experimental error in the measured bond length; the second is the variability of the true bond lengths themselves due to physical perturbations of the crystalline lattice, such as hydrogen bonding.

Suppose that a certain set of m bonds of one bond type have been selected for measurement. Let us fix our attention on the jth bond ($j = 1, ..., m$) and assume it to have a perturbed length y_j. Measurement of y_j will contain experimental error. We assume the errors are such that the measurement on the perturbed length is a conditional Gaussian (normal) variate with a known standard error σ_j, i.e.

$$X|y_j \approx N(y_j,\sigma_j^2) \tag{5}$$

that has density

$$f_{X|y_j}(x) = \frac{1}{(2\pi)^{1/2}\sigma_j}\exp\left\{-\frac{1}{2}\left(\frac{x-y_j}{\sigma_j}\right)^2\right\} \equiv \frac{1}{\sigma_j}\varphi\left(\frac{x-y_j}{\sigma_j}\right) \tag{6}$$

Here we adopt the standard statistical notation of upper-case letters for random variables and the corresponding lower-case letters for their observed values. The notation in (5) means simply that we have a normal population with mean y_j and variance σ_j^2; i.e., repeated measurement of a particular bond length, y_j, will yield a Gaussian distribution of values centered at y_j characterized by a standard error σ_j. φ denotes the standard normal density.

However, the m perturbed bond lengths y_j for $j = 1, ..., m$ also form a population that, from the noncontradictory evidence of sample histograms for N, N′ and for T bond types and the entailed mathematical simplicity, we also assume to be Gaussian with a mean value μ and a variance σ^2, i.e.

$$Y_j \approx N(\mu,\sigma^2) \qquad j = 1, ..., n \tag{7}$$

Both parameters μ and σ^2 are unknown, and their correct estimation from the data is the goal of this analysis. We recognize that the experimental data for a given bond type are a convolution of this distribution with the experimental errors associated with each measurement. From (5) and (7) and the calculus of probabilities we obtain the unconditional distribution of the observation for the jth perturbed bond length to be

$$X_j \approx N(\mu,\sigma_j^2 + \sigma^2) \qquad j = 1, ..., m \tag{8}$$

To obtain the *maximum likelihood estimates* of μ and σ^2, we maximize the likelihood function of the sample data from (8). We maximize

$$L(\mu,\sigma^2) = \prod_{j=1}^{m}\frac{1}{(\sigma_j^2 + \sigma^2)^{1/2}}\varphi\left[\frac{x_j - \mu}{(\sigma_j^2 + \sigma^2)^{1/2}}\right] \tag{9}$$

by setting

$$\frac{\partial L}{\partial \mu} = 0 \qquad \frac{\partial L}{\partial \sigma^2} = 0$$

and solving the coupled equations in μ and σ^2, namely

$$\mu = \sum_{j=1}^{m}\frac{x_j}{\sigma_j^2 + \sigma^2}\Bigg/\sum_{j=1}^{m}\frac{1}{\sigma_j^2 + \sigma^2} \tag{10}$$

and

$$\sum_{j=1}^{m}\frac{1}{\sigma_j^2 + \sigma^2} = \sum_{j=1}^{m}\frac{(x_j - \mu)^2}{(\sigma_j^2 + \sigma^2)^2} \tag{11}$$

Equations 10 and 11 were solved via a computer program to give the estimated 1σ deviation from the mean μ for the various bond types, exhibited in Table IV and Figure 3.

Registry No. $(C_4H_4N_2H)_2Cr_3O_{10}$, 111348-98-2.

Supplementary Material Available: Tables SI and SII, listing thermal parameters and derived hydrogen atom positions, and Figure SI, a diagram of the unit cell packing (3 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Two Monomeric Tungsten(IV) Phenoxide Complexes

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$W(DIPP)_4$ (DIPP = O-2,6-C_6H_3-i-Pr_2) has been prepared by adding LiDIPP to $WCl_4(Et_2S)_2$. $W(DMP)_4$ (DMP = O-2,6-$C_6H_3Me_2$) can be prepared by an analogous procedure or by reducing *trans*-$W(DMP)_4Cl_2$ with sodium in ether. $W(DIPP)_4$ belongs to the space group $C2/c$ with a = 30.557 (5) Å, b = 13.434 (2) Å, c = 23.312 (3) Å, β = 91.99 (1)°, V = 9153.6 Å^3, and Z = 8. Final R_1 = 0.042 and R_2 = 0.046. $W(DIPP)_4$ contains a ruffled distorted square planar WO_4 core with trans O–W–O angles of 168°, cis O–W–O angles of 90–91°, and W–O–C angles of 154–159°. $W(DMP)_4$ belongs to the space group $P4/n$ with a = b = 14.475 (2) Å, c = 7.097 (3) Å, V = 1487.0 Å^3, and Z = 2. Final R_1 = 0.055 and R_2 = 0.057. $W(DMP)_4$ contains an essentially planar WO_4 core in which trans O–W–O angles are 173.7 (3)°, cis O–W–O angles are 89.8 (2)°, and W–O–C angles are 160.7 (4)°. $W(DIPP)_4$ is too crowded to react with a simple substrate such as an internal acetylene while $W(DMP)_4$ reacts with 3-hexyne to yield W(3-hexyne)$(DMP)_4$, with trimethylsilyl azide to yield $W(NSiMe_3)(DMP)_4$, with $(SiMe_3)CHN_2$ to yield $W[N_2CH(SiMe_3)](DMP)_4$, and with O_2, cyclohexene oxide, or iodosylbenzene to yield $W(O)(DMP)_4$. An attempt to replace the DMP ligands by S-2,4,6-$R_3C_6H_2$ (R = Me or i-Pr) ligands yielded $W(S)(DMP)_4$.

Introduction

The group 6 metals are some of the most interesting of the transition metals, in part because of the range of oxidation states that are available. During the last decade their chemistry has been developed extensively. However, molecules of the type MX_4, where X is an alkyl,[1-3] amide,[4] alkoxide,[5] or thiolate[6] group remain relatively scarce, particularly for Mo and W.[7] We have become especially interested in such species because we believe that di-

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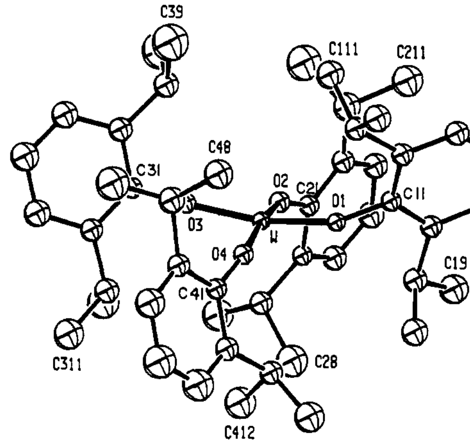

Figure 1. ORTEP diagram of $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ showing the core atom labeling scheme and 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table I. Details of the X-ray Diffraction Study for $W[O\text{-}2,6\text{-}C_6H_3(CHCMe_2)_2]_4$ and $W[O\text{-}2,6\text{-}C_6H_3Me_2]_4$

mol formula	$W[O\text{-}2,6\text{-}C_6H_3(CHCMe_2)_2]_4$	$W[O\text{-}2,6\text{-}C_6H_3Me_2]_4$
mol wt	892.92	668.5
space group	*C*2/*c*	*P*4/*n*
unit cell vol, Å^3	9153.6	1487.0
a, Å	30.557 (5)	14.475 (2)
b, Å	13.434 (2)	14.475 (2)
c, Å	23.312 (3)	7.097 (3)
β, deg	91.99 (1)	
Z	8	2
calcd density, g cm^{-3}	1.296	1.493
cryst dimens, mm	0.1 × 0.2 × 0.25	0.2 × 0.12 × 0.22
data collection temp, °C	−50	−65
Mo Kα radiation, λ, Å	0.71069	0.71069
monochromator	graphite	graphite
abs coeff, cm^{-1}	24.2	37.2
2θ range, deg	3–50	3–55
total no. of reflns measd	8054 ($\pm h,+k,+l$)	1705
no. of reflns with $I > x\sigma(I)$	5006 ($x = 3$)	1435 ($x = 2$)
scan type	ω–2θ	ω–2θ
scan speed, deg min^{-1}	4	4
data/param ratio	20.8	16.9
R	0.042	0.055
R_w	0.046	0.057

