

(100 mL). The solution was stirred vigorously for 1 h. Solvent was removed to yield a deep red solution (50 mL) which was cooled to 0 °C. Large red crystals,  $W(NMe_2)_6$ , ca. 0.6 g, were collected by filtration and dried under vacuum. Anal. Calcd for  $W(NMe_2)_6$ : C, 32.15; H, 8.03; N, 18.75. Found: C, 32.0; H, 8.12; N, 18.5.

$WCl_6 + 6LiNEt_2$ .  $WCl_6$  (34.2 g, 86 mmol) was added slowly to a solution of  $LiNEt_2$  (559 mmol) in hexane (250 mL) and THF (100 mL). The solution was stirred vigorously and cooled in an ice bath. This yielded a dark brown solution and off-white solids. The solution was warmed to room temperature, stirred for 12 h and finally heated to +60 °C for 1 h. The solvent was stripped yielding a black tar. This tar was heated in vacuo: a liquid distilled from 65 to 150 °C at  $3 \times 10^{-3}$  cmHg. The initial liquid was pale yellow and the higher boiling fraction was red; yield 4.39 g of distillate. This distillate was fractionally distilled using a piglet. The initial distillate at 70 °C ( $10^{-4}$  cmHg), ca. 1 mL, was collected.  $^1H$  NMR and  $^{13}C$  NMR were recorded. Anal. Calcd for  $W(NEt_2)_2(NEt)_2$ : C, 34.79; H, 7.30; N, 13.53. Calcd for  $W(NEt_2)_4$ : C, 40.68; H, 8.54; N, 11.68. Calcd for  $W(NEt_2)_3(NEt)$ : C, 37.94; H, 7.96; N, 12.64. Found: C, 39.35; H, 7.87; N, 12.08.

$^1H$  NMR data obtained at 35 °C, 60 HMZ, in  $C_6D_6$ ;  $\delta$  in ppm downfield relative to TMS = 0:  $W=NCH_2CH_3$ ,  $\delta(CH_2)$  4.22, quartet,  $J_{HH} = 7$  Hz,  $\delta(CH_3)$  1.30, triplet,  $J_{HH} = 7$  Hz;  $WN(CH_2CH_3)_2$ ,  $\delta(CH_2)$  = 3.63, quartet,  $J_{HH} = 7$  Hz,  $\delta(CH_3)$  = 1.21, triplet,  $J_{HH} = 7$  Hz.  $^{13}C$  NMR data obtained at 40 °C in  $C_6D_6$ ;  $\delta$  in ppm downfield relative to TMS = 0:  $W=NCH_2CH_3$ ,  $\delta(CH_2)$  57.8,  $\delta(CH_3)$  20.6;  $WN(CH_2CH_3)_2$ ,  $\delta(CH_2)$  55.3,  $\delta(CH_3)$  17.4. These NMR data may be compared to those found for  $Ta(NEt)(NEt_2)_3$ .  $^1H$  NMR data obtained at 30 °C, 60 MHz, in  $C_6D_6$ ;  $\delta$  in ppm relative to TMS = 0:  $Ta=NCH_2CH_3$ ,  $\delta(CH_2)$  4.22, quartet,  $J_{HH} = 7$  Hz,  $\delta(CH_3)$  1.28, triplet,  $J_{HH} = 7$  Hz;  $TaN(CH_2CH_3)_2$ ,  $\delta(CH_2)$  3.37, quartet,  $J_{HH} = 7$  Hz,  $\delta(CH_3)$  1.13, triplet,  $J_{HH} = 7$  Hz.  $^{13}C$  NMR data,  $\delta$  in ppm relative to TMS = 0:  $Ta=NCH_2CH_3$ ,  $\delta(CH_2)$  56.2,  $\delta(CH_3)$  20.4;  $TaN(CH_2CH_3)_2$ ,  $\delta(CH_2)$  47.8,  $\delta(CH_3)$  17.3.

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**Registry No.**  $W(NMe_2)_6$ , 24654-69-1;  $W(NEt_2)_2(NEt)_2$ , 62029-51-0;  $^{13}C$ , 14762-74-4;  $W[N(CD_3)_2]_6$ , 62029-52-1.

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## Some Reactions of Hexakis(dimethylamido)tungsten(VI)

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Hydrocarbon solutions of  $W(NMe_2)_6$  react at room temperature with alcohols ROH to give alkoxides  $W(OR)_6$  (R = Me, Et, *n*-Pr, *i*-Pr, and allyl) which have been characterized by a number of physicochemical studies, including infrared and Raman spectroscopy,  $^1H$  and  $^{13}C$  NMR spectroscopy, and mass spectroscopy. Under similar conditions  $W(NMe_2)_6$  does not react with the alcohols  $Me_3CCH_2OH$ ,  $Me_3COH$ , or  $Et_3SiOH$ . In refluxing benzene  $W(NMe_2)_6$  reacts with  $Me_3COH$  to give  $WO(O-t-Bu)_4$ . From the reaction between  $W(NMe_2)_6$  and methanol at ca. 10 °C,  $W(NMe_2)_3(OMe)_3$  has been isolated and characterized. Reactions with mercaptans RSH (R = Me and Ph) give mercaptides  $W(SR)_3$ .  $CO_2$  and  $CS_2$  give rise to insertion products. An amine-catalyzed mechanism leading to insertion is proposed and supported by the observation that in the presence of an amine trap, such as an alkyl lithium reagent, no  $W-NMe_2$  insertion occurs.  $W(NMe_2)_6$  does not react with each of the following at room temperature and 1 atm: ethylene, carbon monoxide, allene, 1,3-butadiene, phenylacetylene, nitric oxide, and molecular oxygen. The reactions of  $W(NMe_2)_6$  are compared with those reported for  $WMe_6$  by other authors. The reactivity patterns of the two compounds differ quite strikingly:  $WMe_6$  reacts via initial nucleophilic attack at tungsten whereas  $W(NMe_2)_6$  reacts via electrophilic attack at a nitrogen lone pair.

## Introduction

Homoleptic compounds  $ML_n$ , where L = R (alkyl),<sup>2,3</sup>  $NR_2$ ,<sup>4</sup> and  $OR$ ,<sup>5</sup> are known for all of the group 4, 5, and 6 transition metals for certain values of *n*. These compounds afford the unique opportunity of comparing the bonding and reactivity of covalent metal-to-carbon, metal-to-nitrogen, and metal-to-oxygen  $\sigma$  bonds within a series of closely related compounds. For tungsten there exist two known series:  $WL_6$ , where L = Me,<sup>6</sup>  $NMe_2$ ,<sup>7,8</sup> and  $OMe$ ,<sup>7</sup> and  $W_2L_6$ , where L =

$CH_2SiMe_3$ ,<sup>9,10</sup>  $NR_2$ ,<sup>11</sup> and  $O-t-Bu$ .<sup>12</sup> This work arises from our continuing interest in the chemistry of these compounds.<sup>13</sup> We report herein a number of reactions of  $W(NMe_2)_6$ , which, although by no means exhaustive, serve to define the common mode of reaction of the tungsten-to-nitrogen bond in  $W(NMe_2)_6$ . These reactions may be compared with the reactions of  $WMe_6$  reported by Shortland and Wilkinson.<sup>6</sup>

## Results and Discussion

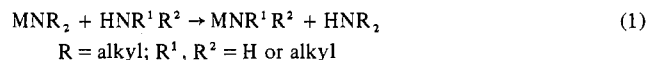
**Aminolysis.** A characteristic of metal dialkylamides is their

