generated by coupling of CO with an alkylidene moiety. The isotope effect on the (**1**):(**3** + **4**) yield ratio is also consistent with, although it does not require, the intervention of an alkyl species. Jeffery et al.[26] have demonstrated the stepwise conversion of an alkylidyne ligand to a bridging acyl ligand via an unsymmetrically bridging alkyl at a Re–W bimetallic center, and the alkylidyne–alkyl–acyl sequence was proposed for a related heterotrinuclear system as well.[27] Recently, we[28] have shown that the sequence can be taken a step further to regenerate an alkylidyne ligand—but containing one more methylene group—by thermal cleavage of the acyl ligand in **1**.

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Registry No. **1**, 93454-10-5; **2**, 80028-15-5; **3**, 85335-18-8; **4**, 104439-75-0; **5**, 104439-76-1; **6**, 104463-65-2; **7**, 86885-48-5; $H_2Os_3(CO)_{10}$, 41766-80-7; $CpW(CO)_2(CTol)$, 60260-15-3; $CpW(CO)_3H$, 12128-26-6; D_2, 7782-39-0.

Supplementary Material Available: Tables of hydrogen atom positions and anisotropic thermal parameters (1 page); a table of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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Contribution from the Central Research and Development Department, E.I. du Pont de Nemours and Company, Inc.,
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Trialkoxynitridomolybdenum Compounds: $(RO)_3Mo{\equiv}N$. Preparation, Structures (R = *t*-Bu and *i*-Pr), and Comparisons with a Tungsten Analogue (R = *t*-Bu)[†]

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The compound $(t\text{-BuO})_3Mo{\equiv}N$ is formed in the reaction between $Cl_3Mo{\equiv}N$ and LiO-*t*-Bu (3 equiv) in THF and is obtained as a white crystalline compound by either sublimation (85 °C, 5×10^{-3} torr) or recrystallization from toluene. In the solid state the compound forms a linear polymer $[(t\text{-BuO})_3Mo{\equiv}N]$ involving alternating short, 1.66 (1) Å, and long, 2.86 (2) Å, Mo–N bonds, corresponding formally to triple and weak dative bonds, respectively. In benzene solution, a cryoscopic molecular weight determination indicates the monomeric species is present. The solubilities of the compounds $[(t\text{-BuO})_3M{\equiv}N]$ where M = Mo and W differ quite markedly, with the molybdenum compound being appreciably more soluble in aromatic solvents. It is suggested that this results from different M≡N—M bonding along the infinite chain with the tungsten compound having a more basic or nucleophilic nitrogen atom. This suggestion finds support from MO calculations employing the Fenske–Hall method. The W≡N distance is significantly longer (1.740 (15) Å) and the W–N distance shorter (2.661 (15) Å). Furthermore, the molybdenum and tungsten compounds differ in their reactivity toward alcohols, yielding, respectively, $(RO)_3Mo{\equiv}N$ and $W(OR)_6$ (R = *i*-Pr, *neo*-Pe, Et) and ammonia. These results are compared with other nitrido compounds of molybdenum and tungsten. Crystal data for $(t\text{-BuO})_3Mo{\equiv}N$ (**1**): at −90 °C, a = 10.125 (3) Å, b = 10.125 (3) Å, c = 9.087 (2) Å, γ = 120.00°, Z = 2, d_{calcd} = 1.356 g cm^{-3}, and the space group is $P6_3cm$; at −160 °C, a = 10.060 (4) Å, b = 10.060 (4) Å, c = 9.035 (3) Å, γ = 120.00°, Z = 2, d_{calcd} = 1.381 g cm^{-3}, and the space group is $P6_3$. Crystal data for $(i\text{-PrO})_3M{\equiv}N$: space group $P6_3cm$, a = 9.877 (3) Å, b = 9.877 (3) Å, c = 8.223 (2) Å, γ = 120.00°, Z = 2, and d_{calcd} = 1.373 g cm^{-3}.

Introduction

The reaction between $(t\text{-BuO})_3W{\equiv}W(O\text{-}t\text{-Bu})_3$ and nitriles in hydrocarbon solvents proceeds[1] according to eq 1. The ni-

$$W_2(O\text{-}t\text{-Bu})_6 + RC{\equiv}N \xrightarrow{25\ ^\circ C} (t\text{-BuO})_3W{\equiv}N + (t\text{-BuO})_3W{\equiv}CR \quad (1)$$

$$R = \text{alkyl or aryl}$$

tridotungsten compound is readily separated from the alkylidyne derivative because the nitride is sparingly soluble in hydrocarbon solvents.

