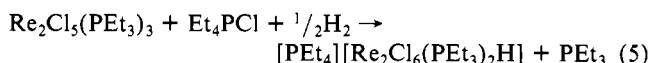
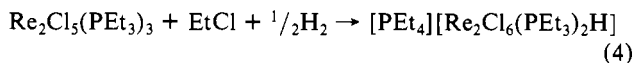


In a very careful study of the electrochemical oxidation of $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ complexes, Walton and his co-workers showed that $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$ undergoes reversible oxidation in dichloromethane to +1 and +2 cations at $E_{1/2} = -0.42$ and $+0.80$ V, respectively.²⁶ Half-wave potentials are referenced to the saturated calomel electrode. In the presence of chloride ion the $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4^+$ cation is rapidly transformed into $\text{Re}_2\text{Cl}_5(\text{PEt}_3)_3$. In the presence of ethyl chloride or chlorotetraethylphosphorane this intermediate could react with elemental hydrogen to give $[\text{PEt}_4][\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2\text{H}]$.



Crucial to our mechanistic hypothesis is the formation of hydrogen chloride and ethyl chloride. The formation of hydrogen chloride and ethyl chloride could occur by the thermodynamically favorable ($\Delta G^\circ = -66.3$ kcal), metal-catalyzed hydrogenation of dichloromethane to give ethyl chloride and hydrogen chloride, $2\text{H}_2(\text{g}) + 2\text{CH}_2\text{Cl}_2(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{Cl}(\text{g}) + 3\text{HCl}(\text{g})$. With deuterium as the reducing agent, the oxidized species would be DCl, and reactions 1 and 2 would lead to the observed deuterio-bridged anion.

The formation of ethyl chloride was suggested by the occurrence of the PEt_4^+ counterion both for the hydrido-bridged anion and the minor product $[\text{PEt}_4][\text{ReCl}_5(\text{PEt}_3)]$. The chlorotetraethylphosphorane, which is required for the formation of the tetra-

ethylphosphonium salts, may form readily by the action of ethyl chloride on triethylphosphine.²⁷ The reaction of phosphines with alkyl halides to form chlorophosphoranes is a reversible reaction²⁸ that can be shifted toward the chlorophosphorane by the formation of stable phosphonium salts similar to those found in this study.

We have established that direct hydrogenation of $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$, a member of the class of compounds containing the electron-rich ($\sigma^2\pi^4\delta^2\delta^*$) Re-Re bond occurs with formation of an air-stable salt $[\text{PEt}_4]^+[\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2\text{H}]^-$. While mechanistic inferences from synthetic studies are limited, our results suggest that formation of the hydrido-bridged anion in dichloromethane is a complex process involving hydrogen chloride and ethyl chloride as intermediates.

Acknowledgment. We are grateful to the SIUC Office of Research and Development and the SIUC Materials Technology Center for financial support at Southern Illinois University and to the National Science Foundation for financial support at Texas A&M University.

Registry No. 1, 109390-22-9; 2, 109390-24-1; $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$, 55400-06-9; *trans*- $\text{ReCl}_4(\text{PEt}_3)_2$, 24551-06-2; Re, 7440-15-5; H_2 , 1333-74-0.

Supplementary Material Available: Listings of bond distances and angles and anisotropic displacement parameters for **1** and anisotropic displacement parameters for **2** and a figure depicting a contoured section of the final difference Fourier map in the disordered region for **2** (5 pages); listings of calculated and observed structure factors for **1** and **2** (21 pages). Ordering information is given on any current masthead page.

(26) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

(27) Lehs, E. A.; Collie, J. N. *Philos. Mag.* **1886**, *22*(5), 183.

(28) Kosolapoff, G. M., *Organophosphorus Compounds*; Wiley: New York, 1950; pp 18, 78-86.