Table I. Analytical Data and Physical Characteristics of Tungsten(VI) Alkoxides

Compd	Physical characteristics	% C		% H	
		Found	Calcd	Found	Calcd
W(OMe) <sub>6</sub>	White crystalline solid, sublimes 50–60 °C, 10 <sup>-3</sup> Torr	19.47	19.46	5.03	4.86
W(OEt) <sub>6</sub>	Clear liquid (freezes near room temp), sublimes <sup>a</sup> 45–70 °C, 10 <sup>-2</sup> Torr	31.61	31.73	6.47	6.66
W(O- <i>n</i> -Pr) <sub>6</sub>	Volatile liquid, sublimes <sup>b</sup> to white solid, 72–85 °C, 10 <sup>-3</sup> Torr	40.33	40.15	8.01	7.86
W(O- <i>i</i> -Pr) <sub>6</sub>	Pale yellow-green solid, sublimes <sup>b</sup> 40–55 °C, 10 <sup>-3</sup> Torr	39.72	40.15	7.51	7.86
W(O(allyl)) <sub>6</sub>	Colorless liquid, sublimes <sup>b</sup> 60–90 °C, 10 <sup>-3</sup> Torr				
WO(O- <i>t</i> -Bu) <sub>4</sub>	Pale yellow waxy solid, sublimes 40–50 °C, 10 <sup>-3</sup> Torr	39.94	39.02	7.34	7.32

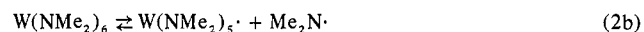
<sup>a</sup> CO<sub>2</sub>(s)-cooled cold finger. <sup>b</sup> N<sub>2</sub>(l)-cooled cold finger.

ability to enter into amine-exchange reactions represented by eq 1.<sup>5</sup> Reactions involving primary amines generally lead to



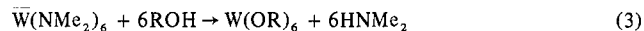
polymeric products involving M–NR–M bridges. However, W(NMe<sub>2</sub>)<sub>6</sub> failed to react with HNET<sub>2</sub> in refluxing benzene and showed no reaction with either HN(CD<sub>3</sub>)<sub>2</sub> or MeNH<sub>2</sub> at room temperature over a period of months. With NH<sub>3</sub> a slow reaction occurred and Me<sub>2</sub>NH was liberated.

The observation that W(NMe<sub>2</sub>)<sub>6</sub> failed to react with HNET<sub>2</sub> is not surprising in view of steric considerations. However, the failure of W(NMe<sub>2</sub>)<sub>6</sub> to react with HN(CD<sub>3</sub>)<sub>2</sub> and MeNH<sub>2</sub> shows that under the experimental conditions W(NMe<sub>2</sub>)<sub>6</sub> does not, to any significant extent, undergo tungsten-to-nitrogen bond cleavage, in either a heterolytic or a homolytic manner. Thus we can eliminate reaction mechanisms based on an initial step, eq 2a or 2b, which would clearly



lead to aminolysis in the presence of HN(CD<sub>3</sub>)<sub>2</sub>.

**Alcoholysis Reactions.** Alkane solutions of W(NMe<sub>2</sub>)<sub>6</sub> reacted smoothly, but relatively slowly, with alcohols ROH to give alkoxides W(OR)<sub>6</sub> according to eq 3 (R = Me, Et,

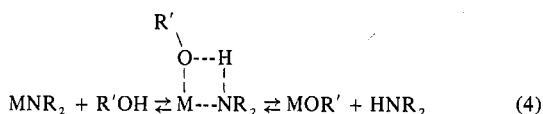


*n*-Pr, *i*-Pr, and allyl).

The alcohols Me<sub>3</sub>CCH<sub>2</sub>OH and Me<sub>3</sub>COH and triethylsilanol failed to react to any appreciable extent at room temperature. Indeed W(NMe<sub>2</sub>)<sub>6</sub> failed to react with a solution of benzene/*tert*-butyl alcohol over a period of 3 years at room temperature. The lack of reactivity of W(NMe<sub>2</sub>)<sub>6</sub> with *tert*-butyl alcohol has been previously noted and may be made use of in the isolation of W(NMe<sub>2</sub>)<sub>6</sub> from mixtures of W(NMe<sub>2</sub>)<sub>6</sub> and W<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>.<sup>8</sup> In refluxing benzene/*tert*-butyl alcohol solution a slow reaction leads to WO(O-*t*-Bu)<sub>4</sub>.

Alcoholysis reactions analogous to (3) have often been employed in the synthesis of metal alkoxides when other procedures are inapplicable, as is the case, for example, in the synthesis of V(OR)<sub>4</sub><sup>14</sup> and M(OR)<sub>3</sub>, where M = Mo<sup>13,15</sup> and W.<sup>12,13</sup> Although W(OMe)<sub>6</sub><sup>16</sup> and W(OPh)<sub>6</sub><sup>17</sup> have been prepared by other methods, it seems that reaction 3 is the most suited for a general synthesis of W(OR)<sub>6</sub> compounds. However, among metal dialkylamides W(NMe<sub>2</sub>)<sub>6</sub> appears uniquely sluggish toward alcoholysis and reaction 3 is not applicable to certain alcohols and triethylsilanol.

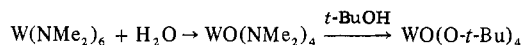
A reasonable reaction pathway leading to alcoholysis is shown in eq 4 and involves an associative mechanism. The



relative importance of the various bond-forming and bond-breaking steps is clearly speculative and would be expected

to vary considerably from one system to another. For a sterically crowded molecule such as W(NMe<sub>2</sub>)<sub>6</sub> (which is the only known mononuclear hexakis(dialkylamido) compound) the associative process, eq 4, is less favored compared to all other known metal dimethylamides M(NMe<sub>2</sub>)<sub>n</sub> (*n* = 1–5). This we believe is the reason for its relative reluctance to undergo alcoholysis reactions and its relative stability toward hydrolysis.

The observed order of reactivity of ROH with W(NMe<sub>2</sub>)<sub>6</sub>, R = Me > Et > Pr >> *t*-Bu, can be understood in terms of eq 4. Both steric factors and acidity (pK<sub>a</sub>(MeOH) = 15.5,<sup>18</sup> 15.09;<sup>19</sup> pK<sub>a</sub>(*t*-BuOH) ≥ 19<sup>19</sup>) clearly favor reaction with MeOH relative to *t*-BuOH. However, the rapid reaction of W(NMe<sub>2</sub>)<sub>6</sub> with (CF<sub>3</sub>)<sub>3</sub>COH (pK<sub>a</sub> = 9.52<sup>18</sup>) suggests that acidity is more important than steric hindrance. Thus the low reactivity of *tert*-butyl alcohol must be mainly due to its very weak acidity. The slow formation of WO(O-*t*-Bu)<sub>4</sub> using refluxing benzene/*tert*-butyl alcohol may be caused by trace hydrolysis:



The water could arise initially from the dehydration of *tert*-butyl alcohol in a heterogeneous reaction catalyzed by the glass reaction vessel. Certainly there is no reason to doubt the existence of W(O-*t*-Bu)<sub>6</sub> since U(O-*t*-Bu)<sub>6</sub> is a stable compound<sup>20</sup> and W(OCH<sub>2</sub>CMe<sub>3</sub>)<sub>6</sub> has been obtained from the reaction involving W<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> and Me<sub>3</sub>CCH<sub>2</sub>OH.<sup>21</sup>

**Methanolysis.** The relatively slow reaction of W(NMe<sub>2</sub>)<sub>6</sub> with methanol was amenable to study by <sup>1</sup>H NMR spectroscopy. At temperatures >50 °C the only tungsten species observed were W(NMe<sub>2</sub>)<sub>6</sub> and W(OMe)<sub>6</sub> but at 40 °C a transient intermediate was detected which at 20 °C had a significant lifetime. By carrying out reactions at ca. 10 °C we were able to isolate this intermediate which proved to be W(NMe<sub>2</sub>)<sub>3</sub>(OMe)<sub>3</sub>.

For a number of group 4 transition metal homoleptic compounds ML<sub>n</sub>, where L = R (alkyl), NR<sub>2</sub>, and OR, the mean bond dissociation energy has been determined and shown to follow the order  $\bar{D}(\text{M-O}) > \bar{D}(\text{M-N}) > \bar{D}(\text{M-C})$ .<sup>22</sup> A similar order apparently exists for the tungsten series WL<sub>6</sub> where L = CH<sub>3</sub>,<sup>23</sup> NMe<sub>2</sub>, and OR.<sup>24</sup> Our isolation of W(NMe<sub>2</sub>)<sub>3</sub>(OMe)<sub>3</sub> and its relative kinetic stability in the reaction between W(NMe<sub>2</sub>)<sub>6</sub> and MeOH are thus particularly interesting. The reaction sequence appears to parallel that found for the reaction between W(NMe<sub>2</sub>)<sub>6</sub> and CO<sub>2</sub> which gives W(NMe<sub>2</sub>)<sub>3</sub>(O<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub> (see later).