Table II. Selected Interatomic Distances (Å) and Angles (deg) in the Core of $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$[a]

W–O(1)	1.851 (6)	O(1)–C(11)	1.386 (10)
W–O(2)	1.866 (5)	O(2)–C(21)	1.366 (9)
W–O(3)	1.851 (5)	O(3)–C(31)	1.378 (9)
W–O(4)	1.849 (5)	O(4)–C(41)	1.354 (9)
O(1)–W–O(2)	91.5 (3)	O(3)–W–O(4)	91.2 (2)
O(1)–W–O(3)	167.7 (2)	W–O(1)–C(11)	154.0 (5)
O(1)–W–O(4)	89.9 (3)	W–O(2)–C(21)	154.5 (5)
O(2)–W–O(3)	90.1 (3)	W–O(3)–C(31)	155.3 (5)
O(2)–W–O(4)	167.6 (2)	W–O(4)–C(41)	159.1 (5)

[a] Atoms are labeled as shown in Figure 1. Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter.

nitrogen is capable of binding to the appropriate d^2 metal center to form a complex of the type $M_2(\mu\text{-}N_2)$, where M is then d^0 and $\mu\text{-}N_2$ a hydrazido(4−) ligand.[8] Such complexes are relevant to the reduction of dinitrogen by nitrogenase to the extent that at least one end of dinitrogen is believed to bind to a molybdenum(IV) center and subsequently be reduced rapidly to ammonia.[9]

The types of MoX_4 complexes that are known are $Mo(NR_2)_4$[10] (R = Me or Et), $Mo(SCMe_3)_4$,[6a,b] $Mo(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_4$,[6c] and $Mo(mes)_4$[11] (mes = mesityl). The alkoxide complexes $Mo(OR)_4$ (R = Me, Et, $CHMe_2$, CH_2CMe_3, CMe_3) have been claimed,[12a] and some reactions of them support that claim,[12b] but none has been shown to be a monomer unambiguously. $Mo_2(OCHMe_2)_8$,[12a,13] $Mo(OR)_4(Me_2NH)_2$[12a] (R = $SiMe_3$ and $SiEt_3$), and $Mo(1\text{-}ada)_4(Me_2NH)$[14] (1-ada = 1-adamantoxy) are well-characterized. $Mo(\eta^3\text{-}all)_4$ (all = allyl) is reasonably well-characterized,[15] although little is known about $Mo(CH_2Ph)_4$.[16] The benzyl ligand can bind in an η^3 fashion, so both $Mo(\eta^3\text{-}all)_4$ and $Mo(CH_2Ph)_4$ must be regarded as special types of MoX_4 complexes. $Mo(mes)_4$[11] has not been structurally characterized, but there is no good reason to suspect that this paramagnetic species is not a tetrahedral monomer.

WX_4 complexes are the rarest, $W(\eta^3\text{-}all)_4$[15a,b] and $W(CH_2Ph)_4$[17] being the only reported examples. Neither is well-characterized, and in each X is not likely to be a simple monodentate ligand.

We chose to attempt to prepare WX_4 complexes first. We anticipated that species with such a low coordination number and low electron count would be highly reactive and perhaps would function as more powerful reducing agents than analogous MoX_4 species. In this paper we report the first examples of authentic monomeric WX_4 species, phenoxide complexes of the type $W(O\text{-}2,6\text{-}C_6H_3R_2)_4$, where R = Me and *i*-Pr, along with some simple reaction chemistry. Some of this work has been reported in preliminary form.[6d]

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(7) (a) The chemistry of Cr(IV) is the best developed by far with numerous examples of $Cr(OR)_4$ (OR = $OCMe_xEt_{3-x}$,[7b,c] $OCHMe(CMe_3)$,[7d] $OCMe_3$,[7e] and $OCH(CMe_3)_2$[7f]) and CrR_4 (R = CH_2CMe_3, CH_2CPh_3, CH_2CMe_2Ph,[7g,h] CH_2SiMe_3,[7i] norbornyl,[7j] *tert*-butyl,[7k,l] and mesityl[7m]) complexes and a few examples of $Cr(NR_2)_4$[7n] complexes being reported in the literature. (b) Basi, J. S.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1963**, 305. (c) Alyea, E. C.; Basi, J. S.; Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A* **1971**, 772. (d) Dyrkacz, G.; Rocek, J. *J. Am. Chem. Soc.* **1973**, *95*, 4756. (e) Hagihara, N.; Yamazaki, H. *J. Am. Chem. Soc.* **1959**, *81*, 3160. (f) Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1863. (g) Mowat, W.; Wilkinson, G. *J. Organomet. Chem.* **1972**, *38*, C35. (h) Mowat, W.; Shortland, A. J.; Hill, N. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 770. (i) Mowat, W.; Shortland, A.; Yagupsky, G.; Hill, N. J.; Yagupsky, M.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 533. (j) Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512. (k) Kruse, W. *J. Organomet. Chem.* **1972**, *42*, C39. (l) Ward, G. A.; Kruse, W.; Bower, B. K.; Chien, J. C. W. *J. Organomet. Chem.* **1972**, *42*, C43. (m) Seidel, W.; Bürger, I. *Z. Anorg. Allg. Chem.* **1976**, *426*, 155. (n) Basi, J. S.; Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A* **1971**, 1433.

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Table III. Final Non-Hydrogen Atom Positional Parameters for $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$

atom	*x*	*y*	*z*
W	0.125350 (10)	0.18269 (2)	0.374310 (10)
O(1)	0.09732 (18)	0.2699 (5)	0.3214 (3)
O(2)	0.13892 (18)	0.2858 (4)	0.4278 (3)
O(3)	0.16341 (17)	0.0992 (4)	0.4167 (2)
O(4)	0.10174 (17)	0.0763 (4)	0.3317 (2)
C(11)	0.0941 (3)	0.3564 (6)	0.2877 (4)
C(12)	0.1178 (3)	0.3641 (7)	0.2363 (4)
C(13)	0.1142 (3)	0.4544 (8)	0.2047 (4)
C(14)	0.0882 (3)	0.5284 (8)	0.2233 (4)
C(15)	0.0634 (3)	0.5181 (8)	0.2740 (4)
C(16)	0.0654 (3)	0.4295 (6)	0.3078 (4)
C(17)	0.0375 (3)	0.4101 (7)	0.3608 (4)
C(18)	−0.0024 (3)	0.3468 (7)	0.3441 (5)
C(19)	0.0235 (4)	0.5063 (9)	0.3933 (5)
C(110)	0.1461 (3)	0.2807 (7)	0.2156 (4)
C(111)	0.1941 (3)	0.2975 (8)	0.2337 (5)
C(112)	0.1413 (4)	0.2595 (8)	0.1475 (5)
C(21)	0.1301 (3)	0.3702 (6)	0.4593 (3)
C(22)	0.1514 (3)	0.4578 (7)	0.4419 (4)
C(23)	0.1412 (3)	0.5443 (8)	0.4740 (4)
C(24)	0.1143 (3)	0.5440 (8)	0.5214 (4)
C(25)	0.0949 (3)	0.4544 (7)	0.5384 (4)
C(26)	0.1032 (3)	0.3658 (7)	0.5078 (4)
C(27)	0.0822 (3)	0.2675 (7)	0.5275 (4)
C(28)	0.0334 (4)	0.2699 (10)	0.5202 (6)
C(29)	0.0948 (4)	0.2411 (10)	0.5909 (6)
C(210)	0.1827 (3)	0.4595 (9)	0.3908 (5)
C(211)	0.1804 (4)	0.5545 (9)	0.3534 (5)
C(21)	0.2274 (4)	0.4383 (11)	0.4129 (6)
C(31)	0.1917 (3)	0.0200 (6)	0.4239 (4)
C(32)	0.1754 (3)	−0.0660 (7)	0.4511 (4)
C(33)	0.2046 (4)	−0.1443 (8)	0.4588 (5)
C(34)	0.2465 (4)	−0.1372 (9)	0.4400 (5)
C(35)	0.2621 (4)	−0.0521 (9)	0.4137 (5)
C(36)	0.2340 (3)	0.0291 (7)	0.4051 (4)
C(37)	0.2500 (3)	0.1250 (8)	0.3763 (4)
C(38)	0.2804 (5)	0.1804 (12)	0.4163 (8)
C(39)	0.2702 (5)	0.1058 (12)	0.3176 (6)
C(310)	0.1300 (3)	−0.0691 (7)	0.4736 (4)
C(311)	0.1096 (4)	−0.1720 (8)	0.4754 (5)
C(312)	0.1283 (4)	−0.0224 (9)	0.5348 (5)
C(41)	0.0836 (3)	−0.0143 (6)	0.3212 (4)
C(42)	0.0402 (3)	−0.0293 (7)	0.3350 (4)
C(43)	0.0218 (4)	−0.1228 (10)	0.3264 (5)
C(44)	0.0481 (5)	−0.1987 (12)	0.3047 (6)
C(45)	0.0896 (4)	−0.1799 (10)	0.2896 (5)
C(46)	0.1095 (3)	−0.0890 (7)	0.2962 (4)
C(47)	0.1543 (3)	−0.0660 (8)	0.2767 (4)
C(48)	0.1542 (4)	−0.0231 (9)	0.2139 (5)
C(49)	0.1852 (4)	−0.1549 (9)	0.2798 (6)
C(410)	0.0121 (3)	0.0553 (8)	0.3595 (4)
C(411)	−0.0328 (4)	0.0619 (9)	0.3295 (5)
C(412)	0.0076 (4)	0.0426 (10)	0.4266 (5)

