Inorg. Chem. **1983**, *22*, 2903-2906

capability of interacting magnetically. As has been stated elsewhere,[21] a major goal in research on bis(μ-halo) copper(II) dimers is the study of the relationship between structure and magnetism, and the preparation of **1**, **2**, and **4** is a contribution to this analysis, which will be more thoroughly discussed in a subsequent publication.

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Registry No. **1**, 86646-35-7; **2**, 86646-36-8; **3**, 86646-37-9; **4**, 86646-38-0; **5**, 86646-39-1.

Supplementary Material Available: Listings of atomic thermal parameters and of observed and calculated structure amplitudes (21 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Molecular Structure Center,
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Isoelectronic Molecules with Triple Bonds to Metal Atoms (M = Mo, W): Crystal and Molecular Structures of Tri-*tert*-butoxytungsten Ethylidyne and Nitride

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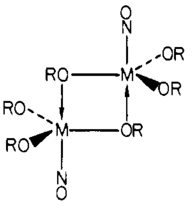
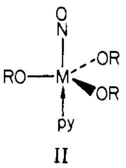
The crystal and molecular structures of $(t\text{-BuO})_3W{\equiv}CMe$ and $(t\text{-BuO})_3W{\equiv}N$ have been determined. In both compounds, tungsten is in a trigonal-bipyramidal geometry with the M≡X function in an axial position. The ethylidyne compound has a centrosymmetric structure involving two trigonal-bipyramidal units joined along a common axial–equatorial edge by a pair of bridging O-*t*-Bu ligands. The nitrido compound is a linear polymer involving alternating short (1.74 (1) Å) and long (2.66 (1) Å) W–N distances corresponding to localized triple and weak dative bonds, respectively. These molecules are members of a more extensive series of compounds containing M≡X functions, where X = NO and $M(OR)_3L$ and M = Mo and W, and structural comparisons are made. For X = CMe, N, and NO trigonal-bipyramidal geometries are found, whereas Lewis base adducts of $M_2(OR)_6$ compounds favor square-based pyramidal geometries with the M≡M bond in the apical position. Crystal data at −160 °C for $(t\text{-BuO})_3W{\equiv}CMe$: $a = 10.317$ (3) Å, $b = 9.517$ (3) Å, $c = 10.891$ (3) Å, $\alpha = 98.90$ (2)°, $\beta = 67.05$ (2)°, $\gamma = 115.24$ (2)°, $Z = 1$, $d_{\text{calcd}} = 1.604$ g cm^{-3} in space group $P\bar{1}$. $(t\text{-BuO})_3W{\equiv}N$: $a = 10.159$ (2) Å, $b = 10.159$ (2) Å, $c = 8.801$ (2) Å, $\gamma = 120.00$ (1)°, $Z = 2$, $d_{\text{calcd}} = 1.761$ g cm^{-3} in space group $P6_3cm$.

Introduction

It has previously been noted[1,2] that NO reacts with hydrocarbon solutions of $M_2(OR)_6$ (M≡M) compounds, where M = Mo[3] and W,[4] to cleave the M≡M bond. In a formal sense, the M≡M bond consisting of one σ and two π components is replaced by two metal–ligand triple bonds, M≡N→O. The structures of $[Mo(O\text{-}i\text{-}Pr)_3NO]_2$[1] and $W(O\text{-}t\text{-}Bu)_3(NO)(py)$[2] are depicted by I and II, which emphasize the trigonal-bipyramidal coordination of the metal atom.


I


II

The recent syntheses[5] of compounds of formula $(t\text{-BuO})_3W{\equiv}CMe$ and $(t\text{-BuO})_3W{\equiv}N$ by cleavage of the W≡W bond in reactions of $W_2(O\text{-}t\text{-}Bu)_6$ with MeC≡CMe and MeC≡N, respectively, provide access to an extensive series of isoelectronic molecules containing the M≡X function supported by strongly π-donating ligands. We show here that the structures of these molecules fall into one of two classes: trigonal bipyramids when X = CMe, N, and NO and square-based pyramids when X = $M(OR)_3L$.