Rather interestingly, alkane- and arenenitriles do not show any reactivity toward $Mo_2(O\text{-t-Bu})_6$, though dimethylcyanamide forms a 1:1 adduct, $Mo_2(O\text{-}t\text{-Bu})_6(NCNMe_2)$.[2,3] We report here simple syntheses of the $(RO)_3Mo{\equiv}N$ compounds together with characterization data and a comparison with a tungsten analogue, $(t\text{-BuO})_3W{\equiv}N$.[4]

Results and Discussion

Synthesis. The compound $(\text{t-BuO})_3Mo{\equiv}N$ is formed by the reactions shown in eq 2.

$$MoCl_4(L)_2 + Y\text{–}N_3 \xrightarrow[\text{solvent = L}]{25\ ^\circ C} MoCl_3(N) + YCl + N_2 + 2L \quad (2i)$$

$$Y = \text{Na or } Me_3Si;\ L = \text{THF or } CH_3CN$$

$$MoCl_3(N) + 3LiO\text{-}t\text{-Bu} \xrightarrow[\text{THF/toluene}]{25\ ^\circ C} (t\text{-BuO})_3MoN + 3LiCl \quad (2ii)$$

The synthesis takes advantage of the established routes to $MoCl_3(N)$[5,6] followed by a metathetic reaction involving LiO-*t*-Bu.

[†] Contribution No. 3833 from the Central Research and Development Department.

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Table I. Summary of Crystal Data

empirical formula	$C_{12}H_{27}MoNO_3$[a]	$C_{12}H_{27}MoNO_3$	$C_9H_{21}MoNO_3$[b]
color of cryst	colorless	colorless	yellow
cryst dimens, mm	0.035 × 0.035 × 0.08	0.035 × 0.035 × 0.08	0.10 × 0.10 × 0.12
space group	$P6_3cm$	$P6_3$	$P6_3cm$
cell dimens			
temp, °C	−90	−160	−154
a, Å	10.125 (3)	10.060 (4)	9.877 (3)
c, Å	9.087 (2)	9.035 (3)	8.223 (2)
Z (molecules/cell)	2	2	2
vol, Å^3	806.70	791.73	694.88
calcd density, g/cm^3	1.356	1.381	1.373
wavelength, Å	0.71069	0.71069	0.71069
mol wt	329.29	329.29	287.21
linear abs coeff, cm^{-1}	7.915	8.062	9.088
scan method			
detector to sample distance, cm	22.5	22.5	22.5
sample to source distance, cm	23.5	23.5	23.5
av ω scan width at half-height, deg	2.0	2.0	
scan speed, deg/min	4.0	4.0	4.0
scan width, deg + dispersion	2.0	2.0	2.0
indiv bkgd, s	6	6	8
aperture size, mm	3.0 × 4.0	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6–55	6–55	6–45
total no. of reflecns collected	1458	3291	1173
no. of unique intens	363	1221	224
no. with $F > 0.0$	309	1045	
no. with $F > 2.33\sigma(F)$	258	763	
no. with $F > 3.00\sigma(F)$			170
no. of parameters	56	94	
$R(F)$	0.0244	0.0348	0.0406
$R_w(F)$	0.0193	0.0256	0.0480
goodness of fit for the last cycle	0.565	0.700	1.831
max Δ/σ for last cycle	0.03	0.02	0.05

[a] $C_{12}H_{27}MoO_3$ = (*t*-BuO)$_3$Mo≡N. [b] $C_9H_{21}MoNO_3$ = (*i*-PrO)$_3$Mo≡N.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for the (*t*-BuO)$_3$Mo≡N Molecule at −160 °C[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
Mo(1)	0*	0*	7508*	9
N(2)	0*	0*	9360 (6)	11
O(3)	162 (3)	−1738(3)	7022 (3)	12
C(4)	115 (5)	−2994 (4)	7874 (4)	14
C(5)	356 (7)	−3986 (6)	6754 (5)	21
C(6)	1384 (6)	−2346 (6)	9030 (6)	19
C(7)	−1460 (6)	−3878 (6)	8617 (7)	24
H(1)	−52 (7)	−439 (7)	574 (7)	42 (14)
H(2)	26 (4)	−477 (5)	718 (5)	6 (9)
H(3)	128 (6)	−352 (6)	613 (6)	17 (10)
H(4)	141 (6)	−316 (6)	963 (5)	23 (13)
H(5)	114 (6)	−170 (6)	981 (8)	30 (12)
H(6)	232 (7)	−167 (6)	863 (6)	23 (12)
H(7)	−226 (6)	−427 (6)	796 (6)	27 (13)
H(8)	−145 (7)	−315 (7)	936 (6)	24 (13)
H(9)	−167 (6)	−477 (6)	924 (5)	11 (10)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated by using the formula give by: Hamilton, W. C.; *Acta Crystallogr.* **1959**, *12*, 609. Parameters marked by an asterisk were not varied.

