y recorder. Cyclic voltammograms were obtained in the drybox in either dichloromethane or acetonitrile (distilled twice from calcium hydride) containing ~0.1 M $[N(n\text{-}Bu)_4][PF_6]$ as supporting electrolyte. $E_{1/2}$ values are referenced to Ag/Ag^+ and uncorrected for junction potentials.

Preparation of Compounds. $\mathbf{W(OC_6F_5)_4Cl_2}$. WCl_6 (0.05 mol, 20 g) in ~50 mL of CCl_4 was added to a three-neck flask equipped with a reflux condenser, pressure-equalizing addition funnel, and gas adapter. The addition funnel was charged with pentafluorophenol (0.2 mol, 37.13 g) in 100 mL of CCl_4. The pentafluorophenol solution was added to the WCl_6 solution slowly over 15 min with stirring. The mixture was then heated to reflux. After 12 h the solvent was removed in vacuo, leaving behind a green residue (48.65 g, 99%). This crude product was recrys-

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tallized from methylene chloride layered with pentane to give large green blocks of $W(OC_6F_5)_4Cl_2$ (42.8 g, 88%): ^{19}F NMR (CD_2Cl_2) δ −148.59 (m, 8), −152.50 (m, 4), −160.70 (m, 8); ^{13}C NMR (CD_2Cl_2) δ 135, 139–140, 143–144 (overlapping multiplets, ring carbons, J_{CF} not calculated). Anal. Calcd for $C_{24}F_{20}O_4Cl_2W$: C, 29.21; H, 0.0; Cl, 7.18. Found: C, 29.13; H, trace; Cl, 7.12.

$W(DCP)_4Cl_2$. WCl_6 (0.076 mol, 30 g) and 2,6-dichlorophenol (1.23 mol, 200 g) were thoroughly mixed in the drybox and transferred to a Schlenk flask. The mixture was heated to ~70 °C, at which point the phenol melted. The resulting solution was stirred rapidly as the temperature was increased to 130 °C. After 11 h the mixture was allowed to cool in vacuo, and the resulting solid was broken up and extracted with 1 L of pentane to remove the excess phenol. The black material that remained was Soxhlet-extracted with pentane for 3 days to remove any remaining phenol. The resulting black microcrystalline $W(DCP)_4Cl_2$ (45.0 g, 65%) was pure enough for further use: ^1H NMR (C_6D_6) δ 6.00 (t, 4, para H), 6.82 (d, 8, meta H); ^{13}C NMR ($CDCl_3$) δ 126.18 (ring carbon), 128.47 (ring carbon), 128.76 (ring carbon) (the ipso carbon resonance was not found). Only the fully decoupled spectrum was acquired due to insolubility of the compound. Anal. Calcd for $C_{24}H_{12}O_4Cl_{10}W$: C, 31.93; H, 1.34; Cl, 39.27. Found: C, 32.33; H, 1.41; Cl, 40.12.

$W(DCP)_4Cl(Et_2O)$. $W(DCP)_4Cl_2$ (2.22 mmol, 2 g) was added all at once to a vigorously stirred suspension of sodium amalgam (0.5%, 2.22 mmol, 10.2 g) in ~100 mL of cold ether (−46 °C). After ~15 min the starting material reacted and the mixture became orange-brown. An orange precipitate was present after 25 min. After 45 min the reaction mixture had darkened considerably. The mixture was filtered through a layer of Celite, and the red solids were dissolved off the frit with methylene chloride. The solvent was then removed from the filtrate in vacuo until red microcrystals formed, which were collected by filtration (1.5 g, 74%). Recrystallization of $W(DCP)_4Cl(Et_2O)$ from methylene chloride yielded a dichloromethane solvate: ^1H NMR (C_6D_6) δ 9.7 (br), 2.7 (br); EPR (20 °C and 77 K) not observed. Anal. Calcd for $C_{29}H_{24}O_5Cl_{11}W$: C, 33.94; H, 2.36; Cl, 38.00. Found: C, 33.96; H, 2.46; Cl, 38.41.