**Tungsten Alkoxides W(OR)<sub>6</sub> and WO(O-*t*-Bu)<sub>4</sub>.** Tungsten(VI) alkoxides are low-melting solids or liquids at room temperature. They are volatile and appear quite thermally stable (<100 °C), allowing their purification by vacuum sublimation or distillation. Analytical and other characterization data are given in Table I.

W(OR)<sub>6</sub> are all soluble in hydrocarbon solvents. A cryoscopic molecular weight determination for W(OMe)<sub>6</sub> indicated its monomeric nature in benzene: found, 373 ± 15; calcd, 370. Higher homologues W(OR)<sub>6</sub>, where R = Et, Pr,

**Table II.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data for Tungsten Alkoxides

Compd	$\delta$ , ppm	
	$^1\text{H}$ NMR <sup>a</sup>	$^{13}\text{C}$ NMR <sup>b</sup>
W(OMe) <sub>6</sub>	4.40 (s)	-CH <sub>3</sub> 61.38
W(OEt) <sub>6</sub>	$\alpha$ 4.73 (q, 2) $\beta$ 1.13 (t, 3)	-CH <sub>2</sub> - 69.79 -CH <sub>3</sub> 18.77
W(O- <i>n</i> -Pr) <sub>6</sub>	$\alpha$ 4.67 (t, 2) $\beta$ 1.55 (m, 2) $\gamma$ 0.87 (t, 3)	-OCH <sub>2</sub> - 76.05 -CH <sub>2</sub> - 26.97 -CH <sub>3</sub> 11.11
W(O- <i>i</i> -Pr) <sub>6</sub>	$\alpha$ 5.08 (septet, 1) $\beta$ 1.17 (d, 6)	-OCH 76.80 -CH <sub>3</sub> 25.02
W(O(allyl)) <sub>6</sub>	5.10 (m) 5.82 (m)	-OCH <sub>2</sub> - 75.51 =CH <sub>2</sub> 111.66
WO(O- <i>t</i> -Bu) <sub>4</sub>	1.36 (s)	-CH= 138.07

<sup>a</sup> At 60 MHz in toluene-*d*<sub>8</sub> and 40 °C; spectra unchanged at -80 °C; ppm downfield from HMDS (hexamethyldisiloxane):  $\alpha$ , protons on C  $\alpha$  to O;  $\beta$ , protons on C  $\beta$  to O;  $\gamma$ , protons on C  $\gamma$  to O.  $J_{\text{H-H}} = 7$  Hz. Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Numbers indicate relative intensities. <sup>b</sup> At 22.6 MHz in C<sub>6</sub>D<sub>6</sub>; in ppm downfield from Me<sub>4</sub>Si; proton-decoupled spectra gave single  $^{13}\text{C}$  resonances.

*i*-Pr, and allyl, are presumed to be monomeric in hydrocarbon solvents. This presumption seems justified in view of their similar physicochemical properties.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra have been obtained for these compounds. In all cases resonances arising from only one kind of alkyl group were observed in the temperature range +90 to -90 °C.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are recorded in Table II.

In the mass spectrometer parent molecular ions W(OR)<sub>6</sub><sup>+</sup> were not generally observed; the ion of highest mass and base peak corresponded to W(OR)<sub>5</sub><sup>+</sup>. (No dinuclear species, W<sub>2</sub>-containing ions, were observed.) Mass spectral data for W(OMe)<sub>6</sub>, including metastable ions, are given in Table III.

Infrared and Raman spectra were also obtained for these compounds; full spectral data are recorded in the Experimental Section. Monomeric compounds W(OR)<sub>6</sub> would be expected to share a common WO<sub>6</sub> octahedral moiety, although in all cases the absolute symmetry would be lower than O<sub>h</sub> due to the arrangements of the alkyl groups. An octahedral WO<sub>6</sub> moiety would give rise to  $\nu_{\text{str}}(\text{W-O})$  of T<sub>1u</sub> and A<sub>1g</sub> symmetry which would be infrared and Raman active, respectively. Assignments of W-O stretching frequencies are given in Table IV for W(OR)<sub>6</sub>, where R = Me, Et, and Pr.  $\nu_{\text{str}}$  increases in the order Me < Et < Pr. A similar trend has been noted in other alkoxides and has been attributed to increased oxygen-to-metal  $\pi$ -bonding as a result of the positive inductive effect of the alkyl group, R = Pr > Et > Me.<sup>25-27</sup> However, these bands may not be pure W-O stretching modes since coupling to other ligand vibrations is possible. We have recently shown that for W(NMe<sub>2</sub>)<sub>6</sub><sup>8</sup> and W<sub>2</sub>(N(CD<sub>3</sub>)<sub>2</sub>)<sub>2</sub>,<sup>11</sup> extensive coupling must exist between  $\nu_{\text{str}}(\text{W-N})$  and other ligand vibrational modes since the strong bands at ca. 550 cm<sup>-1</sup>, qualitatively assignable to  $\nu_{\text{str}}(\text{W-N})$ , shift to ca. 495 cm<sup>-1</sup> upon deuteration. Such a large shift cannot be accounted for by simple mass effects,  $\nu_{\text{str}}(\text{W-NMe}_2)$  vs.  $\nu_{\text{str}}(\text{W-N(CD}_3)_2)$ . In the present study spectra of deuterated alkoxides have not been obtained.

W(NMe<sub>2</sub>)<sub>3</sub>(OMe)<sub>3</sub>. W(NMe<sub>2</sub>)<sub>3</sub>(OMe)<sub>3</sub> is an orange crystalline solid. It is air sensitive, being readily hydrolyzed, and darkens on prolonged storage in screw-cap vials in the drybox. However, it appears indefinitely stable when sealed in ampules in vacuo and stored in the dark at ca. -15 °C. It is volatile and may be sublimed at 60 °C, 10<sup>-3</sup> Torr. In the mass spectrometer it gave a very weak parent ion, W(NMe<sub>2</sub>)<sub>2</sub>(OMe)<sub>3</sub><sup>+</sup>, and a base peak due to W(NMe<sub>2</sub>)<sub>2</sub>(OMe)<sub>3</sub><sup>+</sup>. A weak peak due to W(NMe<sub>2</sub>)<sub>3</sub>(OMe)<sub>2</sub><sup>+</sup> was also observed. The  $^1\text{H}$  NMR spectrum showed two resonances in the integral intensity ratio 2:1 in the temperature range -70

**Table III.** Mass Spectral Data for W(OMe)<sub>6</sub> Obtained by Direct Insertion at 60 °C, 2 × 10<sup>-6</sup> cmHg

<i>m/e</i> ( <sup>184</sup> W)	Ion	Abundance
339	W(OMe) <sub>5</sub> <sup>+</sup>	100
309	W(OMe) <sub>4</sub> H <sup>+</sup>	21
308	W(OMe) <sub>4</sub> <sup>+</sup>	21
307	W(OMe) <sub>3</sub> OCH <sub>2</sub> <sup>+</sup>	9
293	W(OMe) <sub>3</sub> <sup>+</sup>	80
277	W(OMe) <sub>3</sub> <sup>+</sup>	70.2
263	W(OMe) <sub>2</sub> OH <sup>+</sup>	26
261	WO(OMe)OCH <sub>2</sub> <sup>+</sup> , WOH <sub>2</sub> (OMe)CO <sup>+</sup>	18
259	WO(OMe)CO	16
247	WO <sub>2</sub> (OMe) <sup>+</sup>	26.3
245	WOMeOCH <sub>2</sub> <sup>+</sup>	9
243	WOMeCO <sup>+</sup>	Trace
233	WOMeOH <sub>2</sub> <sup>+</sup> (WO <sub>2</sub> OH <sup>+</sup> )	14
232	WOMeOH <sup>+</sup> ·(WO <sub>3</sub> <sup>+</sup> )	3.5
231	WO(OMe) <sup>+</sup>	7
218	W(OH) <sub>2</sub> <sup>+</sup>	2
217	WOOH <sup>+</sup>	3.5
216	WOMeH <sup>+</sup> ; WO <sub>2</sub> <sup>+</sup>	2
202	WOH <sub>2</sub> <sup>+</sup>	1
201	WOH <sup>+</sup>	2
200	WO <sup>+</sup>	2
154	W(OMe) <sub>4</sub> <sup>2+</sup>	13
146	WO(OMe) <sub>2</sub> OCH <sub>2</sub> <sup>2+</sup>	9
138.5	W(OMe) <sub>3</sub> <sup>2+</sup>	Trace