Contribution from the Department of Chemistry,
University of Missouri—Columbia, Columbia, Missouri 65211

Tetrakis(dimethylamido) Complexes of Oxotungsten(VI) and (Phenylimido)tungsten(VI)

David M. Berg and Paul R. Sharp*

Received August 4, 1986

The compound $\text{W}(\text{NPh})(\text{NMe}_2)_4$ (**1**) is formed in a two-step reaction by treating $\text{W}(\text{NPh})\text{Cl}_4 \cdot \text{Et}_2\text{O}$ with 1 equiv of MeOH followed by 4 equiv of LiNMe_2 . $\text{WO}(\text{NMe}_2)_4$ (**2**) can be prepared in a similar manner. An X-ray crystal structure determination shows **1** to have a geometry between square pyramidal and trigonal bipyramidal. The crystals are monoclinic ($C2/c$) with (140 K) $a = 12.383$ (7) Å, $b = 10.262$ (3) Å, $c = 14.278$ (12) Å, $\beta = 107.45$ (5)°, $V = 1731.0$ Å³, and $Z = 4$. The three-dimensional X-ray data were measured at 140 K with the ω - 2θ scan technique and a scintillation detector. The structure was resolved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to give $R(F_o) = 0.019$ and $R_w(F_o) = 0.027$ for 1074 observations above 2σ . A simple bonding analysis is presented to explain the structure of **1**.

Introduction

An important property of many of the early transition metals is their ability to form multiple bonds with themselves¹ and with ligands of the first-period elements C,² N,³ and O.⁴ The major geometrical features of these complexes can be understood in terms of the strong trans influence of the multiply bonded ligands, the maximization of ligand-to-metal π bonding,⁵ and intramolecular steric interactions.⁶ Pentacoordinate complexes containing one triply bonded ligand X ($\equiv\text{O}$,⁷ $\equiv\text{NR}$,⁸ $\equiv\text{N}$,^{7b,9} $\equiv\text{ML}_3\text{L}^{10}$) typ-

ically assume a square-pyramidal geometry with the triply bonded ligand at the apex. When strongly π -donating alkoxides or amides are present, these ligands are oriented so as to π -donate into metal d orbitals not used in forming the triple bond to X. In this paper we report the synthesis of two pentacoordinate complexes of this type and the X-ray crystal structure of one where the introduction of four strongly π -donating amido groups leads to an unusual distortion toward a trigonal-bipyramidal geometry. A simple

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(2) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 1140.

(3) (a) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369-396. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123-175.

(4) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459-517.

(5) Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C.; Janos, J. *J. Am. Chem. Soc.* **1983**, *105*, 1163-1170.

(6) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 709-716.

(7) (a) Hess, V. H.; Hartung, H. Z. *Anorg. Allg. Chem.* **1966**, *344*, 157-166. (b) Knopp, B.; Lorcher, K.-P.; Strahle, J. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1361-1364.

(8) Chou, C. Y.; Huffman, J. C.; Maatta, E. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1184-1185.

(9) Liese, W.; Dehnicke, K.; Rogers, R. D.; Shakir, R.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1061.

(10) (a) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 153-157. (b) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266-2270. (c) Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2075-2077.

Table I. Crystallographic and Data Collection Parameters for **1**

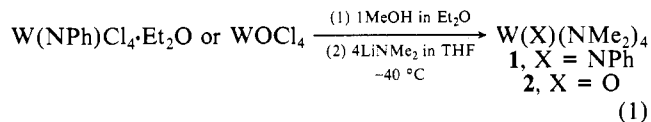
formula (fw)	WN ₃ C ₁₄ H ₂₉ (451.27)
temp	140 K
space group	C2/c
a, Å	12.383 (7)
b, Å	10.262 (3)
c, Å	14.278 (13)
β, deg	107.45 (5)
V, Å ³	1731.0
d _{calcd} , g/cm ³	1.732
Z	4
cryst size, mm	0.2 × 0.3 × 0.3
μ(Mo Kα), cm ⁻¹	68.2
transmission range	87.3–99.7%
scan width in θ, deg	0.70 + 0.35 tan θ
count stats (max time, s)	3% (90)
hkl range (2θ max, deg)	+h,+k,±l (45.0) -h,-k,±l (36.0)
no. of unique data (above 2σ)	1129 (1074)
no. of variables	94
R(F _o) ^a	0.019
R _w (F _o) ^b	0.027
err in unit wt observn ^c	1.182
max shift/esd, final cycle	0.01

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$; $w = 1/\sigma^2 |F_o|$. ^c $[\sum w(|F_o| - |F_c|)^2 / (N_{obs} - N_{par})]^{1/2}$.

bonding analysis is presented to explain the structure.