Results

Preparation and X-ray Structure of $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$. Although a number of logical starting materials of the type WCl_4L_2 (L = RCN,[18] py,[19,20] phosphines,[21] and sulfides[22]) are known, we know of only one report of a successful synthesis of a W(IV) complex starting with one of these molecules; $W(CH_2SiMe_3)_3(PMe_3)Cl$ was isolated in 15–20% yield from the reaction between $Mg(CH_2SiMe_3)Cl$ and $WCl_4(PMe_3)_2$ in diethyl ether.[23] The reason for this behavior is unclear. One possibility is that WCl_4L_2 is readily reduced to W(3+) dimeric species of the type $W_2Cl_6L_4$.[24] This circumstance might be avoided if L is small and/or labile. WCl_4L_2 species where L = Et_2S and tetrahydrothiophene[22] appeared to be the best prospects, the former especially since it is more convenient to prepare and since it is soluble in relatively nonpolar solvents such as toluene.

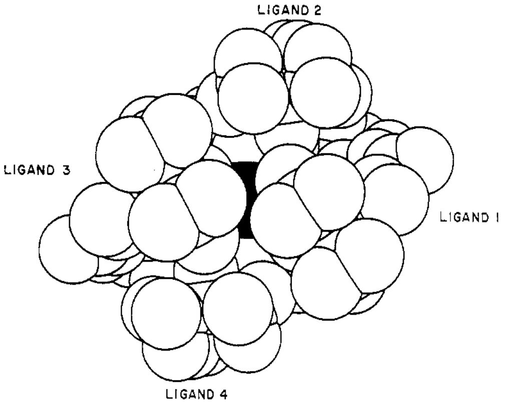

Figure 2. PLUTO space-filling drawing of $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ projected onto the WO_4 plane. Assumed van der Waals radii were as follows (Å): H, 1.20; C, 1.30; O, 1.40; W, 1.80. The W atom is shown shaded at the center of the molecule.

The best procedure for preparing $W(DIPP)_4$ (DIPP = O-2,6-C_6H_3-*i*-Pr_2) is shown in eq 1. Although $WCl_4(Et_2S)_2$ is not

$$WCl_4(Et_2S)_2 + 4LiDIPP\cdot Et_2O \xrightarrow{3:1\ \text{ether/toluene}} W(DIPP)_4 \quad (1)$$

appreciably soluble or stable in ether, the addition of a toluene solution of $WCl_4(Et_2S)_2$ to an ether solution of $LiDIPP\cdot Et_2O$ at −30 °C resulted in an initial rapid reaction followed by a slower step (or steps) that appeared to be complete only after heating the mixture for 16 h at 40 °C in a glass bomb. $W(DIPP)_4$ is obtained in 50% isolated yield from pentane as deep blue crystals. A suitable crystal was selected for an X-ray study. A summary of the data is given in Table I, selected bond distances and angles are given in Table II and final positions in Table III, and an ORTEP drawing is shown in Figure 1.

The geometry about the tungsten atom in $W(DIPP)_4$ is nearly square planar with trans O–W–O angles of 168° and cis angles of 90–91°. The dihedral angle between the planes defined by O(1)–W–O(4) and O(2)–W–O(3) is 17.5°. The W–O–C angles are relatively large (154–159°), a fact that could be taken as indicative of extensive π donation from the oxygen lone pairs to tungsten.[25] The W—O bond lengths are relatively short (1.85–1.87 Å), only slightly longer than the value of 1.79 Å for the W=O bond in WO_4^{2-}.[26] The O–C bond lengths in $W(DIPP)_4$ range from 1.35 to 1.39 Å. For comparison, the relevant parameters for *trans*-$W(OC_6H_5)_4Cl_2$, a molecule considered to exhibit structural effects due to π bonding, are included here: W–O–C angles vary from 155 to 160° (average 158 (5)°), W–O bond lengths vary from 1.72 to 1.90 Å (average 1.82 (7) Å), and O–C bond lengths vary from 1.26 to 1.45 Å (average 1.34 (8) Å).[27]

The four phenyl rings in $W(DIPP)_4$ are "stacked" so that all isopropyl group methine hydrogens project into the central cavities above and below the tungsten atom. The ligand coordination sphere therefore is quite crowded, as illustrated in the PLUTO space-filling diagram shown in Figure 2. Figure 2 further illustrates how difficult it may be for ligands to coordinate to the

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Table IV. Selected Interatomic Distances (Å) and Angles (deg) in the Core of $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$

W–O	1.843 (4)	W–O–C	160.7 (4)
O–C	1.361 (8)	$O–W–O_{cis}$	89.8 (2)
		$O–W–O_{trans}$	173.7 (3)

Table V. Final Positional Parameters for the Non-Hydrogen Atoms of $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$[a]

atom	x	y	z
W	0.2500	0.2500	-0.06235 (10)
O	0.2459 (3)	0.1230 (3)	-0.0766 (6)
C(1)	0.2169 (4)	0.0362 (4)	-0.1210 (9)
C(2)	0.2501 (5)	-0.0035 (5)	-0.2862 (10)
C(3)	0.2214 (6)	-0.0924 (5)	-0.3289 (12)
C(4)	0.1645 (7)	-0.1413 (6)	-0.2102 (13)
C(5)	0.1311 (6)	-0.0994 (6)	-0.0468 (13)
C(6)	0.1576 (5)	-0.0105 (6)	0.0019 (10)
C(7)	0.3165 (6)	0.0497 (6)	-0.4104 (12)
C(8)	0.1238 (6)	0.0357 (7)	0.1813 (14)

[a] Numbers in parentheses are errors in the last significant digit(s).

metal in $W(DIPP)_4$; the isopropyl groups virtually close off access from either the top or the bottom.

$W(DIPP)_4$ appears to be diamagnetic on the basis of sharp signals in its ^1H NMR spectrum. Only one type of methyl group and one type of isopropyl methine resonances are observed; i.e., the DIPP ligands are equivalent on the NMR time scale.

Preparation and X-ray Structure of $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$. In order to determine whether the nearly square planar coordination geometry observed in $W(DIPP)_4$ could be ascribed primarily to steric or electronic factors, we turned to the analogous reaction between $WCl_4(Et_2S)_2$ and LiDMP (DMP = $O\text{-}2,6\text{-}C_6H_3Me_2$) shown in eq 2. Addition of $WCl_4(Et_2S)_2$ to THF is known to

$$WCl_4(Et_2S)_2 + 4LiDMP \xrightarrow[1\ h]{4:1\ toluene/THF} W(DMP)_4 \quad (2)$$

yield $WCl_4(THF)_2$ immediately,[28] so the reaction may proceed via $WCl_4(THF)_2$. The rate of reaction 2 is much greater than that involving LiDIPP. Pentane-soluble $W(DMP)_4$ can be isolated as red cubes. We believe $W(DMP)_4$ to be diamagnetic since a single set of unshifted, sharp DMP signals are observed in its ^1H NMR spectrum.