## Metastable Reactions

1.  $\text{W(OMe)}_5^+ \xrightarrow[m = 281.65]{-\text{OCH}_2} \text{W(OMe)}_4\text{H}^+$
2.  $\text{W(OMe)}_4\text{H}^+ \xrightarrow[m = 305.0]{-\text{H}_2} \text{W(OMe)}_3\text{OCH}_2^+$
3.  $\text{W(OMe)}_3\text{OCH}_2^+ \xrightarrow[m = 249.9]{-\text{OCH}_2} \text{W(OMe)}_3^+$
4.  $\text{W(OMe)}_4\text{H}^+ \xrightarrow[m = 248.3]{-\text{MeOH}} \text{W(OMe)}_3^+$
5.  $\text{W(OMe)}_3^+ \xrightarrow[m = 245.9]{-\text{CH}_4} \text{WO(OMe)OCH}_2^+$
6.  $\text{W(OMe)}_2\text{OH}^+ \xrightarrow[m = 228.2]{-\text{H}_2\text{O}} \text{W(OMe)OCH}_2^+$
7.  $\text{WO(OMe)OCH}_2^+ \xrightarrow[m = 226.24]{-\text{H}_2\text{O}} \text{WOMeCO}^+$
8.  $\text{WOMe(OCH}_2)_2\text{O}^+ \xrightarrow[m = 208.0]{-\text{CO}} \text{WOMeOH}_2^+$

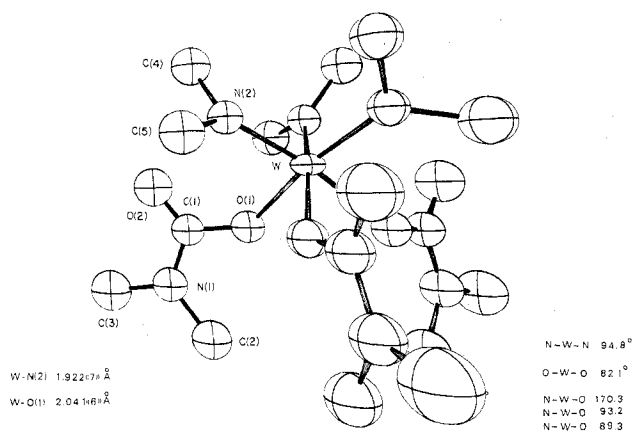
**Table IV.** Infrared and Raman Absorption Maxima (cm<sup>-1</sup>) of Tungsten Alkoxides Assignable to  $\nu_{\text{str}}(\text{W-O})$ 

Compd	Infrared	Raman
W(OMe) <sub>6</sub>	532 <sup>a</sup>	585 <sup>b</sup>
W(OEt) <sub>6</sub>	590 <sup>c</sup>	620 <sup>c</sup> (p)
W(O- <i>n</i> -Pr) <sub>6</sub>	600 <sup>c</sup>	630 <sup>c</sup> (p), 655 <sup>c</sup> (p)
W(O- <i>i</i> -Pr) <sub>6</sub>	595 <sup>a</sup>	615 <sup>b</sup> (p)
W(O(allyl)) <sub>6</sub>	695 <sup>c</sup>	
WO(O- <i>t</i> -Bu) <sub>4</sub> <sup>d</sup>	555 <sup>a</sup>	

<sup>a</sup> Nujol mull. <sup>b</sup> Solid. <sup>c</sup> Neat liquid; p = polarized. <sup>d</sup>  $\nu(\text{W=O})$  940 cm<sup>-1</sup>.

to +40 °C:  $\delta(\text{NMe}_2)$  3.9 and  $\delta(\text{OMe})$  4.2 ( $\delta$  in parts per million relative to HMDS in toluene-*d*<sub>8</sub> at 60 MHz). Infrared data are recorded in the Experimental Section. The experimental data are consistent with the view that W(NMe<sub>2</sub>)<sub>3</sub>(OMe)<sub>3</sub> has a *fac*-WN<sub>3</sub>O<sub>3</sub> octahedral geometry.

**Insertion Reactions. With Carbon Dioxide.** W(NMe<sub>2</sub>)<sub>6</sub> reacts readily with carbon dioxide in alkane solvents to give W(NMe<sub>2</sub>)<sub>3</sub>(O<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub>.<sup>28</sup> This reaction has been the subject of previous study.<sup>29,30</sup> The insertion reaction has been shown



**Figure 1.** Molecular structure of  $W(NMe_2)_3(O_2CNMe_2)_3$  including some important structural parameters. The molecule has  $C_3$  symmetry. Full details are given in ref 28.

to proceed via a catalytic cycle, eq 5, involving dimethylamine



which is generally present in trace quantities in solutions of  $M(NMe_2)_n$  compounds.<sup>30</sup>

The structure of  $W(NMe_2)_3(O_2CNMe_2)_3$ , deduced from single-crystal x-ray studies, is shown in Figure 1. Probably the most significant feature of the molecular structure is the short W-N bond distance, 1.922 (7) Å. This is ca. 0.1 Å shorter than that found in  $W(NMe_2)_6$ , 2.017 (5),<sup>11</sup> 2.032 (25) Å.<sup>7</sup> The very short W-N bond distance, the planarity of the  $WNC_2$  moieties, and the *fac*- $WN_3O_3$  octahedral geometry are all indicative of significant nitrogen-to-tungsten  $\pi$  bonding in  $W(NMe_2)_3(O_2CNMe_2)_3$ . This we believe is an important factor in limiting the insertion reaction. Nitrogen-to-tungsten  $\pi$  bonding leads to decreased basicity of the nitrogen lone pair with respect to acids such as  $Me_2NCOOH$ . A similar explanation could account for our isolation of  $W(NMe_2)_3(OMe)_3$  and its relative kinetic stability in the reaction between  $W(NMe_2)_6$  and MeOH at low temperatures.

Although the tungsten-to-nitrogen bond in  $W(NMe_2)_3(O_2CNMe_2)_3$  is inert to reaction with  $HO_2CNMe_2$  (eq 5ii), it is reactive toward methanolysis:  $W(NMe_2)_3(O_2CNMe_2)_3 + MeOH \rightarrow W(OMe)_6$ . We have found that reaction occurs preferentially at the  $W-NMe_2$  moiety (see Experimental Section). Thus there appears to be a fundamental difference in the reactivities of the  $WNMe_2$  and  $WO_2CNMe_2$  moieties toward MeOH and  $Me_2NCOOH$ .

**With Carbon Disulfide.**  $W(NMe_2)_6$  reacts with  $CS_2$  in hydrocarbon solvents to give an insertion product which, on the basis of elemental analyses, we formulate as  $W(S_2CNMe_2)_4$ . The compound is formed as a finely divided precipitate, which is insoluble in alkane solvents and only very sparingly soluble in benzene. Analytical data, infrared data, and other characterization data are given in the Experimental Section.