Table I. Fractional Coordinates for the $[(t\text{-BuO})_3W{\equiv}CMe]_2$ Molecule

atom	10^4x	10^4y	10^4z
W(1)	1522.0 (2)	4969.8 (3)	3529.4 (2)
C(2)	3055 (7)	4378 (7)	2792 (6)
C(3)	4365 (9)	3879 (10)	2159 (8)
O(4)	2535 (5)	7147 (5)	3305 (4)
C(5)	4080 (7)	8306 (8)	2752 (7)
C(6)	5061 (9)	8174 (10)	3427 (10)
C(7)	3944 (10)	9849 (9)	3032 (10)
C(8)	4708 (10)	8022 (11)	1254 (8)
O(9)	257 (5)	3826 (5)	2531 (4)
C(10)	259 (7)	2680 (7)	1498 (6)
C(11)	1709 (9)	3393 (10)	262 (7)
C(12)	192 (12)	1252 (9)	2002 (9)
C(13)	−1171 (8)	2329 (10)	1208 (8)
O(14)	−693 (5)	5723 (5)	4639 (4)
C(15)	−1212 (8)	6532 (8)	3970 (7)
C(16)	−173 (9)	6860 (9)	2523 (7)
C(17)	−2841 (8)	5433 (10)	4046 (8)
C(18)	−1147 (9)	8046 (8)	4684 (8)

Results and Discussion

Crystals of $(t\text{-BuO})_3W{\equiv}CMe$ were grown by vacuum sublimation, and from an X-ray study, the molecular structure was found to be of type I. An ORTEP view of the molecule is shown in Figure 1. Atomic positional parameters are given in Table I, and pertinent bond distances and angles are reported in Table II. Complete listings of bond distances and angles and anisotropic thermal parameters are available in the supplementary material.

The association by alkoxy bridge formation is very weak, as evidenced by the extremely long W–O (axial) bond distance, 2.484 (4) Å, which occurs with little lengthening of the equatorial W–O bond. Compare W–O = 1.934 (4) Å for the equatorial bridging O-*t*-Bu bond with W–O = 1.89 (1) Å (averaged) for the two other W–O-*t*-Bu ligands. The W–O bridging axial distance, 2.484 (4) Å, may be compared with the related Mo–O distance, 2.195 (6) Å, in $[(i\text{-PrO})_3MoNO]_2$,[1]

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(1) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3354.
(2) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116.
(3) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.
(4) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.
(5) Schrock, R. R.; Listermann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

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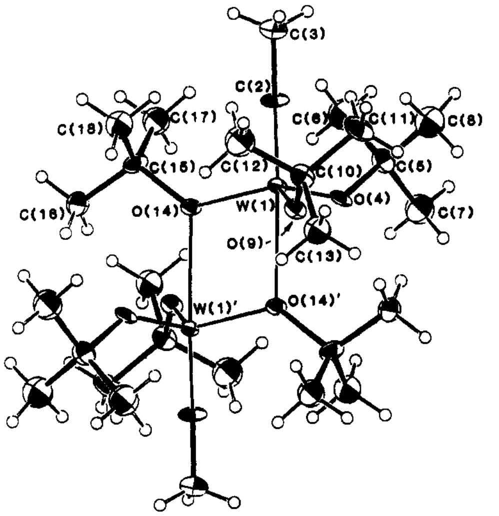

Figure 1. ORTEP view of the centrosymmetric $[(t\text{-BuO})_3W{\equiv}CMe]_2$ molecule showing the atom numbering scheme used in the tables.