$W(DCP)_4Cl(py)$. Pyridine (26 μL, 0.32 mmol) was added to a solution of $W(DCP)_4Cl(Et_2O)$ (300 mg, 0.32 mmol) dissolved in ~10 mL of cold methylene chloride. The color lightened. After ~1.5 h at room temperature the solvent volume was reduced to a minimum in vacuo and the mixture was stored at −46 °C overnight to yield $W(DCP)_4Cl(py)$ (185 mg, 61%) as red cubes: ^1H NMR (CD_2Cl_2) δ 16.5 (br), 10.1 (br), 1.6 (br), −4.5 (br), −10.5 (br); EPR (20 °C and 77 K) not observed. Anal. Calcd for $C_{29}H_{17}O_4Cl_9NW$: C, 36.80; H, 1.81; Cl, 33.71; N, 1.48. Found: C, 36.44; H, 1.57; Cl, 33.35; N, 1.51.

$W(DCP)_4Cl(PMe_3)$. PMe_3 (167 μL, 1.64 mmol) was added rapidly to a solution of $W(DCP)_4Cl(Et_2O)$ (1.54 g, 1.64 mmol) dissolved in ~50 mL of cold methylene chloride. The reaction mixture darkened slightly. After ~1.5 h the solvent volume was reduced to a minimum in vacuo and the mixture cooled to −46 °C overnight to yield $W(DCP)_4Cl(PMe_3)$ (1.26 g, 81%) as red cubes containing one molecule of methylene chloride per tungsten. The product may be recrystallized from methylene chloride layered with pentane: ^1H NMR (CD_2Cl_2) δ 18.8 (br), 15.5 (br), 11.0 (br), 10.1 (br), −5.6 (br), −6.0 (br); EPR (20 °C and 77 K) not observed. Anal. Calcd for $C_{28}H_{23}O_4Cl_{11}PW$: C, 32.70; H, 2.25; Cl, 37.92; P, 3.01. Found: C, 32.77; H, 2.29; Cl, 36.47; P, 2.80.

$W(DCP)_4(PMe_3)$. Sodium amalgam (0.5%, 1.43 mmol, 6.56 g) was added to a solution of $W(DCP)_4Cl(PMe_3)$ (1.352 g, 1.315 mmol) in ~50 mL of cold ether. Yellow solids precipitated as the reaction mixture was allowed to warm to room temperature. After ~1 h the mixture was filtered, and the yellow solids on the frit were dissolved in methylene chloride. The solvent was removed from the filtrate in vacuo. The residue was then dissolved in the minimum volume of dichloromethane, and the solution was stored at −46 °C to give $W(DCP)_4(PMe_3)$ (0.77 g, 64%) as yellow-brown cubes. $W(DCP)_4(PMe_3)$ also may be recrystallized from methylene chloride layered with pentane: ^1H NMR (CD_2Cl_2) δ 18.19 (br), −5.59 (br), −23.43 (br); EPR (20 °C and 77 K) not observed. Anal. Calcd for $C_{27}H_{21}O_4Cl_8PW$: C, 35.72; H, 2.33; Cl, 31.24; P, 3.41. Found: C, 36.03; H, 2.41; Cl, 30.87; P, 3.64.

$[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]$. $W(OC_6F_5)_4Cl_2$ (2.0 mmol, 2.0 g) was added rapidly with stirring to a suspension of sodium amalgam (0.5%, 4.0 mmol, 18.63 g) in 60 mL of ether (−46 °C). As the solution was warmed to room temperature, the color changed from red to yellow. The reaction mixture was stirred at room temperature for 2 h and then was filtered. The solvent was removed from the filtrate in vacuo, leaving a green-yellow residue. The residue was washed with ~75 mL of methylene chloride, which removed some green and yellow impurities and left behind $[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]$ as a light green powder (1.58 g, ~66%). This product was pure enough for further use. It is soluble only in coordinating solvents and decomposes within minutes in tetrahydrofuran and acetonitrile: ^{19}F NMR (CD_3CN) δ −119.50 (m, 8), −146.38 (m, 8), −160.00 (m, 4); EPR (20 °C and 77 K) not observed. Repeated elemental analyses were variable and not satisfactory, we believe because the product is not stable at 25 °C.