Results and Discussion

Preparations. Treating W(NPh)Cl₄·Et₂O¹¹ under dinitrogen with 1 equiv of MeOH in Et₂O gives a pale green solution presumably containing W(NPh)(OMe)Cl₃. Removing all volatiles in vacuo followed by dissolving the residue in Et₂O and adding 4 equiv of LiNMe₂ in THF at -40 °C yields a deep red solution from which W(NPh)(NMe₂)₄ (**1**) can be isolated in a crude yield of 98%. Recrystallization from petroleum ether gives pure, deep red, air-sensitive crystals in a 53% yield. A similar procedure



starting with WOCl₄¹² gives WO(NMe₂)₄ (**2**) in approximately a 25% yield. Alternatively, **2** can be prepared in about the same yield by treating WO(NMe₂)Cl₄⁻ (readily prepared from WOCl₄ and 2 equiv of HNMe₂)¹³ with 3 equiv of LiNMe₂.

Direct amidation of WOCl₄ does not give **2**. Apparently, reduction of the W is the problem since a poor yield of W₂(NMe₂)₆ is isolated when WOCl₄ is treated with 4 equiv of LiNMe₂.¹⁴ The two-step procedure (alcoholysis or aminolysis followed by amidation) described above relies on the greater resistance to reduction of complexes containing π-donating ligands.

Molecular Structure of W(NPh)(NMe₂)₄ (1**).** An X-ray crystal structure determination was performed on **1**, and a drawing of the molecular structure is given in Figure 1. Crystal data and positional parameters are given in Tables I and II. Bond distances and angles are given in Table III. The molecule resides on a crystallographic 2-fold axis that passes through the phenylimido group and the W. Consequently, only half of the phenyl ring and two of the four amido groups are independent. At first glance the structure of **1** appears typical of the square-pyramidal geometry found in this type of complex. However, several features of the structure conflict with this description.

First, the basal-plane trans amido angles are not equivalent. The N2–W–N2 angle of 158.2 (2)° is closest to being linear and is in the range typically observed in square-pyramidal complexes of this type.^{7–10} (Basal-plane trans angles of less than 180° are

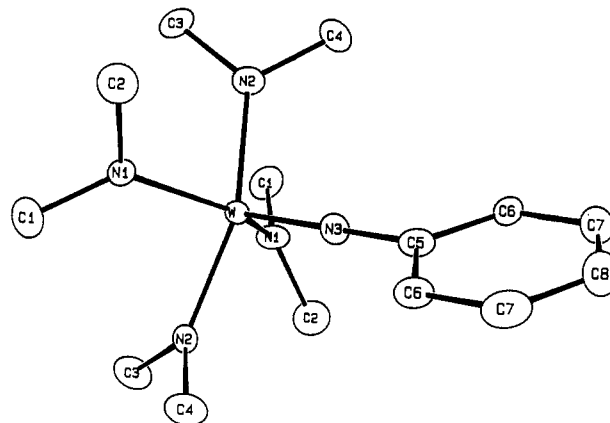


Figure 1. ORTEP view of W(NPh)(NMe₂)₄ (**1**), 50% probability ellipsoids. Atoms with the same name are related by a 2-fold axis passing through the W–imido bond.

Table II. Positional Parameters for Refined Atoms

atom	x	y	z	B ^a , Å ²
W	0.000	-0.07459 (2)	0.250	0.996 (5)
N1	0.0249 (3)	-0.1404 (3)	0.1258 (2)	1.47 (7)
N2	0.1638 (3)	-0.1112 (4)	0.3101 (2)	1.40 (7)
N3	0.000	0.0967 (4)	0.250	1.5 (1)
C1	-0.0457 (3)	-0.2278 (5)	0.0523 (3)	2.08 (9)
C2	0.1229 (4)	-0.1013 (5)	0.0941 (4)	2.4 (1)
C3	0.2236 (3)	-0.2301 (5)	0.2982 (3)	2.11 (9)
C4	0.2380 (4)	-0.0271 (5)	0.3852 (3)	2.2 (1)
C5	0.000	0.2303 (6)	0.250	1.6 (1)
C6	-0.0534 (3)	0.3015 (4)	0.1643 (3)	1.63 (9)
C7	-0.0525 (5)	0.4350 (4)	0.1651 (5)	2.5 (1)
C8	0.000	0.5019 (6)	0.250	2.9 (2)