Table II. Selected Bond Distances (Å) and Angles (deg) for the $[(t\text{-BuO})_3W{\equiv}CMe]_2$ Molecule

A	B	dist
W(1)	W(1)'	3.518 (1)
W(1)	O(4)	1.886 (4)
W(1)	O(9)	1.897 (4)
W(1)	O(14)	1.934 (4)
W(1)	O(14)'	2.484 (4)
W(1)	C(2)	1.759 (6)
O(4)	C(5)	1.441 (8)
O(9)	C(10)	1.441 (7)
O(14)	C(15)	1.497 (8)
C(3)	C(2)	1.499 (9)
C	C	1.52 (1)[a]

A	B	C	angle
O(4)	W(1)	O(9)	118.8 (2)
O(4)	W(1)	O(14)	113.7 (2)
O(4)	W(1)	O(14)'	79.5 (2)
O(4)	W(1)	C(2)	102.3 (2)
O(9)	W(1)	O(14)	114.6 (2)
O(9)	W(1)	C(2)	101.2 (2)
O(14)	W(1)	O(14)'	75.1 (2)
O(14)	W(1)	C(2)	102.8 (2)
W(1)	O(4)	C(5)	138.5 (4)
W(1)	O(9)	C(10)	137.0 (4)
W(1)	O(14)	W(1)	104.9 (2)
W(1)	O(14)	C(15)	129.9 (4)
W(1)	C(2)	C(3)	179.8 (6)

[a] Averaged, *t*-Bu.

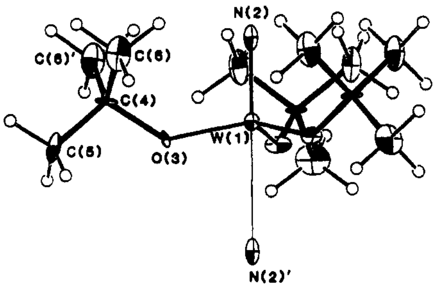

Figure 2. ORTEP view of the repeating unit along the *c* axis of the $[(t\text{-BuO})_3W{\equiv}N]_x$ polymer showing the atom number scheme used in the tables.

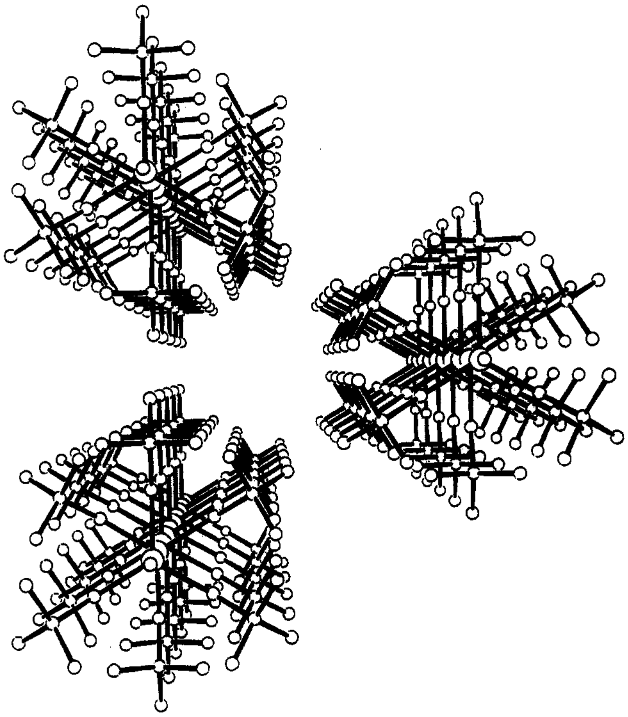

Figure 3. View of the $[W(O\text{-}t\text{-}Bu)_3N]_x$ polymer viewed down the *c* axis from a point at $x = {}^1/_3$, $y = {}^2/_3$. Five cells along the *c* axis are shown. Hydrogen atoms have been omitted. In the space group $P6_3cm$, there is a hexagonal network of tungsten atoms perpendicular to the *c* axis at a translation *c*/2.

Table III. Fractional Coordinates for the $[(t\text{-BuO})_3W{\equiv}N]_x$ Molecule

atom	10^4x	10^4y	10^4z
W(1)	0[a]	0[a]	2492[a]
N(2)	0[a]	0[a]	4469 (17)
O(3)	8195 (7)	8195[a]	2065 (9)
C(4)	6961 (13)	6961[a]	2949 (11)
C(5)	5844 (13)	5844[a]	1858 (19)
C(6)	2350 (13)	−1390 (14)	3987 (16)

[a] Fixed by space-group symmetry.

which adopts the structure depicted by I. Undoubtedly, $(t\text{-BuO})_3W{\equiv}CMe$ is mostly monomeric in solution and the vapor state.