The reaction can be carried out in one reaction vessel without the isolation of the initially formed compound $MoCl_3(N)$. The compound (*t*-BuO)$_3$Mo≡N is obtained as a white crystalline analytically pure material from the crude reaction mixture obtained upon removal of the solvent by either sublimation at 85 °C (5 × 10^{-3} torr) or by extraction with toluene followed by crystallization. Yields based on molybdenum are typically in the range 60–80%.

It was found that less sterically hindered alkoxide derivatives (RO)$_3$Mo≡N could be prepared by alcohol-exchange reactions wherein an excess of alcohol, ROH (where R = *i*-Pr, *neo*-Pe (CH_2CMe_3), and Et) was added to a hydrocarbon solution of (*t*-BuO)$_3$Mo≡N. Purification by sublimation or recrystallization from concentrated hexane solutions gave analytically pure samples of the compound (RO)$_3$Mo≡N.

Physicochemical Properties. (RO)$_3$Mo≡N compounds are moisture-sensitive and should be handled in dry and oxygen-free atmospheres. They are appreciably soluble in aromatic solvents and methylene chloride. A cryoscopic molecular weight determination for (*t*-BuO)$_3$Mo≡N in benzene gave a molecular weight indicative of a monomer. In the infrared spectra obtained from Nujol mull strong sharp absorptions in the region of 1020–990 cm^{-1} are assigned to ν(Mo≡N). The spectrum for (*t*-BuO)$_3$Mo≡N is essentially identical with that of (*t*-BuO)$_3$Mo≡N, which shows ν(W≡N) = 1010 cm^{-1} and ν(W≡^{15}N) = 990 cm^{-1}. (A ^{15}N-labeled Mo compound has not been synthesized.) The ^{1}H NMR spectra for the (RO)$_3$Mo≡N compounds show only one set of signals assignable to the three chemically equivalent alkoxide ligands.

The compounds (*t*-BuO)$_3$M≡N, where M = Mo and W, are very similar in their physical properties, but the molybdenum compound is appreciably more soluble in aromatic hydrocarbon solvents. In toluene at 26 °C, the molybdenum compound shows a solubility of 0.067 mol L^{-1} while the tungsten compound has a solubility of 0.012 mol L^{-1}. It is also interesting to note that the Mo compound is more volatile and sublimes more readily than the tungsten compound: cf. 85 vs. 110 °C at 5 × 10^{-3} torr. Both factors indicate that the dative Mo–N bond is more easily broken than the dative W–N bond.

Solid-State and Molecular Structures of (RO)$_3$Mo≡N Compounds. When they are cooled to −160 °C, crystals of (*t*-BuO)$_3$Mo≡N undergo a reversible phase transition. At −160 °C, the space group is $P6_3$, while at −90 °C, the space group is $P6_3cm$. The latter is the space group observed for (*t*-BuO)$_3$W≡N at −158 °C.[4] Accordingly, crystal data were collected for the molybdenum compound in both space groups and the structures solved in each. The crystal data are summarized in Table I; fractional coordinates and isotropic thermal parameters are given in Tables II and III. The molecular structures at −90 and −160 °C differ by less than 3σ in terms of bond distances and angles. The essential difference

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Table III. Fractional Coordinates and Isotropic Thermal Parameters for the $(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}$ Molecule at −90 °C[a]

atom	x	y	z	B_{iso}, Å^2
Mo(1)	0*	0*	7508*	14
N(2)	0*	0*	9336 (9)	18
O(3)	1809 (4)	1809*	7033 (5)	19
C(4)	3030 (6)	3030*	7871 (6)	22
C(5)	4152 (8)	4152*	6764 (10)	45
C(6)	3778 (7)	2353 (7)	8832 (9)	38
H(1)	492 (9)	492*	733 (13)	33 (16)
H(2)	451 (7)	359 (7)	622 (6)	41 (15)
H(3)	416 (6)	194 (7)	813 (6)	41 (14)
H(4)	466 (6)	314 (6)	933 (4)	26 (11)
H(5)	286 (9)	164 (11)	959 (10)	87 (25)

[a] See footnote *a* of Table II.

Table IV. Comparison of Pertinent Structural Parameters for the Compounds $[(\text{RO})_3\text{M}{\equiv}\text{N}]$, Where M = Mo[a] and W,[b] and R = *t*-Bu, *i*-Pr

	M = W	M = Mo		
param	R = *t*-Bu	R = *t*-Bu	R = *t*-Bu	R = *i*-Pr
space group	$P6_3cm$	$P6_3cm$	$P6_3$	$P6_3cm$
M≡N, Å	1.740 (15)	1.661 (4)	1.673 (5)	1.597 (26)
M—N, Å	2.661 (15)	2.883 (8)	2.844 (5)	2.515 (26)
M—O, Å	1.872 (7)	1.882 (4)	1.888 (3)	1.894 (17)
N≡M—O, deg	101.6 (1)	103.27 (13)	103.45 (9)	101.1 (9)
M—O—C, deg	136.6 (6)	135.1 (3)	134.33 (23)	128.6 (18)
O—M—O, deg	116.1 (2)	114.9 (1)	114.76 (7)	116.4 (6)

[a] This work. [b] From ref 4.