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

Table III. Bond Distances (Å) and Angles (deg) for **1**

W–N1	2.006 (3)	N1–C2	1.473 (6)
W–N2	1.987 (3)	N2–C4	1.466 (6)
W–N3	1.758 (5)	N2–C3	1.463 (5)
N1–C1	1.455 (5)	N3–C5	1.371 (8)
N1–W–N2	84.9 (1)	C1–N1–C2	108.6 (3)
N1–W–N3	109.68 (9)	W–N2–C3	126.5 (3)
N2–W–N3	100.9 (1)	W–N2–C4	122.7 (3)
W–N1–C1	128.8 (2)	C3–N2–C4	110.4 (3)
W–N1–C2	122.7 (3)	W–N3–C5	180

typical and represent the major distortion from a perfect square pyramid.) The N1–W–N1 angle of 140.6 (2)° is considerably smaller. A large decrease in one of the basal-plane trans angles is precisely the type of distortion required to take a square-pyramidal geometry to a trigonal-bipyramidal geometry. A description of the geometry of **1** (and probably **2** as well) as a distorted trigonal bipyramid with the N2 amido groups on the axis and with the imido group and the N1 amido groups in the trigonal plane is possible.

The orientation of the dimethylamido groups of **1** is also unusual. In previously characterized complexes of this type containing π-donating alkoxides or amides, the sp²-hybridized NR₂ or OR groups are nearly planar with the MX group.^{10,15} This is not true of both sets of amido groups in **1**. This can be shown by examining the dihedral angles between the planes containing the dimethylamido groups and W and the planes containing the imido nitrogen N3, W, and the dimethylamido nitrogens. These angles show that the N1 amido group is closer to being perpendicular rather than planar with the imido group (55.7 (3)° out

(11) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483–7490.

(12) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1965**, *18*, 447–452.

(13) Sharp, P. R.; Gaber, F., to be submitted for publication in *Polyhedron*.

(14) Chisholm, M. H.; Cotton, F. A.; Extine, M.; Stults B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477–4485.

(15) Chisholm, M. H.; Chiu, H. T.; Huffman, J. C.; Wang, R. *J. Inorg. Chem.* **1986**, *25*, 1092–1096.

Table IV. Intramolecular Nonbonded Distances (<4 Å)

N1-N1	3.778 (6)	N2-C1	3.997 (5)
N1-N2	2.694 (5)	N2-C1	3.026 (5)
N1-N2	2.770 (4)	N2-C2	2.973 (6)
N1-N3	3.081 (5)	N3-C2	3.665 (6)
N1-C3	3.054 (5)	N3-C4	3.258 (5)
N1-C3	3.674 (5)	C1-C3	3.498 (6)
N1-C4	3.415 (6)	C1-C4	3.461 (6)
N2-N2	3.903 (7)	C2-C3	3.100 (7)
N2-N3	2.891 (5)	C4-C5	3.997 (7)

of the plane or 34.3° from perpendicular). The opposite is observed with the N2 amido group which is 29.8 (4)° out of the plane of the imido group.

Nonbonded intramolecular distances (up to 4 Å) for **1** are given in Table IV. While many of the distances are shorter than the sum of the van der Waals radii, there is one that is remarkably short. The C3 to C2 methyl group contact is 3.10 Å, almost a full angstrom shorter than the sum of the van der Waals radii (4.00 Å). This contact appears to prevent the N1 dimethylamido group from being completely perpendicular to the imido group. This interaction could be relieved by rotation of the N2 dimethylamido group into the plane of the imido group; however, such a rotation would decrease the C1 to C3 and the C4 to N3 contacts, which are already closer than the sum of the van der Waals radii. Thus it seems that the orientation of the amido groups is determined primarily by electronic factors with steric distortions. Intermolecular distances (supplementary material) are not unusual and do not seem to play a role in the molecular geometry.