An alternative preparation of $W(DMP)_4$ is shown in eq 3. It

$$W(DMP)_4Cl_2 + 2Na/Hg \xrightarrow{ether} W(DMP)_4 \quad (3)$$

has been known for 50 years that $W(OC_6H_5)_4Cl_2$ and $W(OC_6H_5)_6$ can be prepared in high yield by simply adding phenol to WCl_6 in carbon tetrachloride.[29] Because the DMP ligand is so much larger than phenoxide itself, *mer*-$W(DMP)_3Cl_3$ is the product of the reaction between 2,6-dimethylphenol and WCl_6 in carbon tetrachloride. More extreme conditions must be employed in order to force four DMP ligands onto the metal (eq 4), and the reaction

$$WCl_6 + 10DMPH \xrightarrow{melt} W(DMP)_4Cl_2 + 4HCl \quad (4)$$

does not proceed beyond $W(DMP)_4Cl_2$ under these conditions. Excess DMPH can be removed by extraction with pentane to give relatively insoluble dark brown $W(DMP)_4Cl_2$ in ~65% yield. We presume $W(DMP)_4Cl_2$ to be trans on the basis of its NMR spectra. Related *trans*-$W(OAr)_4Cl_2$ complexes (Ar = aryl) have been reported by Basset.[30] The reduction shown in eq 3 proceeds smoothly to give $W(DMP)_4$ in ~80% crude yield that is sufficiently pure for further reactions. It is not possible to prepare $W(DIPP)_4$ in an analogous manner, as we have not been able to prepare $W(DIPP)_4Cl_2$ by reactions analogous to that shown in eq 4, presumably for steric reasons.

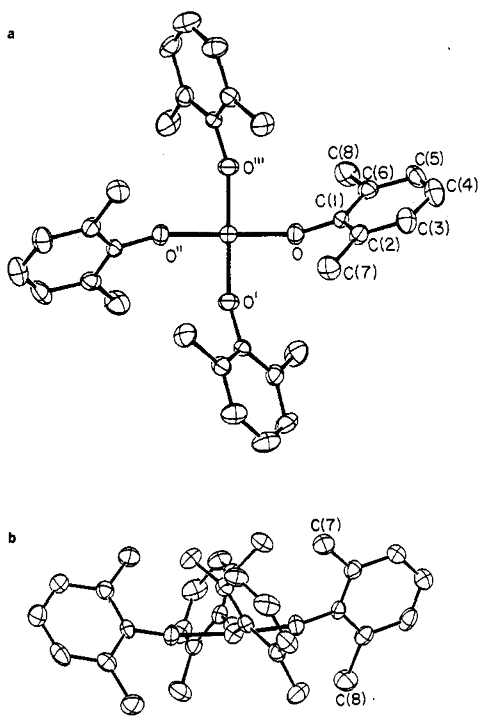

Figure 3. (a) ORTEP diagram of $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ showing the atom labeling scheme and 30% probability thermal ellipsoids. Primed atoms are related to those unprimed by a crystallographically imposed fourfold axis perpendicular to the page running through the W atom. (b) Another view from the side approximately along one of the O–W–O bond axes.

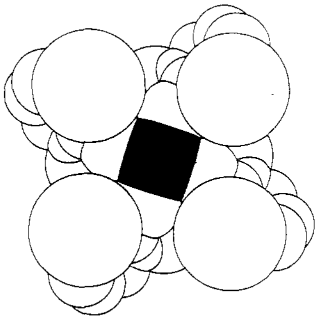

Figure 4. PLUTO space-filling drawing of $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ projected onto the WO_4 plane. Assumed van der Waals radii were as follows (Å): C, 1.30; O, 1.40; W, 1.80; and CH_3, 2.00. The W atom is shown shaded at the center of the molecule.

Details of the X-ray study are provided in Table I and in the Experimental Section. Relevant bond lengths and angles can be found in Table IV and final positional parameters in Table V. Two views of $W(DMP)_4$ are shown in Figure 3. (The molecule has crystallographically imposed fourfold symmetry about the tungsten atom.)

We were surprised to find that the WO_4 core of $W(DMP)_4$ forms an almost perfect square plane. If we define a plane as that containing the four oxygen atoms, then the metal sits only 0.1 Å below that plane, as shown in the side-on view in Figure 3b. Although the W–O and O–C distances (1.843 (4) and 1.361 (8) Å, respectively) in $W(DMP)_4$ do not differ statistically from those in $W(DIPP)_4$, the W–O–C angle (160.7 (4)°) in $W(DMP)_4$ appears to be larger than three of the W–O angles in $W(DIPP)_4$. $O–W–O_{cis}$ angles are essentially 90°, while the $O–W–O_{trans}$ angle (173.7 (3)°) is again larger than analogous angles in $W(DIPP)_4$, as should be the case for the more planar $W(DMP)_4$ species.

The phenyl rings of the DMP ligands are tipped up toward the viewer of Figure 3a so that C_{ipso} is 0.33 Å above the WO_4 plane while C_{para} is 0.98 Å above the WO_4 plane. At the same time the C_6 ring is twisted so that the plane that contains the C_6 ring

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is not close to being perpendicular to the WO_4 plane. The angle between the normals to the WO_4 plane and the C_6 ring plane is 60.0°. All of the above features are shown clearly in the view in Figure 3b. The metal in $W(DMP)_4$ is relatively accessible to external reagents compared to the metal in $W(DIPP)_4$, as suggested by the PLUTO drawing of the molecule from the more hindered side (the same point of view as in Figure 3a) shown in Figure 4.

Reactions of $W(DMP)_4$ and $W(DIPP)_4$. $W(DMP)_4$ reacts immediately with 3-hexyne (eq 5). This diamagnetic molecule

$$W(DMP)_4 + \text{3-hexyne} \rightarrow W(\text{3-hex})(DMP)_4 \qquad (5)$$

appears to be analogous to related $Mo(RC{\equiv}CR)(OAr)_4$ species, one of which, $Mo(PhC{\equiv}CPh)(DIPP)_4$, was shown to be a trigonal bipyramid with the acetylene bound in an equatorial position.[31] The acetylene carbon atom signals are found at 207 ppm in the ^{13}C NMR spectrum of $W(\text{3-hex})(DMP)_4$ (cf. 198 ppm in $Mo(\text{3-hex})(DMP)_4$;[31] 3-hex = 3-hexyne). The ^1H NMR spectrum of $W(\text{3-hex})(DMP)_4$ shows only equivalent phenoxide ligand resonances at 25 °C; they broaden slightly upon cooling the sample to −80 °C. The DMP ligands in $Mo(\text{3-hex})(DMP)_4$ also show no sign of becoming inequivalent at low temperatures. Although it is likely that the $M(\text{3-hex})(DMP)_4$ species (M = Mo and W) are isostructural, we can only assume at this point that they are trigonal bipyramidal species analogous to $Mo(PhC{\equiv}CPh)(DIPP)_4$.[31]

$W(DMP)_4$ reacts with oxygen, cyclohexene oxide, or iodosylbenzene to give $W(O)(DMP)_4$. Authentic $W(O)(DMP)_4$ was prepared straightforwardly from $W(O)Cl_4$ for the purpose of comparison.

The reaction between $W(DMP)_4$ and Me_3SiN_3 proceeds as shown in eq 6. This result contrasts with the reaction between

$$W(DMP)_4 + Me_3SiN_3 \rightarrow W(NSiMe_3)(DMP)_4 \qquad (6)$$

Me_3SiN_3 and WCl_6 to give $WNCl_3$,[32] probably because formation of Me_3SiDMP is not as favorable (thermodynamically and/or kinetically) as formation of Me_3SiCl. Therefore, the result shown in eq 6 is closely related to the reaction between $MoCl_4(THF)_2$ and *p*-tolyl azide to give $Mo(Ntol)Cl_4(THF)$[33] (tol = tolyl).