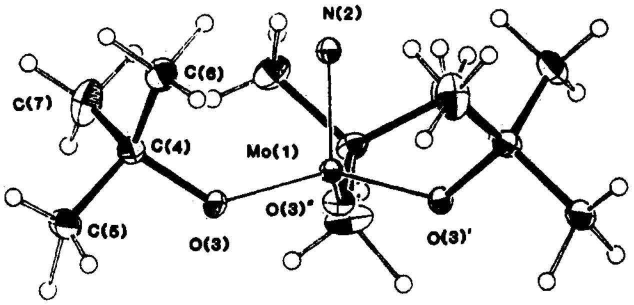


Figure 1. ORTEP drawing of the $(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}$ unit in the $[(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}\cdots]$ polymer viewed perpendicular to the −Mo≡N-----Mo≡N− axis. At −160 °C, the molecular unit has C_3 rather than C_{3v} symmetry; thereby C(6) and C(7) are not symmetry-related by a mirror plane in the low-temperature structure.

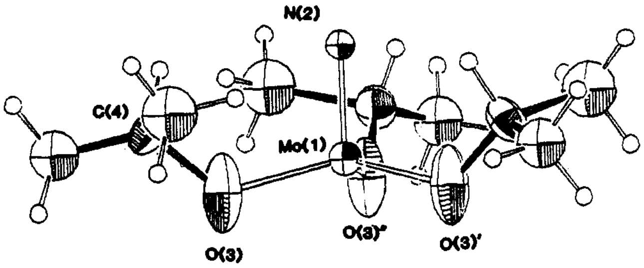


Figure 2. ORTEP drawing of the $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$ molecule giving the atom-numbering scheme used in the tables.

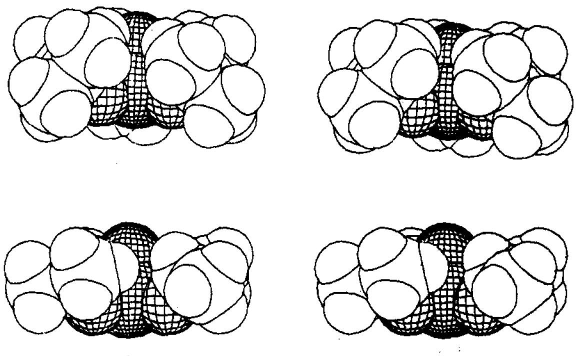


Figure 3. Space-filling drawing of the $(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}$ monomer unit (top) and the $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$ monomer unit (bottom) comparing the crowding around the nitrido ligand.

Table V. Fractional Coordinates and Isotropic Thermal Parameters for the $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$ Molecule[a]

atom	10^4x	10^4y	10^4z	$10B_{\text{iso}}$, Å^2
Mo(1)	10000*	10000*	2508*	18
N(2)	10000*	10000*	4450 (32)	14
O(3)	8118 (17)	8118*	2065 (35)	50
C(4)	7030 (22)	7030*	3175 (31)	29
C(5)	5431 (39)	6241 (37)	2826 (43)	39 (7)
C(5*)	7664 (45)	5851 (46)	3558 (55)	50 (9)
H(1)	716*	759*	419*	39
H(2)	505*	693*	264*	43
H(3)	523*	558*	189*	43
H(4)	484*	555*	373*	43
H(2)′	753*	522*	259*	99
H(3)′	877*	641*	379*	99
H(4)′	713*	517*	443*	99

[a] Parameters marked with an asterisk were not varied.

is that at −90 °C the molecules have crystallographically imposed C_{3v} symmetry while at −160 °C there is only a C_3 axis. The difference arises from the positions of the methyl groups of the O-*t*-Bu ligands. An ORTEP view of the monomeric $(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}$ unit in the lower symmetry space group is given in Figure 1. In the higher symmetry space group, C(6) and C(7) are related by a mirror plane. Each monomeric unit is connected to another, through the agency of long Mo—N bonds which are trans to the short Mo≡N bonds, thus generating an infinite linear chain.

A comparison of pertinent structural parameters for the compounds $[(\text{RO})_3\text{M}{\equiv}\text{N}]$, where M = Mo and W, is given in Table IV. The essential differences are as follows: (i) The M≡N distance is appreciably shorter for M = Mo than for M = W while the long M—N distance is shorter for M = W than for M = Mo. (2) The N≡M—O angle is larger for M = Mo than for M = W while the O—M—O angles are in the reverse order.