When  $CS_2$  was added to an ethereal solution of  $W(NMe_2)_6$  and MeLi,  $W(S_2CNMe_2)_4$  was not formed.  $W(NMe_2)_6$  was recovered from this reaction. We conclude<sup>31</sup> that the reaction between  $W(NMe_2)_6$  and  $CS_2$  to give  $W(S_2CNMe_2)_4$  is catalyzed by the presence of fortuitous  $HNMe_2$  which is typically present in solutions of  $W(NMe_2)_6$ . A reaction sequence, eq 6, which is directly analogous to eq 5 is proposed.

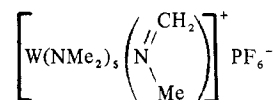


In contrast to the reaction involving  $CO_2$ , reactions with  $CS_2$  lead to reduced tungsten species ( $W(IV)$ ). This observation has parallel in the reactions of  $Cr(NEt_2)_4$ <sup>32</sup> and  $Nb(NMe_2)_5$ <sup>33</sup> with  $CS_2$  which lead to  $Cr(S_2CNMe_2)_3$  and  $Nb(S_2CNMe_2)_4$ , respectively. The sulfur-bonded ligands are more readily oxidized (e.g., to thiuram disulfides,  $R_2NC(S)SS(S)CNR_2$ ) than their oxygen carbamate counterparts.

**With Unsaturated Hydrocarbons.** Hydrocarbon solutions of  $W(NMe_2)_6$  were found to be unreactive at room temperature toward each of the following: ethylene, carbon monoxide, allene, phenylacetylene, 1,3-butadiene, and cyclopentadiene. For these unsaturated molecules an amine-catalyzed insertion mechanism of the type shown in eq 5 and 6 is not possible. However, an alkane solution of  $W(NMe_2)_6$  did prove to be an effective catalyst for the polymerization of hexafluorobut-2-yne.  $W(NMe_2)_6$  was recovered from these reactions and analysis of the acetylene polymer revealed the absence of nitrogen and hydrogen. We believe that polymerization occurred by a reaction which did not involve insertion into the  $W-NMe_2$  bond.

**Miscellaneous Reactions.**  $W(NMe_2)_6$  does not appear labile toward either alkyl substitution or proton abstraction reactions under mild conditions:  $W(NMe_2)_6$  did not react with (i) MeLi in ether, (ii) LiBu in hexane/tetramethylethylenediamine, or (iii) either  $LiCH_2CMe_3$  or  $LiCMe_3$  in refluxing benzene.

Attempts were made to form



by the reaction between  $W(NMe_2)_6$  and  $Ph_3C^+PF_6^-$  in dichloromethane. A reaction did occur but we were unable to characterize a product. Attempts to isolate  $[W(NMe_2)_5NMe_3]^+SO_3CF_3^-$  from the reaction between  $W(NMe_2)_6$  and magic methyl,  $MeSO_3CF_3$ , were similarly unsuccessful.

$W(NMe_2)_6$  in hexane did not react with either nitric oxide or dioxygen at room temperature.

With the mercaptans MeSH and PhSH,  $W(NMe_2)_6$  reacted rapidly giving black (dark brown) hexane-insoluble products which, on the basis of analytical data, are formulated as  $W(SR)_3$  compounds.

**Comparisons with Reactions of Hexamethyltungsten.** An interesting comparison is now possible between the reactions of  $WMe_6$  and  $W(NMe_2)_6$ . The former have been reported by Shortland and Wilkinson.<sup>6</sup>

$WMe_6$  is a red volatile solid which is spontaneously flammable in air and even prone to detonation when stored under nitrogen or under vacuum at temperatures below room temperature.<sup>34</sup>  $W(NMe_2)_6$  on the other hand is thermally stable below 160 °C, is relatively slowly hydrolyzed, and does not react in solution with dry molecular oxygen. Under controlled conditions in solution  $WMe_6$  is reported to react with  $O_2$  to give  $W(OMe)_6$ .  $WMe_6$  also reacts with (is decomposed by)  $CO$ ,  $H_2$ ,  $C_2H_4$ , and terminal acetylenes. With tertiary phosphines  $WMe_6$  reacts to form 1:1 adducts. In the presence of a tertiary phosphine the reaction between  $WMe_6$  and  $H_2$  or  $CO$  is inhibited.  $WMe_6$  reacts with MeOH to give  $W(OMe)_6$ . In all of the above reactions  $WMe_6$  appears more reactive than  $W(NMe_2)_6$ , but toward some substrates the order of reactivity is reversed. For example acetone and  $CS_2$  may be used as inert solvents for  $WMe_6$ .

A fundamental difference in the reactivity patterns of  $WMe_6$  and  $W(NMe_2)_6$  emerges.  $WMe_6$ , which contains a tungsten atom with only 12 valence-shell electrons and is capable of expanding its coordination sphere, readily reacts via initial nucleophilic attack at tungsten. (Alternatively this could be described as electrophilic attack by the electron-deficient

coordinatively unsaturated tungsten atom on a substrate molecule.)  $W(NMe_2)_6$  on the other hand is a sterically crowded molecule and the tungsten attains an 18-electron valence shell as a result of nitrogen p to tungsten dp  $\pi$  bonding. Indeed six  $NMe_2^-$  ligands offer tungsten a total of 24 valence-shell electrons as a result of both  $\sigma$  and  $\pi$  donation. There remains after W-N  $\sigma$  and  $\pi$  bonding a set of six electrons in a triply degenerate, essentially nonbonding molecular orbital belonging to the  $t_u$  representation of the  $T_h$  symmetry group to which the  $W(NC_2)_6$  moiety belongs. Thus the primary mode of reaction of  $W(NMe_2)_6$ , which appears to involve electrophilic attack (protonation) at a nitrogen lone pair, may be rationalized as attack on the filled  $t_u$  nonbonding molecular orbital.

This view of the reactivity patterns for  $WMe_6$  and  $W(NMe_2)_6$  is well illustrated in their reactions with NO and  $CO_2$ .

$W(NMe_2)_6$  does not react with NO under mild conditions.  $WMe_6$  reacts readily consuming 4 equiv of NO to give tetramethylbis(*N*-methyl-*N*-nitrosohydroxylamino)tungsten(VI),  $WMe_4(ON(Me)NO)_2$ . In this reaction tungsten expands its coordination number to 8.<sup>35</sup> This type of reaction has several analogues in the chemistry of transition metal alkyls.<sup>36</sup> For example  $Cp_2ZrMe_2$  reacts<sup>37</sup> with NO to give  $Cp_2ZrMe[ON(Me)NO]$  in which zirconium may be considered to be nine-coordinate. In both instances increasing the coordination number of the metal and number of valence shell electrons renders the remaining metal-carbon (methyl) bonds inert to further reaction with NO.

$WMe_6$  has not been reported to react with  $CO_2$ .  $W(NMe_2)_6$  reacts with  $CO_2$  to give  $W(NMe_2)_3(O_2CNMe_2)_3$  which is inert toward further W- $NMe_2$  insertion. However, the structure of  $W(NMe_2)_3(O_2CNMe_2)_3$  shows that tungsten has not increased its coordination number. The *fac*- $WN_3O_3$  octahedral geometry is adopted presumably because in this geometry nitrogen-to-tungsten  $\pi$  bonding is most favored. This view is certainly supported by the observed short W-N bond distances and long W-O bond distances in  $W(NMe_2)_3(O_2CNMe_2)_3$ . The enhanced N-to-W  $\pi$  bonding in  $W(NMe_2)_3(O_2CNMe_2)_3$  thus renders the  $WNMe_2$  groups inert to substitution by the weak acid  $Me_2NCOOH$ . Similar considerations presumably account for the relative kinetic stability of  $W(NMe_2)_3(OMe)_3$  in the reaction between  $W(NMe_2)_6$  and MeOH.