The molecular structure of $(t\text{-BuO})_3W{\equiv}N$ was determined from an X-ray study on crystals grown from hot toluene solutions. This revealed a fascinating linear polymeric structure, based on II, with alternating short, 1.740 (15) Å, and long, 2.661 (15) Å, W–N distances indicative of triple and weak dative bonds, respectively. A view of the basic repeating unit is given in Figure 2, and a view showing the arrangement of the chains in the lattice is shown in Figure 3. Atomic positional parameters are given in Table III, and pertinent bond distances and angles are given in Table IV. Tables of hydrogen coordinates, anisotropic thermal parameters, and complete listings of bond distances and angles, including H atoms, are given in the supplementary material.

A comparison of the $W(O\text{-}t\text{-}Bu)_3(NO)(py)$[2] and $[W(O\text{-}t\text{-}Bu)_3N]_x$ structures is most interesting. The W—NO (1.732 (8) Å) and the W≡N (1.740 (15) Å) distances are essentially identical, as are the N–W–O and W–O–C angles and the N–W–O–C dihedral angles.

The W–N distance, 2.66 (1) Å, in $[(t\text{-BuO})_3W{\equiv}N]_x$ is barely short enough to call a bond; cf. W–N(py) = 2.323 (7) Å in $(t\text{-BuO})_3W(NO)(py)$.[2] However, it is of comparable length to other distances in compounds where a weak axial ligation occurs trans to a M–M multiple bond. For example, in $W_2(O_2CNMe_2)_6$ there are weak, long W–O axial bonds of length 2.67 (2) Å (averaged).[6] In $[(t\text{-BuO})_3W{\equiv}N]_x$, the

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[6] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4683; *Inorg. Chem.* **1977**, *16*, 603.

Table IV. Bond Distances (Å) and Angles (deg) for the $[(t\text{-BuO})_3W\equiv N]_x$ Molecule

A	B	dist
W(1)	O(3)	1.872 (7)
W(1)	N(2)	1.740 (15)
W(1)	N(2)′	2.661 (15)
O(3)	C(4)	1.475 (14)
C(4)	C(5)	1.487 (20)
C(4)	C(6)	1.527 (13)

A	B	C	angle
O(3)′	W(1)	O(3)	116.1 (2)
O(3)	W(1)	N(2)	101.6 (1)
O(3)	W(1)	N(2)′	78.4 (2)
W(1)	O(3)	C(4)	136.6 (6)
O(3)	C(4)	C(5)	108.0 (8)
O(3)	C(4)	C(6)	108.6 (8)
C(5)	C(4)	C(6)	112.6 (8)
C(6)	C(4)	C(6)	106.5 (12)

axial coordination trans to the $W\equiv N$ group involves the nitride ligand rather than an alkoxy ligand, and the resultant polymeric structure makes the nitride much less soluble in hydrocarbon solvents and also less volatile than the alkylidyne compound.

To our knowledge, $(t\text{-BuO})_3W\equiv N$ is the first compound of formula $[X_3M\equiv N]_n$, $X_3LM\equiv N$, or $[X_4M\equiv N]^-$ to adopt a structure based on a trigonal-bipyramidal geometry. All known structures are based on square-based pyramidal geometries with the $M\equiv N$ group in the axial position.[6] The difference may be a result of the strong π-donating ability of the alkoxy ligands.