$[N(n\text{-}Bu)_4]_2[W(OC_6F_5)_4Cl_2]$. $[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]$ (0.43 mmol, 500 mg) was added to a stirred acetonitrile solution of tetra-*n*-butylammonium bromide (0.85 mmol, 275 mg) at −46 °C. The complex dissolved, and a white precipitate formed immediately. The reaction mixture was filtered and the solvent removed in vacuo, leaving behind a light green oily material that was recrystallized with difficulty from methylene chloride layered with toluene as light green cubes (260 mg, 41%) that contain 1.5 equiv of toluene per tungsten: ^1H NMR (CD_2Cl_2) δ 1.51 (m, 16), 0.87 (m, 16), 0.71 (m, 24), 0.59 (m, 16); ^{19}F NMR (CD_2Cl_2) δ −122.50 (br, 8), −150.41 (br, 8), −163.86 (br, 4); EPR (20 °C and 77 K) not observed. Anal. Calcd for $C_{56}H_{72}F_{20}O_4N_2W$: C, 47.08; H, 5.05; Cl, 4.67; N, 1.84. Found: C, 47.32; H, 4.95; Cl, 4.48; N, 2.17.

$[AsPh_4]_2[W(OC_6F_5)_4Cl_2]$. $[Na(Et_2O)_x]_2[W(OC_6F_5)_4Cl_2]$ (1 mmol, 1.2 g) was added to a stirred solution of tetraphenylarsonium chloride (2 mmol, 0.856 g) in 20 mL of acetonitrile at −46 °C. The complex dissolved, and a white precipitate formed immediately. Stirring was continued for 1 h at room temperature, after which time the reaction mixture was filtered. Any solids remaining on the frit were washed with acetonitrile. The volume of the filtrate was reduced to ~30 mL, and the solution was cooled to −46 °C overnight to give yellow cubes (1.2 g, 67%) of $[AsPh_4]_2[W(OC_6F_5)_4Cl_2](CH_3CN)$. Alternatively the complex may be recrystallized from methylene chloride, affording $[AsPh_4]_2[W(OC_6F_5)_4Cl_2](CH_2Cl_2)$ as yellow needles: ^1H NMR (CD_2Cl_2) δ 7.68 (t, 8), 7.54 (t, 16), 7.30 (d, 16); ^{19}F NMR (CD_3CN) δ −122.04 (m, 8), −150.37 (m, 8), −162.93 (m, 4); EPR (20 °C and 77 K) not observed. Anal. Calcd for the acetonitrile solvate $C_{74}H_{43}F_{20}O_4As_2Cl_2NW$: C, 49.52; H, 2.42; Cl, 3.95; As, 8.35. Found: C, 49.87; H, 2.45; Cl, 3.75; As, 8.54.