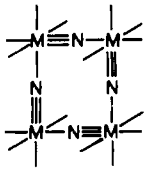
One must view the results of the $[(t\text{-BuO})_3\text{W}{\equiv}\text{N}]$ structure with some caution in view of the observed phase transition for M = Mo. It may well be that the larger than anticipated esd's for the M = W structure occur because it lies near a phase transition. Two points should be clear, however; (i) a reexamination of the data for M = W confirms that the space group was chosen properly (i.e. the extinction for *hh0l* was indeed present); (2) as seen in the present structure, the M≡N distance is essentially the same for both phases.

In view of the differences between the tungsten and molybdenum compounds for $(t\text{-BuO})_3\text{M}{\equiv}\text{N}$, the crystal structure for $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$ was performed. $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$ also crystallizes as a linear polymer with the space group $P6_3cm$. Unfortunately, a disorder was discovered in the position of the two terminal methyl groups of the isopropoxide ligand. Figure 2 shows only one of the possible ordered states, with the alternate having the "screw" axis of the molecule going in the opposite sense. This has again given esd's that are larger than those anticipated. Crystal data are summarized in Table I; fractional coordinates and isotropic thermal parameters are given in Table V, and selected bond distances and angles are given in Table IV.

The trends observed for the *tert*-butoxide continue for $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$. The M—O bond lengths (1.894 (17) Å) and N≡M—O bond angles (101.1 (9)°) are similar. The Mo≡N triple bond and dative bond cannot be exactly placed, but the Mo≡N bond is short (1.597 (26) Å). The closest distance between neighboring Mo atoms was accurately placed at 4.112 (2) Å, which is much smaller than that seen in $(t\text{-BuO})_3\text{M}{\equiv}\text{N}$ (4.40 Å, M = W; 4.54 Å, M = Mo). This may be understood in terms of steric factors, which lie in the order *t*-BuO > *i*-PrO. As can be seen in the space-filling diagrams in Figure 3, the *tert*-butoxide ligands shield the M–N core to a greater extent. This may cause a lengthening of the M–N dative bond in the order *t*-BuO > *i*-Pr.

Comments on M–N Bonding. It is interesting to speculate about the origin of these small but significant differences in the structures, for these most surely underscore the physicochemical properties of the compounds and, as we show elsewhere, the different reactivities of the M≡N bond.

First, it is important to recognize that the covalent radii of molybdenum and tungsten are essentially identical and it is unreasonable to invoke size or steric arguments. Evidence supporting this statement is seen here in the observed M–O distances, which are identical by the 3σ criteria. For M–M multiple bonds of high order, e.g. of order 4 and 3, however, the M–M distance is longer by up to 0.1 Å for M = W compared to that for M = Mo. This has been suggested to result from core–core repulsions, which become more important for M = W due to the higher number of electrons associated with the heavier atoms.[7] Could a similar phenomenon be invoked for M≡N bonds? In principle, yes, but there are a number of closely related pairs of M═O- and M≡N-containing compounds that have been structurally characterized that do not reveal evidence of this effect.[8,9] The Mo═O and M≡N distances are generally the same when the 3σ criteria is applied, and at most a 0.01-Å difference could be invoked based on previous findings. For example, in the compounds of formula $[L(Cl)_3M{\equiv}N]_4$, where L = $OPCl_3$ and M = Mo[9] and W,[11] which adopt the cyclic structure shown in I, the M≡N distances are 1.66 (1) Å (M = Mo) and 1.67 (1) Å (M = W) and the M—N distances are 2.16 (1) Å (M = Mo) and 2.15 (1) Å (M = W). Also in the latter compounds ν(M≡N) is at 1080 cm^{-1} for M = W and at 1049, 1042 cm^{-1} for M = Mo, whereas in the compounds $(t\text{-BuO})_3M{\equiv}N$, the values of ν(M≡N) are lower and differ by only a small amount but in the reverse order for the two metals: 1020 cm^{-1} for M = Mo and 1010 cm^{-1} for M = W. We conclude that electronic factors must be invoked and suggest the following.



I

It is now well-recognized that π-acceptor ligands, such as NO and CO, bind more strongly to $W(OR)_3$ centers than to $Mo(OR)_3$ centers in either mononuclear or dinuclear compounds. One manifestation of this effect is that in closely related pairs of molecules the values of ν(CO)[12] or ν(NO)[13] differ by ca. 70–80 cm^{-1} with those for M = W lying lowest; e.g., for $[(t\text{-BuO})_3M{-}NO]_x$, ν(NO) = 1565 cm^{-1} (M = W)[14] and 1632 cm^{-1} (M = Mo).[15] This reflects the greater π-back-bonding capabilities of W relative to Mo in its middle and higher oxidation states. The present observation is complementary to the above. In oxidation state +6, molybdenum will have a higher effective positive center and will bond more tightly to the π-donating N^{3-} ligand. Tungsten in oxidation state +6 is a weaker oxidizing agent than molybdenum and will interact less strongly with the N^{3-} ligand, leaving some net negative charge on the nitride ligand. This supposition is supported by MO calculations using the Fenske–Hall method. The model compound $(HO)_3MN$ was employed for the calculation using the bond angles and lengths found in the crystallographic studies. In a comparison of the difference for M = Mo and W it was found that a greater negative charge was located on the N ligand when the metal was W. This was consistent for both long M≡N lengths (1.74 Å) and short M≡N lengths (1.66 Å) for both Mo and W parameters. Mo, being more electronegative than W, matches the energy of the nitride ligand better than W; thus, there is less charge separation and more covalent bonding in the Mo case.