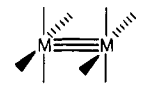
Table V. Summary of Crystallographic Data[a]

	I	II
fw	860.48	417.200
space group	$P\bar{1}$	$P6_3cm$
a, Å	10.317 (3)	10.159 (2)
b, Å	9.517 (3)	
c, Å	10.891 (3)	8.801 (1)
α, deg	98.90 (2)	
β, deg	67.05 (2)	
γ, deg	115.24 (2)	
Z	1	2
V, $Å^3$	890.58	786.62
d(calcd), g/cm^3	1.604	1.761
cryst size, mm	0.03 × 0.03 × 0.04	0.24 × 0.06 × 0.04
cryst color	colorless	colorless
radiation	Mo Kα (λ = 0.710 69 Å), graphite monochromator	
linear abs coeff, cm^{-1}	66.24	74.98
transmission factors	no absorption corr	0.656–0.737
temp, °C	−160	−160
instrument	Picker 4-circle diffractometer, locally modified and interfaced	
detector aperture	3.0 mm wide × 4.0 mm high, 22.5 cm from cryst	
sample to source dist	23.5 cm	
takeoff angle, deg	2.0	2.0
scan speed, deg/min	3.0	3.0
scan width, deg	1.8 + 0.692 tan θ	1.8 + 0.692 tan θ
bkgd counts, s	4 at each end of scan	4 at each end of scan
2θ range, deg	6–45	6–45
data collected	2502 total	2231 total
unique data	2322	208
unique data with $F_o > 3\sigma(F_o)$	2273	173
no. of variables	284	53
$R(F)$	0.026	0.017
$R_w(F)$	0.028	0.012
goodness of fit	1.194	1.695
largest Δ/σ	0.05	0.05

[a] Compound I = $[(t\text{-BuO})_3W\equiv CMe]_2$; compound II = $[(t\text{-BuO})_3W\equiv N]_x$.

If the axial $M\equiv X$ bond is taken to be coincident with the *z* axis, metal atomic d_{z^2}, d_{xz}, and d_{yz} orbitals will be used to form the triple bond. The M–OR σ bonds may use metal atomic s, p_x, and p_y orbitals, and the in-plane d_{xy} and $d_{x^2-y^2}$ orbitals may be used to form π bonds by interaction with filled oxygen p orbitals. Note that if the oxygen is considered to be sp^2 hybridized, which is consistent with the W–O–C angle of 136°, then one sp^2 hybrid orbital, the lone pair, is directed away from tungsten. (It is this lone pair that is used to form the RO bridges in $[(t\text{-BuO})_3W\equiv CMe]_2$.) The remaining three oxygen p orbitals (one per oxygen) are confined to the *xy* plane and may be used to π-donate to the vacant tungsten d_{xy} and $d_{x^2-y^2}$ orbitals. Thus, as a result of forming a triple bond $M\equiv X$ and three σ bonds supplemented by two π bonds to the *t*-BuO ligands, a monomeric species $(t\text{-BuO})_3W\equiv X$ would yield a 16-electron valence shell for tungsten. In the absence of strongly π-donating ligands, the formation of an additional M–L bond could occur by coordination in either the equatorial plane or the axial position to give square-based pyramidal and trigonal-bipyramidal geometries, respectively. Simple considerations of trans influence[8] would lead one to expect the former, and this surely accounts for the observation of the square-pyramidal geometries in the anions $[MNX_4]^-$, where M = Mo, Re, Ru, Os and X = F, Cl, Br, I.[7,9] However, when the equatorial ligands are strong π donors, the formation of a new M–L σ bond in the *xy* plane would occur with loss of a π bond. Thus, a weak association may be preferred in the axial position, providing this does not significantly weaken the trans $X\equiv M$ bond. This trigonal-bipyramidal geometry is seen in the isoelectronic series $[M(OR)_3(NO)]_2$, $M(OR_3\text{-}(NO)L$, $[W(O\text{-}t\text{-Bu})_3(CMe)]_2$, $[W(O\text{-}t\text{-Bu})_3N]_x$, and $[M(O\text{-}t\text{-Bu})_2(NAr)(\mu\text{-NAr})]_2$,[10] and in each instance RO ligands occupy equatorial positions.

The compounds $M_2(OR)_6$ ($M\equiv M$), which may be viewed as members of the series $(RO)_3M\equiv X$, where X = $M(OR)_3$, expand their coordination geometries by forming bonds in the *xy* plane as depicted by III (no rotational preference is implied). This has been seen in a number of structures of amine, pyridine, or phosphine adducts of formula $M_2(OR)_6L_2$[11] and also in the compounds $M_2(OR)_4(O_2CX)_2$, where X = OR[12] and Ph.[13]



III

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(7) Dehnicke, K.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413 and references therein.