Bonding Analysis. We start with the usual analysis for an idealized square-pyramidal complex,^{3a,16} which takes the axial W imido triple bond as coincident with the *z* axis. Only the π -bonding interactions will be considered. The two π bonds to the imido group are formed from the empty metal d_{xz} and d_{yz} atomic orbitals and the filled imido nitrogen p_x and p_y orbitals. For the amido groups on the *x* and *y* axes, the only remaining empty metal *d* orbital for π donation from their lone-pair *p* orbitals is the d_{xy} . For proper overlap the amido groups must lie nearly in a plane with the imido group.

Such a bonding situation is fine if there is only one amido group donating into the metal d_{xy} orbital, but in **1** there would be four amido groups all competing for the same metal orbital. It must be this problem that leads to the distortion toward a trigonal-bipyramidal geometry. Two of the amido groups (the N2 pair) in **1** are aligned as expected for overlap with the d_{xy} orbital. The other two (the N1 pair) have rotated into a perpendicular position and have bent down away from the imido group such that their lone-pair *p* orbitals are pointed toward the vacant metal site¹⁷ along the *z* axis trans to the imido group. Several new interactions result.

First, and what must be the driving force for the distortion, is the formation of metal-N1 amido π bonds by donation into the vacant orbital along the *z* axis trans to the imido group. Some σ interaction with the metal d_{xz} or d_{yx} orbital, one of the orbitals used to form a metal-imido π bond, is also introduced by the bend down. In addition, a π interaction with the metal $d_{x^2-y^2}$ orbital is possible. This orbital is used for the σ bonds to the N2 amido groups. These competitive interactions should, to some extent, weaken the metal-imido π bond and the metal-N2 amido σ bonds. Thus, the formation of the metal-N1 amido π bonds comes at some sacrifice in the π bonding to the imido group and in the σ bonding to the N2 amido groups.

Comparison with Other Structures. A few complexes related to **1** adopt trigonal-bipyramidal geometries. Two of these, WN(O-*t*-Bu)₃ and W(CR)(O-*t*-Bu)₃, are pentacoordinate by virtue of bridging ligands but, unlike the triply bonded group of **1**, which is in the trigonal plane, the triply bonded groups are axial with

a weakly σ -bonded bridging ligand in the trans position.¹⁸

Two other complexes have distorted trigonal-bipyramidal geometries similar to that of **1**. However, the geometry of these molecules appear to result from intramolecular steric interactions of the ligands. The most closely related is MoO[OC(CF₃)₃]₄.¹⁹ A minimal π -bonding contribution is likely for this complex, given the expected decreased π -donating ability of a fluoro-substituted alkoxide. Consistent with this, all four alkoxy ligands are planar with the molybdenum-oxo bond indicating that additional π -bonding interactions, as were observed in **1**, are not present.

The second complex is Re(N)(PPh₃)₂Cl₂.²⁰ The intramolecular distances in this complex are very similar to those of related 6-coordinate complexes, whose geometry could be reasonably explained by intramolecular packing of the ligands. On the basis of this comparison, it was concluded that the geometry of the 5-coordinate complex was also explainable by intramolecular packing. Ligand-to-metal π donation would not be a factor in this structure.

The best complex for a comparison of the W-amido bond distances is W₂(NMe₂)₆.¹⁴ This complex is related to **1** in that, other than the triply bonded ligand (in this case an identical metal fragment), there are only dimethylamido ligands. The W-N distances in this complex are all equivalent at 2.017 Å, just slightly longer than the distances in **1** (2.006 (3) and 1.987 (3) Å). These distances are at the long end of the range (1.92–2.02 Å),^{13,14,21} suggesting relatively weak double bonds. This is to be expected, considering the competition of the amido groups for donation to the W (see the bonding analysis above). This competition is also apparent in the relatively long W-imido bond distance (1.758 (5) Å) in **1** which is at the long end of the observed range (1.61–1.77 Å).²² (A similar bond lengthening from competition between oxo and alkoxy groups has been observed.²³)

Finally, the structure of a Ta analogue of **1**, Ta(N-*t*-Bu)(NMe₂)₃, has been communicated.²⁴ The normal tetrahedral geometry (closely related to the geometry about the W atoms in W₂(NMe₂)₆) maximizes N-M π bonding. A long Ta-imido distance (1.77 (2) Å) is noted and, as in **1**, probably results from the competition with the amido and imido groups for donation to the metal.