## Experimental Section

Anhydrous  $Me_2NH$ ,  $MeNH_2$ , and  $NH_3$  were obtained in lecture bottles from Matheson and used as is. *n*-Butyllithium (ca. 2.4 M in hexane), methylolithium (ca. 2.0 M in ether), and *tert*-butyllithium (1.5 M in pentane) were purchased from Alfa Inorganics.  $(CD_3)_2NH$  was purchased from Merck Sharp and Dohme;  $(CF_3)_3COH$ , from PCR, Inc.  $W(NMe_2)_6$  was prepared as previously described.<sup>8</sup>

**Preparation of Tungsten(VI) Alkoxides.  $W(NMe_2)_6 + MeOH$ .** Freshly crystallized  $W(NMe_2)_6$  (0.69 g, 1.55 mmol) was dissolved in hexane (80 mL). This solution was heated (hot water bath) and MeOH (5 mL, 77 mmol) was added via syringe. The solution quickly lost its deep red color and liberated dimethylamine. The solution was heated to reflux and stirred for 2 h. The solvent was stripped from the straw-colored solution, and the off-white residue was dissolved in freshly distilled pentane (70 mL). The solution was concentrated to 20 mL, allowed to cool undisturbed to room temperature, and then placed at  $-20^\circ C$  in the refrigerator. After 24 h the solution was opaque; some crystal formation was apparent. The solution was filtered using a coarse frit. A grayish white solid and clear filtrate were obtained. Solids were discarded and the filtrate was placed at  $-20^\circ C$  for 24 h in the refrigerator. White crystals of  $W(OMe)_6$  formed and were filtered from this solution using a coarse frit. Analytical and NMR data are given in Tables I and II, respectively.

Infrared absorption bands in the region 200–1500  $cm^{-1}$ , obtained from a Nujol mull using CsI plates: 230 (w, br), 305 (w), 368 (m), 476 (w), 532 (s), 580 (w), 1070 (vs), 1085 (sh), 1152 (m), 1418 (w), 1475 (s).

Raman bands, solid sample, 100–1200  $cm^{-1}$ : 238 (w), 305 (m), 372 (m), 476 (w), 585 (vs), 1068 (vw), 1129 (w), 1165 (vw).

**$W(NMe_2)_6 + EtOH$ .**  $W(NMe_2)_6$  (0.918 g, 2.05 mmol) was dissolved in benzene (60 mL). Ethanol (1.43 mL, 25 mmol) was added, and the solution immediately turned deeper red. Dimethylamine was liberated. After 14 h the solution was pale yellow-orange. The solvent was stripped and the pale orange residue was sublimed at 45–70  $^\circ C$  at low vacuum ( $10^{-2}$  Torr), onto a  $CO_2(s)$  cold finger. Upon warming of the cold finger to room temperature, the white sublimate melted to yield a clear liquid. Analytical data and NMR data are given in Tables I and II, respectively.

Infrared bands in the region 300–1500  $cm^{-1}$ , neat liquid between CsI plates: 315 (w), 410 (w), 550 (s, sh), 590 (vs, br), 810 (w), 915 (s), 1060 (vs), 1100 (vs), 1150 (s), 1260 (w), 1270 (w), 1355 (s), 1375 (s), 1445 (m), 1470 (m).

Raman bands in the region 250–1500  $cm^{-1}$ , neat liquid in a sealed capillary: 305 (m, br, p), 620 (s, p), 915 (w, sh, p), 935 (w, p), 1080 (vs, p), 1140 (m, p), 1160 (s, p), 1270 (w, br, dp), 1355 (w, dp), 1375 (w, p), 1450 (m, dp), 1470 (m, dp). (Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad; p, polarized; dp, depolarized.)

**$W(NMe_2)_6 + n$ -PrOH.**  $W(NMe_2)_6$  (1.05 g, 2.34 mmol) was dissolved in benzene (60 mL). *n*-PrOH (2.16 mL, 28 mmol) was added. The solution darkened slightly on addition of the alcohol and liberated dimethylamine. After 72 h the solution was pale orange. The solvent was stripped to yield a red liquid. This was sublimed at 75–85  $^\circ C$ ,  $10^{-3}$  Torr onto a liquid-nitrogen-cooled cold finger. Upon warming the cold finger to room temperature, the white solid melted to yield a clear liquid. Analytical data and NMR data are given in Tables I and II, respectively.

Infrared bands in the region 400–1500  $cm^{-1}$ , neat liquid, between KBr plates: 455 (w, sh), 600 (s, br), 805 (s), 850 (m), 888 (w), 905 (vw), 965 (vs), 1070 (vs, vbr), 1260 (s), 1325 (w), 1340 (w), 1360 (m), 1375 (m), 1465 (m).

Raman bands in the region 200–1500  $cm^{-1}$ , neat liquid sealed capillary: 260 (s), 420 (s), 630 (vs), 655 (vs), 870 (m), 895 (w), 1010 (s), 1030 (s), 1110 (s), 1140 (vs), 1155 (vs), 1170 (vs), 1330 (m), 1345 (m), 1370 (m).

**$W(NMe_2)_6 + i$ -PrOH.**  $W(NMe_2)_6$  (1.183 g, 2.64 mmol) was dissolved in benzene (60 mL). *i*-PrOH (2.43 mL, 32 mmol) was added; the solution darkened slightly, and liberated dimethylamine. After 64 h, the solution was pale orange and somewhat cloudy due to a small amount of fine solid in the solution. The solvent was stripped. The pale solid residue was sublimed at 40–55  $^\circ C$ ,  $10^{-3}$  Torr, onto a liquid-nitrogen-cooled cold finger to yield a yellow-green solid. Analytical data and NMR data are given in Tables I and II, respectively.

Infrared bands in the region 400–1500  $cm^{-1}$ , from a Nujol mull between KBr plates: 470 (w, br), 595 (s), 805 (w, br), 845 (m), 975 (s), 1020 (w, br), 1115 (vs), 1125 (sh), 1165 (m), 1260 (m), 1325 (m), 1365 (m), 1375 (s), 1460 (s).

A strong, sharp band was found in the Raman spectrum at 615  $cm^{-1}$  ( $\nu_{str}(W-O)$ ).

**$W(NMe_2)_6 + Allyl Alcohol$ .**  $W(NMe_2)_6$  (0.787 g, 1.76 mmol) was dissolved in benzene (50 mL). Allyl alcohol solution (8 mL) (benzene azeotrope, 17% allyl alcohol, 10.54 mmol) was added. Dimethylamine was liberated; the solution was heated occasionally (heat lamp). After 24 h the pale orange solution was stripped to leave a pale brown residue. This residue was distilled at 60–90  $^\circ C$ ,  $10^{-3}$  Torr, to yield a pale green liquid. At room temperature the compound appeared yellow. The compound,  $W(OCH_2CH=CH_2)_6$ , was characterized by  $^1H$  and  $^{13}C$  NMR spectroscopy and mass spectroscopy. The heaviest ion corresponded to  $W(OCH_2CH=CH_2)_6^+$ .

Infrared bands in the region 400–2000  $cm^{-1}$ , neat liquid between KBr plates: 460 (m), 540 (m), 695 (vs), 805 (w, br), 903 (m, sh), 920 (s), 940 (s, vbr), 1020 (vs, vbr), 1040 (vs, vbr), 1115 (s, vbr), 1240 (w), 1260 (w), 1285 (w), 1340 (m), 1355 (m), 1400 (s), 1420 (m), 1440 (w), 1645 (m, br, asym).

**$W(NMe_2)_6 + t$ -BuOH.**  $W(NMe_2)_6$  (2.0 g, 4.46 mmol) was added to *t*-BuOH/benzene azeotrope (50 mL, 36.6% *t*-BuOH, 280 mmol). The red solution was refluxed for 64 h. Dimethylamine was liberated and the solution became less red. On removal of the solvent under vacuum, an orange solid remained. This was placed on the high vacuum line and a pale yellow solid (1.0 g) sublimed at 40–50  $^\circ C$ ,  $10^{-3}$  Torr. Anal. Calcd for  $W(O-t-Bu)_4$ : W, 37.40; C, 39.02; H, 7.32; N, 0.00. Calcd for  $W(O-t-Bu)_6$ : W, 29.58; C, 46.30; H, 8.75;

N, 0.00. Found: W, 37.30; C, 39.94; H, 7.34; N, 0.18. In the mass spectrum the ion of highest mass corresponded to  $WO(O-t-Bu)_3^+$ .