(8) Appleton, T. G.; Clark, H. C.; Manzer, L. M. *Coord. Chem. Rev.* **1973**, *10*, 335.

(9) A number of polymeric structures are also found in which a square-based pyramidal unit is weakly ligated in the position trans to the $M\equiv N$ bond. This may give rise to square-planar tetrameric structures as in $MoNCl_3$ or linear polymers as in $ReNCl_4$. See Strahle and Liese et al., respectively: Strahle, J. *Z. Anorg. Allg. Chem.* **1970**, *375*, 238; **1971**, *380*, 96. Liese, W.; Dehnicke, K.; Walker, I.; Strahle, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 693.

(10) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratermann, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 1305; *Inorg. Chem.* **1982**, *21*, 978.

(11) $Mo_2(OSiMe_3)_6(HNMe_2)_2$: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 153. $W_2(OPr)_6(py)_2$: ref 4. $W_2(OCH_2\text{-}t\text{-Bu})_6(PMe_3)_2$: Chetcuti, M. J.; Chisholm, M. H.; Huffman, J. C.; Leonelli, J., submitted for publication in *J. Am. Chem. Soc.* Other structures include $Mo_2(O\text{-}i\text{-Pr})_6(py)_2$, $Mo_2(OCH_2\text{-}t\text{-Bu})_6(py)_2$, and $W_2(O\text{-}i\text{-Pr})_6(HNMe_2)_2$: Leonelli, J. Ph.D. Thesis, Indiana University, Bloomington, IN, 1982.

(12) M = Mo, R = *t*-Bu, *i*-Pr, CH_2-*t*-Bu and M = W, R = *t*-Bu: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 1727.

(13) Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C., submitted for pulication in *Inorg. Chem.*

Clearly, III is not favored by either steric factors or RO-to-M π bonding. The difference in geometry may result from the fact that the $M\equiv M$ bond, which is weaker than $M\equiv N$, $M\equiv C$, and M—NO bonds in these compounds, is more sensitive to bond weakening by axial ligand coordination. The structures of $W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$ show that axial coordination is avoided relative to coordination in the *xy* plane.[6]

Detailed studies of the electronic structures of these fascinating molecules are planned.

Experimental Section

The compounds $(t\text{-BuO})_3W\equiv CMe$ and $(t\text{-BuO})_3W\equiv N$ were prepared from the reactions between $W_2(O\text{-}t\text{-Bu})_6$ and $MeC\equiv CMe$ and $MeC\equiv N$ as described by Schrock.[5]

The alkylidyne complex was purified by vacuum sublimation (40 °C, 10^{-4} torr). Because it is extremely soluble in hydrocarbon solvents, crystallization from solution was not successful. Crystals suitable for X-ray studies were obtained by sublimation.

The nitrido compound was purified by sublimation (110 °C, 10^{-4} torr) and crystallized from hot toluene. (It is only very sparingly soluble in hydrocarbon solvents at room temperature.) Long hexagonal rods were obtained in this manner.

X-ray Crystallography. General procedures and a library of programs have been given previously.[14]

$[(t\text{-BuO})_3W\equiv CMe]_2$. Colorless crystals were transferred to a nitrogen-filled glovebag in sealed ampules. The sample appeared highly reactive, darkening immediately when the ampules were opened, although subsequent examination indicated crystals of excellent quality. A systematic search of a limited hemisphere of reciprocal space revealed no systematic absences or symmetry, leading to the assignment of the triclinic space group. Complete crystallographic data are given in Table V. The structure was solved by Patterson and Fourier techniques. ψ scans of several reflections indicated a maximum variation of 5% in ψ, so no absorption correction was applied. All hydrogen atoms were located, and the final full-matrix refinement included all postional parameters, isotropic thermal parameters for hydrogen atoms, and anisotropic thermal parameters for non-hydrogen atoms. A final difference Fourier was featureless, the largest peak (1.3 e/Å^3) lying 0.4 Å from the tungsten.