Concluding Remarks. Clearly, **1** does not conform perfectly to either a square-pyramidal or a trigonal-bipyramidal geometry. In addition, ¹H NMR data show that in solution **1** and **2** have dynamic structures since a singlet is observed for the dimethylamido groups down to -90 °C. Still, we feel that the simple arguments presented above provide a reasonable explanation as to why **1** would show a distortion from the usual square-pyramidal geometry toward a trigonal-bipyramidal geometry. Certainly a detailed molecular orbital analysis would more thoroughly explain the geometry of **1**.

Apart from its structure, the reaction chemistry of **1** appears promising. Amido complexes are valuable as starting materials for a variety of complexes.²⁵ Although **1** and **2** are formally

(16) (a) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223 (see p 57). (b) Kon, H.; Sharpless, N. E. *J. Phys. Chem.* **1966**, *70*, 105–111. (c) Gray, H. B.; Hare, C. R. *Inorg. Chem.* **1962**, *1*, 363–368.
(17) This site is often readily occupied by solvent or halides in these types of complexes.

(18) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903–2906.
(19) Johnson, D. A.; Taylor, J. C.; Waugh, A. B. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1271–1275.
(20) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204–210.
(21) (a) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 782–792. (b) Chisholm, M. H.; Cotton, F. A.; Extine, M.; Millar, M.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4486–4491. (c) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 989–999.
(22) (a) Nielson, A. J.; Waters, J. M.; Bradley, D. C. *Polyhedron* **1985**, *4*, 285–297. (b) Nielson, A. J.; Waters, J. M. *Aust. J. Chem.* **1983**, *36*, 243–251. (c) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 103–104. (d) Drew, M. G. B.; Moss, K. C.; Rolfe, N. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1219–1222. (e) Drew, M. G. B.; Fowles, G. W. A.; Rice, D. A.; Rolfe, N. *J. Chem. Soc., Chem. Commun.* **1971**, 231–232.
(23) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021–1037.
(24) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579–580. Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965–969.
(25) Bradley, D. C. *Metal and Metalloid Amides*; Horwood-Wiley: New York, 1979.

W(VI) complexes, they are electron rich. The reactions of **1** and **2** with acidic and electrophilic species will be the subject of a future report.²⁶

Experimental Section

General Procedures. All experiments were performed under a dinitrogen atmosphere in a VAC drybox or by Schlenk techniques. Solvents were dried and purified under dinitrogen by using standard procedures. Methanol was dried by distillation from CaH₂. The petroleum ether had a boiling range of 35–60 °C. Dimethylamine was obtained from commercial sources and was used as received. WCl₄¹² and W(NPh)Cl₄·Et₂O¹¹ were prepared by reported procedures. LiNMe₂ was prepared from BuLi and NMe₂H in hexane/petroleum ether.

¹H NMR shifts are reported in ppm referenced to TMS and were recorded on a JEOL FX90Q or Varian EM360 at ambient temperature (35 ± 5 °C). IR spectra were recorded on a Nicolet 20DXB FT-IR, and mass spectra, on a Kratos MS 25. Analyses (drybox techniques) were by Galbraith Microanalytical Laboratories.

Preparation of W(NPh)(NMe₂)₄ (1). W(NPh)Cl₄·Et₂O (3.89 g, 7.90 mmol) was dissolved in 20 mL of Et₂O. A solution of MeOH (0.30 g, 9.36 mmol) in 5 mL of Et₂O was added dropwise with stirring. The original orange solution lightened and became pale yellow-green. All volatiles were removed in vacuo. The solid residue was redissolved in 20 mL of Et₂O and cooled to -40 °C. A solution of LiNMe₂ (0.40 g, 7.9 mmol) in THF was added dropwise with stirring. All volatiles were removed from the resulting deep red solution, and the solid residue was extracted with several portions of petroleum ether. Reducing and cooling (-40 °C) the extracts gave 3.56 g (97%) of crude **1**. Recrystallization from petroleum ether gave large red crystals in a 53% yield.