The residue after the sublimation was placed on the high vacuum line and at 60–80 °C,  $10^{-3}$  Torr, unreacted  $W(NMe_2)_6$  (0.5 g, 1.12 mmol) was sublimed.

For  $WO(O-t-Bu)_4$ , infrared bands in the region 3000–200  $cm^{-1}$  obtained from a Nujol mull between CsI plates: 305 (m), 366 (m), 468 (m), 475 (m, sh), 555 (s), 779 (s), 895 (m), 908 (m), 940 (vs, br), 1021 (w), 1170 (vs), 1231 (s), 1360 (s), 1378 (m), (2850–3000 (s)).

**$W(NMe_2)_6$  + *t*-BuOH (Sealed Flask, 3 Years).**  $W(NMe_2)_6$  (0.958 g, 2.14 mmol) was dissolved in benzene (80 mL) in a 250-mL round-bottom flask. *t*-BuOH (26 mmol) in *t*-BuOH/benzene azeotrope (36.6%, 5.2 mL) was added via syringe. The solution was frozen and the flask was sealed under vacuum, and stored at room temperature for 3 years. A  $^1H$  NMR spectrum of the reaction mixture taken upon opening the flask showed unreacted starting material and *t*-BuOH. Some additional unidentified resonances were present. The solution was stripped; the resulting red residue was dried for 10 h at  $10^{-3}$  Torr and then dissolved in hexanes. After 96 h at –20 °C, the solution was filtered and crystals of  $W(NMe_2)_6$  were isolated.

**$W(NMe_2)_6$  + Neopentyl Alcohol.** (1) **Preparation of Neopentyl Alcohol Solution.** Neopentyl alcohol (36.46 g, 0.41 mmol) was placed in an oven-dried flask. Benzene (150 mL, dry, oxygen free) and molecular sieves were added to the neopentyl alcohol, and the solution was placed under nitrogen. The solution was 28% neopentyl alcohol by weight.

(2) **Reaction with  $W(NMe_2)_6$ .**  $W(NMe_2)_6$  (0.31 g, 0.69 mmol) was dissolved in benzene (30 mL) in a 50-mL airless flask. Neopentyl alcohol solution (1.47 mL, 4.1 mmol) was added via syringe. The solution was stirred for 3 h at room temperature; no change was observed. The solvent was stripped to 15 mL, and formation of small red crystals ( $W(NMe_2)_6$ ) was apparent. Additional neopentyl alcohol solution (1.47 mL, 4.1 mmol) and benzene (25 mL) were added. The solution was stirred with refluxing at 80 °C for 16 h. The solvent was stripped to 20 mL. The deep red solution was kept at –20 °C for 2 days and then filtered on a coarse frit; crystals of  $W(NMe_2)_6$  were isolated.

A similar reaction was carried out using a sixfold excess of neopentyl alcohol and refluxing in benzene for 60 h.  $W(NMe_2)_6$  was recovered.

**$W(NMe_2)_6$  +  $Et_3SiOH$ .**  $W(NMe_2)_6$  and  $Et_3SiOH$  were reacted in benzene as above. No apparent reaction occurred at room temperature over a period of 72 h. (No reaction was apparent from  $^1H$  NMR spectra recorded during this time.) The solution was then refluxed for 36 h. The solution turned pale yellow. The solvent was stripped to yield an orange oil. Attempts to vacuum distill a tungsten triethylsiloxide led at ca. 100 °C to apparent decomposition:  $(Et_3Si)_2O$  and  $Et_3SiOH$  were distilled leaving behind a black sticky gum. The reaction was not pursued further.

**$W(NMe_2)_6$  + Perfluoro-*tert*-butyl Alcohol (*t*- $C_4F_9OH$ ).**  $W(NMe_2)_6$  (0.32 g, 0.69 mmol) was dissolved in benzene (30 mL) in a 50-mL bantamware flask, with stirring and warming (hot water bath) to aid dissolution. (Not all of the  $W(NMe_2)_6$  went into solution.) After removing the flask from the water bath, *t*- $C_4F_9OH$  (5.3 mmol) in *t*- $C_4F_9OH$ /benzene solution (5 mL) was added via syringe over a period of 5 min. The solution immediately turned green, then after 1 min turned brown, then lightened to red-brown over 30 min. The solution was stirred for 1.5 h. When stirring was stopped, the solution separated into two layers: an orange benzene solution above a heavy brown oil. The solvent was stripped off to give a yellow-orange powder. At 60 °C,  $10^{-3}$  Torr, a white salt was isolated by sublimation. Anal. Calcd for  $(CF_3)_3COH_2N(Me)_2$ : C, 25.62; H, 2.84; N, 4.98; O, 5.69; F, 60.85. Found: C, 25.72; H, 2.99; N, 5.05; F, 61.07.

At 110–120 °C,  $10^{-3}$  Torr, a mixture of the white salt and an oil, varying in color from orange to brown, was obtained upon further sublimation. We were unable to obtain a pure tungsten compound from this mixture.

The above reaction was repeated using a twofold excess of *t*- $C_4F_9OH$  and hexane as solvent. After sublimation of  $(CF_3)_3COH_2NMe_2$ , a small amount of an orange crystalline material sublimed at 120 °C. In the mass spectrometer the highest mass ion was at  $m/e$  805, which corresponds to  $WO[OC(CF_3)_3]^+$ . Cf. mass spectrum of  $WO(O-t-Bu)_4$ .

**$W(NMe_2)_3(OMe)_3$ .**  $W(NMe_2)_6$  (0.588 g, 1.31 mmol) was dissolved in benzene (45 mL) in a 50-mL airless flask. This was cooled in an ice bath to ca. 4 °C. (Not all of the  $W(NMe_2)_6$  went into solution.)

MeOH (1.6 mL, 67 mmol) was added; the solution lightened to orange over a 5-min period. After 15 min the ice bath was removed and replaced with a cold water bath at 8 °C. This was not allowed to warm above 13 °C. After 1 h of stirring, the  $^1H$  NMR spectrum showed no  $W(NMe_2)_6$  or  $W(OMe)_6$ , thus confirming the presence of only an intermediate species. The solvent was stripped without removal of the cold water bath and placed under high vacuum ( $10^{-3}$  Torr) for 10 h. The orange residue showed only two peaks in the  $^1H$  NMR spectrum,  $\delta$  3.9 and 4.2 in the integral ratio 2:1, respectively. Anal. Calcd for  $W(NMe_2)_3(OMe)_3$ : C, 26.41; H, 6.60; N, 10.27. Found: C, 25.88; H, 6.31; N, 9.89.

$W(NMe_2)_3(OMe)_3$  is very soluble in alkane solvents but may be crystallized from pentane at low temperatures. In the mass spectrometer it showed a very weak parent ion  $W(NMe_2)_3(OMe)_3^+$ , a base peak  $W(NMe_2)_2(OMe)_3^+$ , and a weak peak corresponding to  $W(NMe_2)_3(OMe)_2^+$ .

Infrared bands in the region 400–1500  $cm^{-1}$ , obtained from a Nujol mull between CsI plates: 405 (w), 460 (vs), 520 (vs), 800 (w, br), 960 (vs), 970 (vs), 1015 (s), 1035 (s), 1075 (vs), 1095 (vs), 1120 (s), 1140 (s), 1230 (w), 1265 (m), 1380 (vs), 1410 (m), 1460 (vs, br).

In an NMR tube  $W(NMe_2)_3(OMe)_3$  was reacted with MeOH (>3 equiv) in benzene at ca. 35 °C. Reaction was rapid and quantitative to give  $W(OMe)_6$  and  $Me_2NH$ .

**$W(NMe_2)_3(O_2CNMe_2)_3$ .** The preparation of  $W(NMe_2)_3(O_2CNMe_2)_3$  from the reaction between  $CO_2$  and  $W(NMe_2)_6$  and its exchange reactions with  $CO_2$  have been described previously.<sup>30</sup> Note:  $W(NMe_2)_3(O_2CNMe_2)_3$  is an extremely reactive compound and is prone to decomposition at room temperature even when stored under  $N_2$  or in sealed ampules in vacuo. It appears indefinitely stable, however, when sealed in ampules in vacuo and stored in the dark at –15 °C.