The addition of (trimethylsilyl)diazomethane to $W(DMP)_4$ yields what we believe to be an imido-like complex containing the $[N_2CH(TMS)]^{2-}$ ligand (eq 7) on the basis of elemental analyses

$$W(DMP)_4 + N_2CHSiMe_3 \rightarrow (DMP)_4W{=}N{-}N{=}CHSiMe_3 \qquad (7)$$

and observation of a $W[N_2CH(TMS)]$ resonance in the ^{13}C NMR spectrum at 184 ppm with J_{CH} = 145 Hz. There is precedent for this type of reaction. The product of the reaction between $[Mo(OCMe_3)_4]_x$ (*x* unknown) and Ph_2CN_2 has been shown to be a trigonal bipyramidal complex with the imido ligand in an axial position and an N-N-C bond angle of ~140°.[12]

The attempt to prepare thiolate complexes analogous to $W(DMP)_4$ by treating $W(DMP)_4$ with mesitylene thiol or 2,4,6-triisopropylbenzenethiol (cf. the reaction between $[Fe(DMP)_4]^-$ and benzenethiol to give $[Fe(SPh)_4]^{-}$[34]) gave the surprising result shown in eq 8 (Ar = 2,4,6-$C_6H_2R_3$; R = Me and *i*-Pr). $W(S)(DMP)_4$ was prepared independently by the reaction between $W(DMP)_4$ and elemental sulfur (eq 9). Mesitylene was identified by ^1H NMR and gas chromatography and shown to be formed essentially quantitatively. This result does not bode well for the preparation of W(IV) thiolate complexes, at least via a ligand-exchange reaction.

$$W(DMP)_4 + ArSH \rightarrow W(S)(DMP)_4 + ArH \qquad (8)$$

$$W(DMP)_4 + S_8 \rightarrow W(S)(DMP)_4 \qquad (9)$$

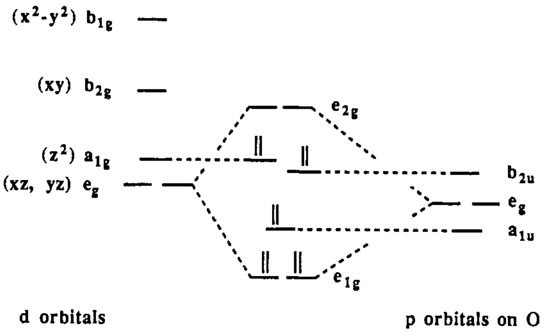

Figure 5. Simple MO description of π bonding between a metal in a square planar complex and four π-bonding ligands, each containing one electron pair in a p orbital *perpendicular* to the MO_4 plane.

In contrast to $W(DMP)_4$, $W(DIPP)_4$ is relatively unreactive. $W(DIPP)_4$ does not react with 3-hexyne. The fact that $W(DIPP)_4$ only decomposes in the presence of dry oxygen gas to give unidentified products instead of $W(O)(DIPP)_4$ suggests that the most likely intermediate in a reaction between MX_4 and O_2 to give $M(O)X_4$, i.e., $(MX_4)_2(\mu\text{-}O_2)$, can form when X = DMP but not when X = DIPP. These few negative results, along with the results of the X-ray studies, were enough to convince us that $W(DIPP)_4$ is simply too crowded a molecule to react as easily with small molecules as $W(DMP)_4$ does. Therefore, although we have not compared the reactivity of $W(DIPP)_4$ with $W(DMP)_4$ side by side for many substrates, we feel that further study of $W(DIPP)_4$ cannot be justified if we are interested primarily in μ-N_2 complexes; $[W(DIPP)_4]_2(\mu\text{-}N_2)$ could not possibly form.

Discussion

The feature of $W(DIPP)_4$ and $W(DMP)_4$ that requires some discussion is the fact that they are both almost square planar. To put this result in perspective, we should point out that we know of only one other example of a nearly square planar tungsten complex where the four ligands themselves are not constrained to lie in the same plane in the absence of a metal (e.g., as in a porphyrin ligand). Ibers[35] found that the WS_4 core in $[W_3S_8]^{3-}$ was nearly square planar with displacements of the S ligands alternately above and below an ideal plane by 0.17–0.21 Å. To make matters more interesting, we should point out that $W(SCMe_3)_4$ is a slightly flattened tetrahedron[6d] ($Mo(SCMe_3)_4$ is isostructural[6a,b]) and $Mo(NMe_2)_4$ has a strictly tetrahedral core with the planar π-bonding NMe_2 ligands nested so as to give the molecule D_{2d} symmetry.[10] $W(SCMe_3)_4$, $Mo(SCMe_3)_4$, and $Mo(NMe_2)_4$ are all diamagnetic, or apparently so, judging from the fact that ^1H NMR signals are sharp and unshifted.

A reasonable proposal is that $W(DIPP)_4$ and $W(DMP)_4$ are square planar because of the large amount of energy gained in establishing a delocalized π system over the WO_4 core above and below the WO_4 plane. Although the large W-O-C angles and short W-O bonds are not a priori indicative of strong π bonding between W and O—one could simply say that O is sp-hybridized for reasons that have nothing to do with π bonding between W and O—it makes more sense to assume that they *are* indicative of significant W-O π bonding, since group 6 metals are known to form strong double and triple W-O, W-N, and W-C bonds in general (e.g., oxo, nitrido, alkylidyne, etc.). In the MO diagram in Figure 5 we have assumed that the oxygen in the phenoxide ligand is sp-hybridized (i.e., that the core W-O-C symmetry is D_{4h}) and that only the p orbitals that are perpendicular to the WO_4 plane are involved in π bonding between W and O (i.e., for now we ignore completely p orbitals on O that lie in the WO_4 plane). Overlap between the e_g set of p orbitals perpendicular to the WO_4 plane and the e_g set of d orbitals yields a strongly bonding e_{1g} set into which four of the total of eight p π electrons can be placed. Four more can then be placed in the nonbonding a_{1u} and b_{2u}

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combinations of p orbitals, leaving the metal-based nonbonding a_{1g} orbital to accept the two d electrons. Therefore, W(DIPP)$_4$ and W(DMP)$_4$ should be diamagnetic. The fact that W(DIPP)$_4$ is distorted from planarity could be interpreted in steric terms; that is, a W(phenox)$_4$ complex (phenox = phenoxide) will be square planar *until* interligand interactions force it to distort toward tetrahedral. But if the phenoxide ligand in W(phenox)$_4$ is not large *enough*, then it can bridge to give a dimer, W$_2$(phenox)$_8$, the structure of which should be analogous to that of Mo$_2$(OCHMe$_2$)$_8$.[12a]

Let us assume that MoX$_4$ and WX$_4$ complexes are isostructural (the only case where both are known is where X = SCMe$_3$), i.e., that as yet unknown Mo(DMP)$_4$ would be square planar. Why then is Mo(NMe$_2$)$_4$ tetrahedral? Dimethylamide ligands are probably even better π-electron donors than phenoxide ligands. We propose that tetrahedral Mo(NMe$_2$)$_4$ is in fact a compromise, since the electronically preferred square planar molecule with all N and C atoms lying in the same plane as the metal is sterically impossible. Therefore, two trans NMe$_2$ ligands rotate by 90° about their M–N bonds and the MoN$_4$ core distorts to give the observed D_{2d} structure.

The next question is why are Mo(SCMe$_3$)$_4$, W(SCMe$_3$)$_4$, and Mo(S-2,4,6-C$_6$H$_2$-*i*-Pr$_3$)$_4$ all slightly flattened tetrahedra? The most consistent answer is that the amount of π bonding between M and S is not great enough to cause a square planar species to be completely favorable electronically, yet enough M–S π bonding is present to cause the severely bent thiolate ligands (M–S–R $\approx$ 110°) to orient in a particular fashion relative to one another, to lower the symmetry of the molecule (lift the e_g degeneracy), and to slightly flatten the MS$_4$ core. The electronic and/or steric factors that result in the MoN$_4$ core in Mo(NMe$_2$)$_4$ being strictly tetrahedral while the MoS$_4$ core in Mo(SCMe$_3$)$_4$ is flattened must be relatively subtle. Although Enemark has suggested that thiolates are powerful π-bonding ligands,[36] our results suggest that while M–S π bonding may be significant enough to orient thiolate ligands and even raise the activation energy for rotation of the thiolate ligand about the M–S bond to the point where rotational isomers can be observed, π bonding is not as overwhelming as in the case of alkoxides or amide ligands, where the p orbitals employed in π bonding to the metal are better matched electronically and spatially with those on the metal. It is interesting to note that Mo(mes)$_4$ is paramagnetic,[11] as its proposed tetrahedral structure and lack of π bonding between Mo and C require it to be.