Solid **1** is highly air sensitive, decomposing rapidly to a sticky white solid on contact with air. In solution (C₆H₆), **1** begins to decompose at 60 °C.

¹H NMR (C₆D₆): 6.9–7.8 (m, 5, NPh), 3.40 ppm (s, 24, NMe₂). IR (mineral oil mull): 1585 m, 1481 s, 1411 w, 1363 s, 1236 m, 1144 m, 974 m, 945 s, 753 m cm⁻¹. Analyses were marginally successful and gave the following results. Anal. Calcd (found) for WN₃C₁₄H₂₉: C, 37.26 (36.46); H, 6.48 (6.17); N, 15.52 (14.50).

Preparation of WO(NMe₂)₄ (2). A procedure similar to that given for **1** but starting with WCl₄ gives red **2** in about a 25% yield. Alternatively, **2** is obtained in about the same yield by adding 3 equiv of LiNMe₂ in THF to a solution of [WO(NMe₂)Cl₄]NH₂Me₂¹² in THF at -40 °C followed by the same workup as given for **1**. Sublimation of **2** at 50–60 °C is accompanied by decomposition. In solution (C₆H₆) **2** begins to decompose at 55 °C.

¹H NMR (C₆D₆): 3.0 ppm (s, 2, NMe₂). IR (mineral oil mull): 1448 m, 1414 m, 1395 w, 1237 w, 1147 m, 1044 w, 944 s cm⁻¹. Analyses of

this highly air-sensitive complex were not successful and gave the following results. Anal. Calcd (found) for WON₄C₈H₂₄: C, 25.54 (24.22); H, 6.43 (6.06); N, 14.90 (13.77). A chemical ionization (CH₄) mass spectrum gave peaks with the correct W isotopic pattern at (tungsten-184): *m/z* 404 (M + 27), 345 (M - 32), 316 (M - 61).

Structure Analysis. An outline of crystallographic and data collection parameters is given in Table I. Crystals of **1** were grown by cooling a solution of the complex in Et₂O to -40 °C. These crystals were very unstable in air but could be easily handled in the air if they were well coated with grease (Apiezon N). A large red crystal was cleaved under the grease to give a suitable fragment. The fragment was mounted on a glass rod with the grease and transferred to a CAD4 diffractometer equipped with a liquid-N₂ cold stream. Cell dimensions were based upon a Delaunay reduction of a cell obtained from the centering of 25 reflections on the diffractometer.

Intensity data (140 K) were measured with Mo K α radiation from a graphite monochromator (ω - 2θ scan, 96 steps/scan, 16 steps/side background). The intensities of three standard reflections were measured after each 7200-s exposure to the X-rays and showed no intensity decay during the experiment. An empirical absorption correction was applied based on ψ scans. A total of 1272 reflections were measured and averaged ($R = 0.013$) to give 1129 independent reflections. The Enraf-Nonius SDP program package was used for all calculations.

The structure was resolved by Patterson and Fourier methods. Hydrogen atoms were placed in calculated fixed positions. Those for the methyl groups were based on the location of at least one peak in a reasonable hydrogen atom position. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ converged to the R values given in Table I. An isotropic extinction correction was refined. The final difference Fourier map had the two largest peaks (1.06 and 0.90 e/Å³) in the vicinity of the W atom. Final atomic positional parameters for the refined atoms are included in Table II. Selected interatomic bond distances and angles are given in Table III. Other data are included as supplementary material.

Acknowledgment. We acknowledge the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank Dr. J. L. Templeton and a reviewer for the helpful comments on the bonding. D.M.B. acknowledges the support of a Nightingale summer fellowship. The purchase of the X-ray equipment was partially funded by a grant from the National Science Foundation (CHE-7820347).

Registry No. **1**, 109585-85-5; **2**, 109585-86-6; W(NPh)Cl₄·Et₂O, 83634-25-7.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom positional parameters, additional bond distances and angles, intermolecular distances, torsion angles, and least-squares planes (4 pages); a listing of structure factors (6 pages). Ordering information is given on any current masthead page.

(26) Berg, D. M.; Sharp, P. R., to be submitted for publication in *Inorg. Chem.*