$[(t\text{-BuO})_3W\equiv N]_x$. A hexagonal needle approximately 0.05 mm in diameter was cleaved to yield a well-formed prism 0.24 mm in length. A systematic search of limited hemispheres of reciprocal space revealed a trigonal lattice with a general pseudoextinction such that all *hkl* for $l = 2n + 1$ were weak. It was difficult to determine what, if any, space group extinctions were present because of the psuedoextinction. Crystal and diffractometer data are given in Table V.

The structure was initially solved in space group $P3c1$ by placing the tungsten atom at $z = {}^1/_4$ on the *c* axis. A difference Fourier phased on the tungsten ($R(F) = 0.14$) revealed all remaining non-hydrogen atoms. Full-matrix refinement converged to $R(F) = 0.028$. Examination of the coordinates at this stage revealed that all atoms were within 1 σ of a higher order symmetry, and the space group was thus transformed to $P6_3cm$. Full-matrix refinement in this setting rapidly converged to $R(F) = 0.017$, indicating the proper setting. A final difference Fourier was featureless, the largest peak being 0.6 e/Å^3.

Acknowledgment. We thank the National Science Foundation and the Wrubel Computing Center for support.

Registry No. $(t\text{-BuO})_3W\equiv CMe$, 86669-24-1; $(t\text{-BuO})_3W\equiv N$, 86669-26-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, fractional coordinates, and thermal parameters for hydrogen atoms, complete tables of distances and angles, and listings of observed and calculated structure amplitudes for $[(t\text{-BuO})_3W\equiv CMe]_2$ and $[(t\text{-BuO})_3W\equiv N]_x$ (24 pages). Ordering information is given on any current masthead page. Crystallographic data are also available, in microfiche form, from the Chemistry Library, Indiana University Chemistry Department. Request MSC Report No. 82083 for $[(t\text{-BuO})_3W\equiv CMe]_2$ and 82087 for $[(t\text{-BuO})_3W\equiv N]_x$.

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Dinuclear Aryloxide Chemistry. 1. A Direct Comparison of Aryloxide and Alkoxide Coordination to a Dimetal Center. Synthesis and Structure of 1,2-Bis(isopropoxy)tetrakis(2,6-dimethylphenoxy)dimolybdenum ($Mo\equiv Mo$)

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The preparation and characterization of the compound 1,2-$Mo_2(O\text{-}i\text{-}Pr)_2(OAr)_4$ (OAr = 2,6-dimethylphenoxide) are reported. Structural analysis of the compound has allowed a direct comparison of alkoxide and aryloxide coordination to a dimetal center from which it was concluded that although not expected to be as good a π-donor ligand as alkoxide, aryloxide has a greater ability to form large M–O–C angles and thus relieve steric strain at the metal. Crystal data for $Mo_2(O\text{-}i\text{-}Pr)_2(OAr)_4$ at −163 °C were $a = 18.169$ (6) Å, $b = 11.327$ (3) Å, $c = 10.678$ (3) Å, $\alpha = 99.58$ (2)°, $\beta = 57.82$ (2)°, $\gamma = 97.63$ (2)°, $Z = 2$, and $d_{\text{calcd}} = 1.441$ g cm^{-3}, with space group $P\bar{1}$.

Introduction

One important characteristic of early-transition-metal alkoxide chemistry is the ability of the ligand to undergo oxygen p-to-metal-d π bonding.[1] This has been used to account for a number of physical and chemical properties of alkoxides. Structural studies have shown that M–O distances associated with alkoxy groups can be very short, implying varying amounts of multiple bond character. Similarly π donation by the alkoxy group is associated with large M–O–C angles, sometimes 160°, and this is rationalized as being due to partial rehybridization at the oxygen to promote the nonbonding lone pairs into p orbitals of correct symmetry for overlap with metal d orbitals. In the extreme case, a linear M–O–C unit con-

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