The facile reaction shown in eq 8 has little precedent. Although S–C bond cleavage in alkane thiolates is relatively common,[37-39] S–C bond cleavage in arenethiolates appears to be limited to certain clusters[40] or to cobalt-catalyzed borohydride reductions.[41] Although we cannot be justified in writing a complete mechanism for the reaction shown in eq 8, the reaction shown in eq 10 is a

$$\text{W(DMP)}_4 + \text{ArSH} \rightarrow \text{W(DMP)}_3\text{(HOAr)(SAr)} \quad (10)$$

plausible first step. We feel that spontaneous, unassisted cleavage of the S–aryl bond is unlikely. While it might seem reasonable to postulate that the aryl ring migrates to the metal, where it can be protonated by metal-bound or free ArOH, the fact that the reaction is as successful for much more crowded triisopropylbenzenethiol as for mesitylenethiol would argue against this interpretation. We suggest that the S–aryl bond is attacked directly by a proton in metal-bound ArOH or, perhaps even more plausibly, by a hydride in a tungsten(VI) derivative (eq 11). (It is known that WCl$_5$(SPh) decomposes slowly to W(S)Cl$_4$ and presumably chlorobenzene.[39]) The first step in the reaction therefore might be described more accurately as an oxidative addition of an ArSH bond to W(IV) followed by elimination of ArH from a H–W–SAr complex. Peculiarly, although we have prepared Mo(TIPT)$_4$ by reducing Mo(TIPT)$_4$Cl[6c] (TIPT = 2,4,6-C$_6$H$_2$-*i*-Pr$_3$), we have not yet been able to prepare W(TIPT)$_4$ by reducing W(TIPT)$_4$Cl (unpublished results). Therefore, it is still possible that W(IV) arenethiolate complexes may be inherently unstable. In that case we would have to propose that the aryl ring is activated (possibly even intramolecularly) by interaction with the metal and/or that more complex reactions involving C–H bond cleavages, even in the alkyl groups in the 2- and 6-positions, might be part of the mechanism.

What bearing do our findings have on bonding of dinitrogen to give (MX$_4$)$_2$(μ-N$_2$) complexes? It appears now that if X contains electron pairs on the atom attached to M, then we not only must guard against intermolecular binding of X to give (e.g.) dimers of the type M$_2$X$_8$ but we also must prevent intramolecular "π inhibition" of N$_2$ binding via donation of π electrons to M and/or decomposition of the X ligand. How such intramolecular "π inhibition" can be circumvented at this stage is not clear. Ultimately, one could hope to prepare a rigid MX$_4$ core that is close to the MX$_4$ conformation in the resulting N$_2$ complex and that as a result of its rigid structure also prevents a significant amount of π bonding between M and X. (It is interesting to note that at least part of the set of donor ligands to Mo in nitrogenase is likely to be relatively rigid.[9]) An alternative is to employ an X that has no π electrons that are as readily available as they are on O, N, or S, i.e., X = alkyl. In fact the only apparent example of dinitrogen binding to a d^2 metal is binding to incipient "WCp*Me$_3$" to give (WCp*Me$_3$)$_2$(μ-N$_2$) (Cp* = η^5-C$_5$Me$_5$).[8] The fact that Mo(mes)$_4$ apparently does not bind N$_2$ is not inconsistent; Mo(mes)$_4$ must be an exceedingly crowded and (it was noted[11]) a surprisingly thermally stable and relatively unreactive species.

An interesting question is whether Mo and W compounds will be isostructural (e.g., Mo(SCMe$_3$)$_4$ and W(SCMe$_3$)$_4$) in all cases. Unfortunately, in spite of much effort, we have been unable to prepare Mo(DIPP)$_4$ or Mo(DMP)$_4$. These findings are as puzzling as the fact that we have not been able to prepare W(TIPT)$_4$, as noted above. At present we can think of no good reason why Mo(DMP)$_4$ should not exist and be isostructural with W(DMP)$_4$.

We will continue to search for monomeric complexes of the type MX$_4$ in which M is Mo or W and X is a simple monodentate ligand in an effort to understand their structures and in order to determine under what circumstances, if any, such species might bind dinitrogen.

Experimental Section

General Details. All operations were performed under nitrogen in a Vacuum Atmospheres drybox or by standard Schlenk or vacuum line techniques. Commercial pentane (washed with 5% HNO$_3$/H$_2$SO$_4$ and dried over CaCl$_2$), reagent grade THF, toluene, DME (predried by passage through a column of 13X sieves and storage over sodium chunks), and anhydrous ether were distilled from dark purple sodium benzopenone ketyl under nitrogen. Reagent grade methylene chloride and diethyl sulfide were distilled from CaH$_2$, while reagent grade carbon tetrachloride and dichloromethane were distilled from P$_2$O$_5$ and deaerated with nitrogen. Phenols were purchased commercially and sublimed or distilled before use. Cyclohexene oxide, trimethylsilyl azide, and (trimethylsilyl)diazomethane (10% hexane solution) were purchased commercially and used as received.

Only nonroutine coupling constants (in Hz) are reported. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm downfield of Me$_4$Si.

Preparation of *mer*-W(O-2,6-C$_6$H$_3$Me$_2$)$_3$Cl$_3$. 2,6-Dimethylphenol (20.2 mmol, 2.46 g) in 30 mL of CCl$_4$ was added as rapidly as possible to a stirred solution of WCl$_6$ (5.04 mmol, 2.00 g) in 100 mL of CCl$_4$. The solution turned dark brown immediately, and the WCl$_6$ dissolved rapidly. The solution was then heated to reflux for 1 h. The CCl$_4$ was

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removed in vacuo, and the residue was extracted with dichloromethane. The extracts were combined and filtered, and the dichloromethane was removed in vacuo. The residue was placed on a sintered-glass frit and extracted with pentane in order to remove the excess phenol. The resulting 2.94 g (89%) of dark brown microcrystalline material was pure enough for further use. The analysis sample was twice recrystallized from dichloromethane. ^{1}H NMR (C_6D_6): δ 2.48 (s, 6, Me); 2.87 (s, 12, Me); 6.3–6.5 (2 overlapping triplets, 3, H_p); 6.625 (d, 2, H_m); 6.765 (d, 4, H_m). Anal. Calcd for $WC_{24}H_{27}O_3Cl_3$: C, 44.10; H, 4.16. Found: C, 44.33; H, 4.34.

Preparation of *trans*-W(O-2,6-$C_6H_3Me_2$)$_4$$Cl_2$. 2,6-Dimethylphenol (0.252 mol, 30.8 g) and WCl_6 (0.0252 mol, 10.0 g) were thoroughly mixed in the drybox and transferred to a Schlenk flask equipped with a magnetic stirring bar. The flask was heated until the phenol melted. The resulting solution was stirred vigorously. After ~10 min, the mixture rapidly solidified. Heating was continued at a somewhat reduced level for 10 min more, and the flask was then cooled under vacuum. The solid mass was broken up, placed on a sintered-glass frit, and extracted with ~500 mL of pentane to remove the bulk of the phenol. The resulting dark brown powder was then Soxhlet-extracted with pentane for 2 days to remove the last of the phenol. The resulting dark brown powder (12.2 g, 65%) was pure enough for further use. The sparingly soluble powder can be "recrystallized" from dichloromethane. ^{1}H NMR (C_6D_6): δ 2.60 (s, 24, Me); 6.53 (t, 4, H_p); 6.775 (d, 8, H_m). Anal. Calcd for $WC_{32}H_{36}O_4Cl_2$: C, 51.98; H, 4.90; Cl, 9.58. Found: C, 51.69, 50.21; H, 4.97, 4.77; Cl, 11.28, 10.29. Erratic analytical results on samples that are "pure" by ^{1}H NMR suggest that the product is contaminated by some impurity (perhaps paramagnetic) with a high chloride content. The amorphous material so far has refused to crystallize.

Preparation of W(O-2,6-C_6H_3-*i*-Pr_2)$_4$. A solution of $WCl_4(Et_2S)_2$[22] (0.593 mmol, 0.300 g) in 3 mL of toluene was cooled to −30 °C and added rapidly to a solution of Li(O-2,6-C_6H_3-*i*-Pr_2)(Et_2O) (2.37 mmol, 0.613 g) in 20 mL of ether that had been cooled to −30 °C. After the mixture was stirred for 1.5 h at 25 °C, it was transferred to a glass bomb and maintained at 40 °C for 14 h. Light tan solids slowly deposited from the dark red solution. The mixture was filtered, the solvents were removed from the filtrate in vacuo, and the dark red residue was recrystallized from pentane at −30 °C to afford 0.250 g (47%) of extremely dark blue crystals. The product sometimes is contaminated with a small amount of unidentified orange material, in which case solutions will appear green or even yellow-brown. ^{1}H NMR (C_6D_6): δ 1.10 (d, 48, CH*Me*$_2$); 3.57 (sept, 8, C*H*Me_2); 7.04 (m, 12, aromatic H). ^{13}C NMR (dioxane-*d*$_8$): δ 23.56 (q, CH*Me*$_2$); 30.52 (d, *C*HMe_2); 123.66 (d, ring C); 136.30 (s, ortho C); 157.88 (s, ipso C). Anal. Calcd for $WC_{48}H_{68}O_4$: C, 64.57; H, 7.68. Found: C, 64.48; H, 7.75.