The effective positive charge at the metal center is also influenced by the nature of the ancillary ligands, and in this case the π-donating alkoxide ligands are important, for with chloride, as in $[Cl_3W{\equiv}N(OPCl_3)]_4$ compounds, both M≡N bonds are essentially the same (1.66 Å). The stabilizing influence of RO ligands is seen in the compound $WI_2(O\text{-}t\text{-Bu})_4$, which provides a rare example of I–W bonds involving a W(6+) center.[16]

In the present work we note that the reactivity of the M≡N moiety is dependent on both the metal and the ligand. Addition of alcohol (>6 equiv) to a hydrocarbon solution of $(t\text{-BuO})_3W{\equiv}N$ gives $W(OR)_6$ and NH_3, while under directly analogous conditions the related reactions employing $(t\text{-BuO})_3Mo{\equiv}N$ give $(RO)_3Mo{\equiv}N$ (eq 3 and 4). This difference in reactivity may in part be due to the greater negative charge located on the nitride for $(t\text{-BuO})_3W{\equiv}N$, making it easier to protonate.

$$(t\text{-BuO})_3W{\equiv}N + 6ROH \rightarrow W(OR)_6 + 3t\text{-BuOH} + NH_3 \qquad (3)$$

$$(t\text{-BuO})_3Mo{\equiv}N + ROH\ (\text{excess}) \rightarrow (RO)_3Mo{\equiv}N + 3t\text{-BuOH} \qquad (4)$$

$$R = Et,\ i\text{-Pr},\ neo\text{-Pe}$$

Experimental Section

Dry and deoxygenated solvents and atmospheres (N_2) were used throughout. NMR spectra were obtained with a Nicolet 360 spectrometer. Infrared spectra were recorded from Nujol mulls between CsI plates using a Perkin-Elmer 283 spectrometer. Elemental analyses were performed by Alfred Bernhard Analytical Laboratories, Elbach, West Germany.

Preparation of $(t\text{-BuO})_3Mo{\equiv}N$. $Cl_3Mo{\equiv}N$ was prepared in situ via previously published methods.[5,6] Following the metathetic reaction with LiO-*t*-Bu the white crystalline compound $(t\text{-BuO})_3Mo{\equiv}N$ can be obtained by either sublimation from the crude reaction mixture or by crystallization from a toluene extraction of the crude residue after filtration to remove LiCl and any other insoluble materials. The overall yields based on Mo are typically in the range 60–80%. A specific procedure is given below.

To a suspension of $MoCl_4(CH_3CN)_2$[5] (4.80 g, 15.0 mmol) in CH_3CN (50 mL) was added NaN_3 (1.17 g, 18.0 mmol). There was an immediate slow evolution of dinitrogen, and the color of the reaction mixture gradually turned to a clear burgundy. After the mixture was stirred for 1 h at room temperature, the solvent was removed in vacuo, yielding a dark red-brown solid. Toluene (70 mL) was added, giving a dark red suspension, followed by LiO-*t*-Bu (3.50 g, 43.8 mmol). The reaction mixture was stirred for 1 h, and THF (70 mL) was added. The reaction mixture was filtered through Celite, and the solvent was removed from the filtrate by dynamic vacuum, yielding a brown solid (5.2 g). The crude product was heated in vacuo (85 °C, 5 x 10^{-3} torr), and $(t\text{-BuO})_3Mo{\equiv}N$ (4.0 g, 80% yield based on Mo) sublimed as a white crystalline compound (mp 160–162 °C). Anal. Calcd for $C_{12}H_{27}O_3NMo$: C, 43.8; H, 8.26; N, 4.25; Mo, 29.1. Found: C, 43.6; H, 8.22; N, 4.22; Mo, 28.7. ^1H NMR data ($CDCl_3$ solvent, Me_4Si reference): δ 1.50 (singlet). IR data (cm^{-1}, Nujol mull): 370 (w, br), 470 (w), 598 (s), 712 (m), 782 (s), 909 (vs), 920 (vs, br), 1020 (s), 1160 (s), 1234 (m), 1255 (w).