$W(OC_6F_5)_4(3\text{-hxy})(Et_2O)$. (a) $WCl_4(3\text{-hxy})(Et_2O)$[11] (2.074 mmol, 1.0 g) was added rapidly with stirring to a 50-mL ether solution (−46 °C) of potassium pentafluorophenoxide (8.3 mmol, 1.843 g). The reaction mixture immediately turned bright red. The solution was warmed to room temperature, stirred for 2 h, and then filtered through a layer of Celite. The filtrate volume was reduced to ~20 mL and cooled to −46 °C to yield $W(OC_6F_5)_4(3\text{-hxy})(Et_2O)$ as large red blocks (1.2 g, 54%) in two crops: ^1H NMR (C_6D_6, 20 °C) δ 1.00 (t, 6), 1.10 (t, 6), 3.35–3.47 (overlapping quartets, 8); ^1H NMR (toluene-d_8, −90 °C) δ 0.61 (br, 6), 1.12 (br, 6), 3.07 (br, 4), 4.12 (br, 4); ^{19}F NMR (C_6D_6, 20 °C) δ −158.79 (m, 8), −163.95 (m, 8), −164.62 (m, 4); ^{13}C NMR (C_6D_6, 20 °C) δ 13.54, 15.16, 29.00, 65.80, 134–142 (m, ring carbons, J_{CF} not calculated), 232.8 ($CH_3CH_2C{\equiv}CCH_2CH_3$); IR (Nujol) $\nu_{C≡C}$ not found. Anal. Calcd for $C_{34}H_{20}F_{20}O_5W$: C, 38.08; H, 1.88; Cl, 0.0. Found: C, 37.77; H, 2.00; Cl, <1%. Note: ^1H NMR downfield chemical shifts are concentration dependent.

(b) 3-Hexyne (1.64 mmol, 186 μL) was added slowly to $[Na(Et_2O)_x]_2[WCl_2(OC_6F_5)_4]$ (~0.85 mmol, 1 g) in 15 mL of ether at −46 °C with stirring. The reaction mixture was allowed to warm to room temperature, during which time it slowly became red. Stirring was continued for 12 h, and then the mixture was filtered and the solvent removed from the filtrate in vacuo. The residue thus obtained was recrystallized from a minimum of ether to give $W(OC_6F_5)_4(3\text{-hxy})(Et_2O)$ as red blocks (450 mg, ~47%). All spectroscopic data were identical with those for the complex prepared from $WCl_4(3\text{-hxy})(Et_2O)$ and 4 equiv of potassium pentafluorophenoxide.

X-ray Study of $[W(DCP)_4Cl(Et_2O)]\cdot CH_2Cl_2$. Data were collected at −65 °C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo Kα radiation. The crystal was mounted by using a technique similar to that reported elsewhere.[16] Details of the data collection, reduction, and refinement procedures were similar to those described elsewhere.[15] A total of 3202 reflections (+*h*,+*k*,+*l*) were collected in the range $3° < 2\theta < 50°$ with 2595 having $I_o > 2\sigma(I_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (210 variables) using SHELX-76. Final $R_1 = 0.082$ and $R_2 = 0.090$. Hydrogen atoms were ignored while all other atoms were refined anisotropically. Two methylene chloride molecules of crystallization are present in each unit cell at full occupancy. The final difference-Fourier map contained no chemically significant features. Crystal data are $a = 12.241$ (9) Å, $b = 8.643$ (2) Å, $c = 17.408$ (8) Å, $\beta = 102.25$ (5)°, $V = 1799.8$ Å^3, space group $P2/n$, $Z = 2$, mol wt = 860, ρ(calcd) = 1.587 g cm^{-3}, $\mu = 37.2$ cm^{-1}. A

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semiempirical absorption correction was applied.

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Supplementary Material Available: A fully labeled drawing of $W(DCP)_4Cl(Et_2O)$ and a table of final positional and thermal parameters (2 pages); a table of final observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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A New Mixed Molybdenum–Tungsten Dinuclear Complex, Bis(μ-oxo)(μ-ethylenediaminetetraacetato-*N*,*N'*)oxomolybdenum(V)oxotungstate(V)