Preparation of W(O-2,6-$C_6H_3Me_2$)$_4$. From $WCl_4(Et_2S)_2$. A −30 °C solution of $WCl_4(Et_2S)_2$ (1.0 mmol, 0.50 g) in ~40 mL of toluene was added rapidly to a −30 °C solution of Li(O-2,6-$C_6H_3Me_2$) (4.0 mmol, 0.51 g) in 5 mL of THF. The red mixture was stirred for 1 h at room temperature, during which time the color darkened and light tan solids precipitated. Pentane was then added (45 mL), the solution was filtered through Celite, and the solvents were removed in vacuo. The dark red oil residue was dissolved in the minimum amount of toluene, and 5 volumes of pentane was added. The solution was filtered to remove some additional traces of tan solids, and the solvents were removed from the filtrate in vacuo to afford a dark red sticky solid. The crude yield is ~75% by NMR integration versus an internal standard. The product may be recrystallized from ether as dark red blocks. ^{1}H NMR (C_6D_6): δ 2.26 (s, 24, Me); 6.77 (t, 4, H_p); 6.89 (d, 8, H_m). ^{13}C NMR (dioxane-*d*$_8$): δ 20.51 (q, Me); 123.01 (d), 126.17 (s), 128.66 (d), and 160.43 (s) (all ring C). Anal. Calcd for $WC_{32}H_{36}O_4$: C, 57.50; H, 5.43. Found: C, 57.00; H, 5.52.

From W(DMP)$_4$$Cl_2$. W(DMP)$_4$$Cl_2$ (1.35 mmol, 1.00 g) was added rapidly as a solid to 50 mL of ether at −30 °C containing sodium amalgam (0.5%, 2.70 mmol, 12.4 g). The solution was stirred vigorously for 2 h at 25 °C. The mixture was filtered, the solvent was removed in vacuo, and the residue was extracted with ether. The extracts were combined, and the ether was removed in vacuo to yield 0.74 g (82%) of microcrystalline product that was identical with that prepared from $WCl_4(Et_2S)_2$ and LiDMP above.

Preparation of W(EtC≡CEt)(O-2,6-$C_6H_3Me_2$)$_4$. 3-Hexyne (0.45 mmol, 51 μL) in 2 mL of ether was added all at once to a solution of W(DMP)$_4$ (0.45 mmol, 0.30 g) in 15 mL of ether that had been cooled to −30 °C. The solution promptly turned bright red. The solution was warmed to 25 °C. After 1 h the solvent was removed in vacuo and the bright red residue was recrystallized from ether to give 0.160 g (47%) of red-orange flakes. The yield is virtually quantitative by ^{1}H NMR. ^{1}H NMR (C_6D_6): δ 0.88 (t, 6, CH_2*C**H*$_3$); 2.13 (s, 24, Me); 2.92 (q, 4, *C*H_2CH_3); 6.73 (t, 4, H_p); 6.92 (d, 8, H_m). ^{13}C NMR (CD_2Cl_2): δ 14.3 (q, CH_2*C*H_3); 17.74 (q, DMP Me); 26.42 (t, *C*H_2CH_3); 121.73 (d), 127.44 (s), 128.71 (d), and 162.65 (s) (all ring C); 207.06 (s, Et*C*≡*C*Et). $\nu_{C\equiv C}$ was too weak to observe in an IR spectrum of a sample in Nujol. Anal. Calcd for $WC_{38}H_{46}O_4$: C, 60.80; H, 6.18. Found: C, 61.38; H, 6.20.

Preparation of W(O)(O-2,6-$C_6H_3Me_2$)$_4$. From W(DMP)$_4$ and Cyclohexene Oxide. Cyclohexene oxide (0.45 mmol, 45 μL) in 2 mL of ether was added rapidly dropwise to W(O-2,6-$C_6H_3Me_2$)$_4$ (0.45 mmol, 0.30 g) in 15 mL of ether that had been cooled to −30 °C. The solution turned bright red. After the reaction mixture was stirred for 2 h at 25 °C, the solvent volume was reduced in vacuo and a bright red precipitate was isolated by filtration (yield 0.25 g, 81%). The analysis sample was recrystallized from a mixture of toluene and pentane. ^{1}H NMR (C_6D_6): δ 2.34 (s, 24, Me); 6.59 (t, 4, H_p); 6.74 (d, 8, H_m). ^{13}C NMR ($CDCl_3$): δ 16.72 (q, Me); 123.34 (d), 128.05 (d), 128.23 (s), and 160.80 (s) (all ring C). IR (Nujol, cm^{-1}): 967 ($\nu_{W=O}$). Anal. Calcd for $WC_{32}H_{36}O_5$: C, 56.15; H, 5.30. Found: C, 55.92; H, 5.33.

Analogous reactions involving 1 equiv of iodosylbenzene or 0.5 equiv of dry O_2 gas gave W(O)(DMP)$_4$ in similar high yield.

From W(O)Cl_4. A solution of $WOCl_4$ (0.87 mmol, 0.30 g) in 5 mL of ether was added rapidly dropwise to a solution of Li(O-2,6-$C_6H_3Me_2$) (3.5 mmol, 0.45 g) in 15 mL of ether that had been cooled to −30 °C. The solution turned bright red instantly. The solution was warmed to room temperature and after 1.5 h was filtered. The solvent was removed in vacuo, and the resulting bright red residue was recrystallized from a mixture of toluene and ether to yield 0.44 g (71%) of a material identical in all respects with that prepared from W(O-2,6-$C_6H_3Me_2$)$_4$ and cyclohexene oxide.

Preparation of W(N_2CHSiMe_3)(O-2,6-$C_6H_3Me_2$)$_4$. (Trimethylsilyl)diazomethane (0.45 mmol, 515 μL of a 10% solution in hexane) was added rapidly dropwise to a solution of W(O-2,6-$C_6H_3Me_2$)$_4$ (0.45 mmol, 0.30 g) in 15 mL of ether that had been cooled to −30 °C. The solution turned bright red immediately. After the solution stood for 1 h at 25 °C, the solvents were removed in vacuo and the residue was recrystallized from pentane to afford 0.186 g (53%) of small dark red cubes. ^{1}H NMR (C_6D_6): δ −0.099 (s, 9, SiMe_3); 2.37 (s, 24, Me); 6.65 (t, 4, H_p); 6.87 (d, 8, H_m); 7.49 (s, 1, C*H*SiMe_3). ^{13}C NMR (CD_2Cl_2): δ −2.87 (q, SiMe_3); 17.15 (q, DMP Me); 122.40 (d), 127.33 (s), 128.46 (d), and 162.56 (s) (all ring C); 184.28 (d, J_{CH} = 145, *C*HSiMe_3). Anal. Calcd for $WC_{36}H_{46}N_2O_4Si$: C, 55.24; H, 5.92; N, 3.58. Found: C, 55.23; H, 6.02; N, 4.37.

Preparation of W(NSiMe_3)(O-2,6-$C_6H_3Me_2$)$_4$. Trimethylsilyl azide (0.60 mmol, 79 μL) in 2 mL of ether was added rapidly dropwise to a solution of W(O-2,6-$C_6H_3Me_2$)$_4$ (0.60 mmol, 0.40 g) in 20 mL of ether that had been cooled to −30 °C. The solution immediately turned bright red. The mixture was warmed to 25 °C and stirred for 1 h. The solvent was removed in vacuo, and the residue was recrystallized from ether to afford 0.32 g (71%) of clear bright red cubes. ^{1}H NMR (C_6D_6): δ 0.59 (s, 9, SiMe_3); 2.33 (s, 24, Me); 6.63 (t, 4, H_p); 6.83 (d, 8, H_m). ^{13}C NMR (CD_2Cl_2): δ 1.79 (q, SiMe_3); 17.64 (q, Me); 122.30 (d), 127.84 (s), 128.38 (d), and 161.95 (s) (all phenoxide ring C). Anal. Calcd for $WC_{35}H_{45}NO_4Si$: C, 55.64; H, 5.98. Found: C, 56.22; H, 5.94.