$(t\text{-BuO})_3W{\equiv}N$ + *i*-PrOH. $(t\text{-BuO})_3W{\equiv}N$ (0.40 g) was suspended in hexane (10 mL), and excess *i*-PrOH (2 mL) was added to the solution, causing the solids to dissolve immediately. The solvent was removed under a dynamic vacuum, and the resultant solids were heated in vacuo

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(60–80 °C, 10^{-4} torr), yielding a white fluffy solid (sublimate), which was identified as $\text{W(O-}i\text{-Pr)}_6$ by elemental analyses and a comparison of IR and NMR data with those of a sample prepared by the previously described route employing $\text{W(NMe}_2)_6$.[16]

$(t\text{-BuO})_3\text{Mo}{\equiv}\text{N} + i\text{-PrOH}$. $(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}$ (0.325 g) was suspended in hexane (10 mL), and excess i-PrOH (2 mL) was added and the resultant solution stirred for 2 h at room temperature. The solvent was removed under a dynamic vacuum, and the resultant solids were redissolved in hexane (ca. 5 mL). Cooling to −15 °C yielded white needles, ca. 150 mg, of $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$. Anal. Calcd for $\text{C}_9\text{H}_{21}\text{O}_3\text{NMo}$: C, 37.64; H, 7.37; N, 4.87. Found: C, 37.47; H, 7.33; N, 4.95. ^{1}H NMR data (benzene-d_6): δ 5.40 (septet); 1.44 (doublet, $J_{\text{HH}} = 7$ Hz). IR data (cm^{-1}): 340 (w, br), 455 (w), 560 (w), 600 (sh), 640 (vs), 720 (w), 788 (w), 850 (s), 940 (sh), 965 (vs), 992 (s), 1108 (s), 1170 (m), 1238 (w), 1332 (m).

$(t\text{-BuO})_3\text{Mo}{\equiv}\text{N} + \text{EtOH}$. $(\text{EtO})_3\text{Mo}{\equiv}\text{N}$ was prepared in a manner analogous to that for $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$ (described above) employing ethanol. Anal. Calcd: C, 29.40; H, 6.17; N, 5.71. Found: C, 29.52; H, 6.06; N, 5.65. ^{1}H NMR data (benzene-d_6): δ 5.18 (quartet); 1.48 (triplet). IR data (cm^{-1}): 1258 (w), 1150 (w), 1195 (sh), 1189 (s), 1158 (s), 1145 (s), 1125 (m), 983 (vs), 908 (m), 872 (m), 800 (w), 720 (w), 610 (m), 582 (m), 562 (m), 482 (w).

$(t\text{-BuO})_3\text{Mo}{\equiv}\text{N} + \text{HOCH}_2\text{CMe}_3$ (HO-*neo*-Pe). $(neo\text{-PeO})_3\text{Mo}{\equiv}\text{N}$ was prepared in a manner analogous to that for $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$ employing neopentyl alcohol. Anal. Calcd: C, 48.51; H, 8.95; N, 3.77. Found: C, 48.29; H, 8.35; N, 4.08. ^{1}H NMR data (benzene-d_6): δ 4.90 (singlet), 0.91 (singlet). IR data (cm^{-1}, Nujol mull): 1258 (w), 1239 (m), 1165 (s), 1042 (vs), 1020 (vs), 982 (s), 932 (vs), 915 (sh), 790 (s), 746 (w), 720 (m), 670 (s), 600 (s), 482 (m), 380 (w).

Crystallographic Studies. General procedures and listings of programs have been reported.[18] Crystal data are summarized in Table I.

$(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}$ at −160 °C. A suitable small crystal was selcted, transferred to the goniostat, cooled to −160 °C, and characterized in the usual way. The unit cell was hexagonal, with cell dimensions very similar to those of the previously characterized compound $(t\text{-BuO})_3\text{W}{\equiv}\text{N}$.[4] It was therefore assumed that the two compounds were isomorphous, and the data collection was undertaken.

The W compound crystallized in the space group $P6_3cm$; however, when the Mo data were processed, it was apparent that the extinction of h–$h0l$ for $l = 2n + 1$ was not present. The maximum intensity for an extinction was 131.5 with a σ value of 11.3, and the average intensity for an extinction was 14.0. Also the R value for the averaging of equivalent reflections was 0.117 for 644 unique reflections observed more than once. This R value is unusually high for data collected in this laboratory, and closer inspection of the data led to the conclusion that the space group was $P6_3$. Reprocessing of the data now gave an R value of 0.042 for 1118 unique reflections observed more than once. The main difference between the two space groups is the fact that the molecule (for $Z = 2$) must have $3m$ symmetry in $P6_3cm$, whereas the molecular symmetry in $P6_3$ is 3. The structure was solved by standard heavy-atom methods, starting out with the Mo atom in the same position as the W atom in $(t\text{-BuO})_3\text{W}{\equiv}\text{N}$. In both space groups the metal atom must lie on the z axis, and the z coordinate is arbitrary; thus, the same coordinate was chosen for ease of comparison. The remainder of the atoms were located by standard Fourier methods, and all hydrogen atoms were located after initial refinement of the heavy atoms. The least-squares refinement was completed with anisotropic thermal parameters on the non-hydrogen atoms and isotropic hydrogen atoms. Since the space group $P6_3$ is noncentrosymmetric and polar, the refinement was carried out for both enantiomers with use of data where the Friedel pairs were not averaged; i.e. we used hkl and $hk{-}l$ data. The structure shown in this report led to the lowest R value. It should also be mentioned that the refinement was carried out with use of 1045 non-zero reflections.