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Neutralization by aqueous 2 M Na_2CO_3 of an aqueous solution of $(pyH)_2[MoOCl_5]$ (py = pyridine), $(NH_4)_2[WOCl_5]$, and disodium dihydrogen ethylenediaminetetraacetate (Na_2H_2edta) under a nitrogen atmosphere gave a mixture of $[Mo_2O_4(edta)]^{2-}$, $[W_2O_4(edta)]^{2-}$, and the new mixed-metal title complex. The new complex was purified by the use of an anion-exchange column (QAE-Sephadex A-25). The mixed-metal structure was confirmed by the XPS spectra, ^1H and ^{13}C NMR spectra, and the X-ray crystal structure determination. The sodium salt of the complex anion, $WMoNa_2O_{16.5}N_2C_{10}H_{21}$, crystallizes in the monoclinic space group $P2_1$ with $a = 9.133$ (1) Å, $b = 32.119$ (3) Å, $c = 7.128$ (1) Å, $\beta = 101.97$ (1)°, $V = 2045.4$ (4) Å^3, and $Z = 4$. The structure was solved by using 2691 unique reflections with $|F_o| > 3\sigma(F_o)$ to give $R = 0.031$. Two metal ions were statistically disordered. Each metal ion has a heavily distorted octahedral structure. The metal–metal distance is 2.55 (1) Å, indicating the existence of a direct metal–metal bond. $[MoWO_4(edta)]^{2-}$ exhibits an absorption peak at 288 nm (ϵ = 8200 M^{-1} cm^{-1}) and a distinctive shoulder at 352 nm (ϵ = 980 M^{-1} cm^{-1}). Both transitions are located between the corresponding peaks of the dimolybdenum(V) (298, 388 nm) and the ditungsten(V) (276, 342 nm) complexes. Cyclic voltammetry in an aqueous solution at pH 7.5 (phosphate buffer) shows one irreversible oxidation wave at +0.56 V vs SCE with a glassy-carbon electrode. ^{95}Mo and ^{183}W NMR signals appear at higher and lower field, respectively, than the corresponding signals of the two homonuclear dimers. The Mo 3d electron binding energies are smaller than those of the dimolybdenum(V) complex, while the W 4d and 4f electron binding energies are larger than those of the ditungsten(V) complex. Metal NMR and XPS data indicate that molybdenum and tungsten ions in the mixed-metal complex are in somewhat lower and higher oxidation states than those of the dimolybdenum and ditungsten complexes, respectively.

Introduction

Mixed-metal clusters without strong σ-donating and/or π-accepting ligands such as CO are important for investigating the nature of interactions between different metal atoms and regioselective redox and ligand substitution reactions. We have recently reported two types of new mixed-metal trinuclear complexes, $[Mo_nW_{3-n}(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ (n = 1, 2)[1] and $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ (L = H_2O, pyridine).[2] The important feature of these complexes is that their structural characteristics, such as bond lengths and angles, are very similar to those of their homonuclear analogues. It is thus possible in these cases to compare the electronic structures and the reactivities of the mixed-metal complexes with those of the homonuclear analogues without considering different steric factors. The X-ray photoelectron (XPS)[3] and metal (^{95}Mo and ^{183}W) NMR spectra[4] of the mixed Mo–W clusters revealed that a shifting of negative charge takes place from tungsten to molybdenum. This may result from the difference in electronegativities of the two metal atoms. It is interesting that the extent of the charge shift is large enough to be observed by the two techniques and yet the structural features are not significantly affected. A similar charge shift was not observed by XPS for the mixed Ru–Rh complex.[2] It was suggested that this may be because the metal–metal direct bond is essentially absent in this system (the Ru–Rh distance is expected to be ca. 3.3 Å,[2] while the Mo–W distances in the Mo–W clusters are ca. 2.73 Å[5]).[6] The rate of the substitution of methanol for the terminal water ligand is very similar between Ru and Rh sites in the Ru–Rh trinuclear complex.[2] In marked contrast, the Mo–W clusters show significant regioselectivity in their ligand substitution reactions (terminal water ligand substitution).[5] Obviously it is important to extend the research to other heterometallic systems to find more general examples.

Molybdenum and tungsten are unique in the sense that they give stable clusters in a wide range of oxidation states and that the structural characteristics of the corresponding clusters are very similar between the two elements.[7-10] In lower oxidation states (bivalent and tervalent), there have been a variety of mixed molybdenum–tungsten dinuclear complexes reported with metal–metal multiple bonds.[11-21] Trinuclear mixed Mo–W complexes,

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