Preparation of W(S)(O-2,6-$C_6H_3Me_2$)$_4$. From Mesitylenethiol. 2,4,6-Trimethylbenzenethiol (0.53 mmol, 79 μL) was added to a solution of W(DMP)$_4$ (0.53 mmol, 355 mg) in ether at −30 °C. The solution was warmed to room temperature and stirred for 6 h. A red powder precipitated out and was isolated by filtration (234 mg, 63%). This crude product can be recrystallized from methylene chloride (120 mg, 32%) as red needles. ^{1}H NMR (C_6D_6): δ 2.31 (s, 24, Me); 6.59 (t, 4, H_p); 6.75 (d, 8, H_m). ^{13}C NMR (CD_2Cl_2): δ 17.44 (q, J_{CH} = 127 Hz, Me); 123.73 (d, J_{CH} = 161 Hz, ring C); 128.54 (d, J_{CH} = 159 Hz, ring C); 128.60 (s, ortho C); 162.08 (s, ipso C). IR (Nujol, cm^{-1}): 520 ($\nu_{W=S}$). Anal. Calcd for $WC_{32}H_{36}O_4S$: C, 54.87; H, 5.18; S, 4.58. Found: C, 54.75; H, 5.08; S, 4.88.

An analogous reaction involving 2,4,6-triisopropylbenzenethiol gave W(S)(DMP)$_4$ in similar yield.

From Elemental Sulfur. Elemental sulfur (1.5 mmol, 48 mg) was added to a solution of W(DMP)$_4$ (1.5 mmol, 1 g) in methylene chloride (−30 °C) while the solution was stirred rapidly. The reaction mixture was allowed to warm to room temperature and then stirred for 3 h, during which time the color became deep red. The volume of solvent was then reduced to a minimum, and the solution was cooled to −30 °C to give red needles (350 mg, 33%) of W(S)(DMP)$_4$ that are spectroscopically identical with the complex prepared from 2,4,6-trimethylbenzenethiol.

X-ray Study of W(O-2,6-C_6H_3-*i*-Pr_2)$_4$. Data were collected on an Enraf-Nonius CAD4F-11 diffractometer. (See Table I for details.) Data collection, reduction, and refinement procedures used in this laboratory have been detailed elsewhere.[42] A blue crystal was mounted under a

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nitrogen atmosphere on the end of a glass fiber with epoxy and quickly transferred to the nitrogen stream of the cooling device. Under these conditions no crystal decay was observed during the course of the data collection. Refinement was by full-matrix least-squares techniques (241 variables) using SHELX-76. The W and O atoms were refined anisotropically, and all hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and constrained to "ride" on their respective carbon atoms. The largest peak on the final difference-Fourier map was 0.89 e/Å^3. An empirical absorption correction was appled on the basis of Ψ scans of two reflections located near $\chi = 90°$.

X-ray Study of $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$. See Table I for details. Refinement was by full-matrix least-squares techniques (85 variables) using SHELX-76. Hydrogen atoms were ignored while all other atoms were refined anisotropically. The final difference-Fourier map contained no chemically significant electron density. A semiempirical absorption correction was applied.

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Registry No. *mer*-$W(DMP)_3Cl_3$, 102307-42-6; *trans*-$W(DMP)_4Cl_2$, 82972-39-2; $W(DMP)_4$, 99248-59-6; $W(EtC{\equiv}CEt)(DMP)_4$, 99248-63-2; $W(O)(DMP)_4$, 111557-27-8; $W(N_2CHSiMe_3)(DMP)_4$, 111557-26-7; $W(NSiMe_3)(DMP)_4$, 111557-29-0; $W(S)(DMP)_4$, 111557-28-9; $W(DIPP)_4$, 99248-58-5; $WCl_4(Et_2S)_2$, 40354-86-7; S, 7704-34-9; O_2, 7782-44-7; iodosylbenzene, 536-80-1; cyclohexene oxide, 286-20-4; mesitylenethiol, 1541-10-2.

Supplementary Material Available: Numbering scheme for carbon atoms (Figure 1) and final thermal parameters (Table S1) and final hydrogen atom positions (Table S2) for $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ and final thermal parameters (Table S4) for $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$ (5 pages); observed and calculated structure factors for the two compounds (Tables S3 and S5) (27 pages). Ordering information is given on any current masthead page.

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Reaction of H_2S with $[Ir(H)_2(Me_2CO)_2(PPh_3)_2]BF_4$. Crystal and Molecular Structures of $[Ir_2(SH)_2(H)_3(PPh_3)_4]BF_4\cdot 2(CH_3)_2CO$, $[Ir_2S(SH)(H)_3(PPh_3)_4]\cdot 1.5C_6H_6$, and $[Ir_2(SH)(SC_3H_7)(H)_3(PPh_3)_4]BF_4\cdot (CH_3)_2CO$ and Their Reactions with Organic Reagents

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The reaction of H_2S with $[Ir(H)_2(Me_2CO)_2(PPh_3)_2]BF_4$ in acetone solution led to the formation of the hydrido- and sulfhydryl-bridged dimeric complex $[Ir_2(SH)_2(H)_3(PPh_3)_4]BF_4$ (**1**) as a major product, which upon deprotonation of one bridging SH ligand produced $[Ir_2S(SH)(H)_3(PPh_3)_4]$ (**2**). A minor product isolated from the H_2S reaction was the propane-2-thiolato-bridged dimeric complex $[Ir_2(SH)(SC_3H_7)(H)_3(PPh_3)_4]BF_4$ (**3**). All three complexes were characterized by single-crystal X-ray diffraction [**1**$\cdot 2(CH_3)_2CO$, triclinic $P\bar{1}$, $a = 14.919$ (8) Å, $b = 23.63$ (2) Å, $c = 18.835$ (4) Å, $\alpha = 92.09$ (5)°, $\beta = 113.95$ (4)°, $\gamma = 79.16$ (7)°, $Z = 2$, $R = 0.056$; **2**$\cdot 1.5C_6H_6$, monoclinic $P2_1/n$, $a = 17.377$ (6) Å, $b = 24.658$ (6) Å, $c = 18.220$ (5) Å, $\beta = 92.76$ (2)°, $Z = 4$, $R = 0.046$; **3**$\cdot (CH_3)_2CO$, monoclinic $P2_1/a$, $a = 20.154$ (9) Å, $b = 18.349$ (9) Å, $c = 21.690$ (7) Å, $\beta = 108.08$ (3)°, $Z = 4$, $R = 0.046$] and ^1H and ^{31}P NMR spectroscopy. In all three complexes, the coordination geometry about each Ir atom is approximately pseudooctahedral, being bound to a terminal hydride, a bridging hydride, two cis phosphines, and two bridging sulfur atoms. The planes that contain an iridium atom and the two bound phosphines in each half of compounds **1** and **2** are approximately orthogonal, the dihedral angle equaling 82.9° in **1** and 84.0° in **2**. In **3** this angle is opened up somewhat to 108.8°. The dihedral angle between the planes containing the two iridium atoms and each sulfur atom is 73.9° in **1** and 77.0° in both **2** and **3**. Neither the iridium hydrides nor the sulfhydryl hydrogen atoms were located in the X-ray analyses of any of the complexes; however, their positions could be deduced by a combination of X-ray and NMR data. ^{31}P and ^1H NMR indicates the presence of three isomers for **1**, two isomers for **2**, and three isomers for **3** with respect to the orientation of the SR groups ($R = H, C_3H_7$) relative to the metal–metal axis. Compounds **1** and **2** reacted with various organic reagents such as CH_2I_2, $BrCH_2CH_2Br$, and CH_3I to give high yields of products in which the sulfur ligands were alkylated.

Introduction

Interest in the chemistry and reactivity of sulfhydryl- (SH^--) containing complexes[1–12] is due in part to efforts to understand possible modes of reaction of SH groups on metal sulfide hydrodesulfurization catalysts[1,5,6] and also to their potential in serving

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