When the data collection was completed at −160 °C, the crystal was warmed to ca. −90 °C, where the crystal underwent a phase transition to the $P6_3cm$ space group. During the warmup the crystal was driven to the angular settings for one of the h–$h0l$ reflections and the phase transition was observed when the intensity gradually disappeared as the temperature increased. The structure determination of the $P6_3cm$ species is described below. The main difference between the structures is the torsion angle N(2)–Mo(1)–O(3)–C(4), which is 7.5° in the $P6_3$ species and by symmetry required to be 0.0 in the $P6_3cm$ species.

$(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}$ at −90 °C. A full set of data were collected at −90 °C and processed in the usual manner, except that Friedel-related reflections were not average since the space group is noncentric and polar. A total of 1458 reflections were measured; 162 of these were space group extinctions, the average intensity for an extinction was −4.8, and the maximum was 30.4 with a σ value of 11.4. After averaging 363 unique reflections were obtained; the R value for the averaging was 0.044 for 358 reflections measured more than once.

The structure was solved by standard heavy-atom methods, with use of the Mo position from the low-temperature structure. All hydrogen atoms were located after initial refinement, and full-matrix least-squares refinement led to the final R value of 0.0244 for 309 non-zero reflections. All non-hydrogen atoms were refined with use of anisotropic thermal parameters, and hydrogen atoms were isotropic.

$(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with $6/mmm$ symmetry and systematic absences corresponding to $P6_3cm$. Subsequent solution and refinement of the structure confirmed this choice. The structure was solved by placing the Mo atom at 1, 1, 0.2508 (to correspond to the position observed for the $\text{WN(O-}t\text{-Bu)}_3$ and $\text{MoN(O-}t\text{-Bu)}_3$ molecules). It was noted that the thermal parameter of the Mo atom had to be fixed for the first few cycles, as was the case in the earlier studies.

A disorder was discovered in the position of the two terminal methyl groups. The drawings reflect only one of the possible ordered states, with the alternate having the "screw" axis of the molecule going in the opposite sense. Many of the hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen parameters, even though the atoms are of half-occupancy. For the final cycles of refinement, half-weight hydrogens were placed in idealized fixed positions, although no attempt was made to readjust the positions after each cycle.

A final difference Fourier was featureless, the largest peak being 0.65 e/Å^3.

Computational Details. The model system $(\text{HO})_3\text{MN}$ was used to investigate the nature of the $\text{M}{\equiv}\text{N}$ bonding. The coordinations were idealized to C_{3v} symmetry, but otherwise bond lengths and angles were taken from the crystal structures of $(t\text{-BuO})_3\text{M}{\equiv}\text{N}$ (M = Mo, W). Nonempirical Hartree–Fock molecular orbital calculations were performed with use of the self-consistent field Fenske–Hall method[19] (program MEDIEVEL). SCF calculations were performed in the atomic basis. Basis functions for the atoms were generated by a best fit to Herman Skillman atomic calculations. Contracted double-ζ representation were used for the Mo and W 4d and 5d AO's as well as O and N 2p AO's. The basis functions for the metal atoms were derived for a +1 oxidation state with the valence s and p exponents fixed at 1.8 for each of the Mo and W s and p orbitals.

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Registry No. $(t\text{-BuO})_3\text{Mo}{\equiv}\text{N}$, 82209-31-2; $\text{Cl}_3\text{Mo}{\equiv}\text{N}$, 14259-70-2; $\text{MoCl}_4(\text{CH}_3\text{CN})_2$, 19187-82-7; $(t\text{-BuO})_3\text{W}{\equiv}\text{N}$, 82209-24-3; $\text{W(O-}i\text{-Pr)}_6$, 52321-90-1; $(i\text{-PrO})_3\text{Mo}{\equiv}\text{N}$, 103590-79-0; $(\text{EtO})_3\text{Mo}{\equiv}\text{N}$, 103590-80-3; $(neo\text{-PeO})_3\text{Mo}{\equiv}\text{N}$, 103590-81-4; $(\text{HO})_3\text{Mo}{\equiv}\text{N}$, 103590-82-5; $(\text{HO})_3\text{W}{\equiv}\text{N}$, 103590-83-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and complete listings of bond angles and distances (4 pages); a table of F_o and F_c values (1 page). Ordering information is given on any current masthead page.

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