**NMR Tube Reactions of  $W(NMe_2)_3(O_2CNMe_2)_3$ .**  **$W(NMe_2)_3(O_2CNMe_2)_3$  + *t*-BuOH.**  $W(NMe_2)_3(O_2CNMe_2)_3$  (ca. 30 mg) was placed in an NMR tube and dissolved in benzene (ca. 0.5 mL) with HMDS (hexamethyldisiloxane) as an internal standard. To this solution, *t*-BuOH (0.2 mL) in a 36% *t*-BuOH/benzene azeotrope was added through a serum cap. The  $^1H$  NMR spectrum recorded after 24 h showed only starting materials.

**$W(NMe_2)_3(O_2CNMe_2)_3$  + MeOH (Deficient in MeOH).**  $W(NMe_2)_3(O_2CNMe_2)_3$  (ca. 30 mg) was placed in an NMR tube and dissolved in benzene (ca. 0.5 mL) with HMDS as an internal standard. To this solution, MeOH (0.09 mmol) in benzene (0.9 M, 100  $\mu$ L) was added via microsyringe, through a serum cap. The  $^1H$  NMR spectrum, recorded after 24 h, showed  $W(OMe)_6$ ,  $Me_2NH$ , and an intermediate species; no  $W(NMe_2)_3(O_2CNMe_2)_3$  was observed. The intermediate is formulated as  $W(OMe)_5(O_2CNMe_2)$  on the basis of  $^1H$  NMR data:  $\delta(OMe)$  4.56,  $\delta(O_2CNMe_2)$  2.75 ppm relative to HMDS.

**$W(NMe_2)_3(O_2CNMe_2)_3$  + MeOH (Excess MeOH).**  $W(NMe_2)_3(O_2CNMe_2)_3$  (ca. 30 mg) was placed in an NMR tube and dissolved in benzene (ca. 0.5 mL) with HMDS added as an internal standard. The sample was frozen in liquid nitrogen. Methanol (100  $\mu$ L) was added via microsyringe through a serum cap to the frozen sample. The reaction was monitored by  $^1H$  NMR spectroscopy at 40 °C; the sample was placed in the probe as soon as it had all melted and had been shaken to ensure mixing. Formation of  $W(OMe)_6$  and  $Me_2NH$  was rapid and quantitative.

**$W(NMe_2)_3(O_2CNMe_2)_3$  +  $CD_3OD$  (Excess  $CD_3OD$ ).**  $W(NMe_2)_3(O_2CNMe_2)_3$  (ca. 30 mg) was placed in an NMR tube and dissolved in benzene (ca. 0.5 mL) with HMDS added as an internal standard. The solution was capped with a serum cap, removed from the drybox, and frozen with liquid nitrogen.  $CD_3OD$  (50  $\mu$ L) was added via microsyringe. As soon as the sample was permitted to melt, it was shaken and placed in the NMR probe at 40 °C. The reaction was monitored by NMR spectroscopy. In this reaction the formation of  $W(OCd_3)_6$  could not be followed directly but was inferred by loss of  $W-NMe_2$  and  $W-O_2CNMe_2$  resonances. From the relative rate of disappearance of  $NMe_2$  signals we conclude that reaction with MeOH proceeds preferentially at the  $W-NMe_2$  moiety. This might have been inferred from reaction with  $CH_3OH$ . However, there is here some ambiguity concerning the assignment of resonances at  $\delta$  ca. 4 ppm which might otherwise be assigned to either  $W-NMe_2$  or  $W-OMe$  protons. It is on this basis that we conclude that the reaction between  $W(NMe_2)_3(O_2CNMe_2)_3$  and MeOH to give  $W(OMe)_6$  proceeds via an intermediate with a significant lifetime,  $W(OMe)_5(O_2CNMe_2)$ .

**W(NMe<sub>2</sub>)<sub>6</sub> + CS<sub>2</sub>.** W(NMe<sub>2</sub>)<sub>6</sub> (0.429 g, 0.96 mmol) was dissolved in hexane (50 mL). A large excess of CS<sub>2</sub> (2 mL, 35 mmol) was added via syringe. No immediate change was apparent. Over 3 h the solution turned mustard color and a flocculent precipitate was formed. This was permitted to sit 1 day to aid in the separation of precipitate from the solvent. However, little change was observed. The mixture was syringed into centrifuge tubes and centrifuged for 3.5 h. The solvent layer was discarded. The solids obtained from centrifugation were heated to 110 °C at 10<sup>-3</sup> Torr. Anal. Calcd for W(S<sub>2</sub>CNMe<sub>2</sub>)<sub>4</sub>: C, 21.69; H, 3.61; N, 8.43. Found: C, 21.40; H, 3.45; N, 8.27.

ESR parameters obtained at 25 °C in CH<sub>2</sub>Cl<sub>2</sub>:  $g_{av} = 1.896$ ,  $A_{av} = 76$  G (<sup>183</sup>W, 15% natural abundance,  $I = 1/2$ ).

Infrared bands in the region 200–2000 cm<sup>-1</sup>, obtained from a Nujol mull between CsI plates: 215 (sh), 235 (s), 260 (w), 360 (m), 375 (w), 395 (w), 445 (s), 525 (m), 575 (m), 725 (m), 805 (s), 890 (w), 935 (w), 975 (s), 1155 (s), 1250 (s), 1375 (s), 1400 (s), 1460 (s), 1550 (s).

**W(NMe<sub>2</sub>)<sub>6</sub> + MeSH.** W(NMe<sub>2</sub>)<sub>6</sub> (0.125 g, 0.28 mmol) was dissolved in benzene (40 mL). This solution was frozen with liquid nitrogen and MeSH (1.84 mmol) was condensed using a calibrated vacuum manifold. The solution was allowed to warm to room temperature under reduced pressure. No immediate change was apparent, but after 8 h of stirring the reaction mixture had turned black. The solvent was stripped. Hexane (35 mL) was added to the black residue and the solution was then filtered. The brown-black precipitate was collected and dried under high vacuum for 8 h. Anal. Calcd for W(SMe)<sub>3</sub>: C, 11.01; H, 2.77. Found: C, 11.30; H, 3.00.

The black powder was insoluble in hexane and benzene but sparingly soluble in methylene chloride.

In CH<sub>2</sub>Cl<sub>2</sub> this material gave an ESR signal at room temperature:  $g_{av} = 2.005$ . No <sup>183</sup>W hyperfine splitting was observed.

Infrared bands at the region 200–2000 cm<sup>-1</sup>, obtained from a Nujol mull between CsI plates: 215 (sh), 230 (s), 255 (m), 340 (m, br), 415 (w), 440 (w), 455 (w), 470 (m), 485 (s), 500 (sh), 615 (m), 725 (m), 805 (s), 945 (s), 1015 (sh), 1190 (s), 1260 (s), 1295 (s), 1375 (vs), 1410 (sh), 1455 (vs).

**W(NMe<sub>2</sub>)<sub>6</sub> + PhSH.** W(NMe<sub>2</sub>)<sub>6</sub> (0.198 g, 0.442 mmol) was dissolved in benzene (35 mL). PhSH (0.40 mL, 3.90 mmol) was added via syringe. The color changed immediately to deep purple, darkening to black over the next several hours. A precipitate was visible. The solvent was stripped and the black residue was dried under vacuum for 8 h. Hexane (35 mL) was added, and the mixture was stirred for 2 h and then filtered using a medium frit. The compound was completely insoluble in hexane. Anal. Calcd for W(SPh)<sub>3</sub>HNMe<sub>2</sub>: C, 43.24; H, 3.78; N, 2.52; S, 17.29. Found: C, 41.75; H, 4.52; N, 2.37; S, 17.38.

In CH<sub>2</sub>Cl<sub>2</sub> the compound gave an unsymmetrical ESR signal:  $g_{av} = 1.96$ , at room temperature.

Infrared bands in the region 200–2000 cm<sup>-1</sup>, obtained from a Nujol mull and CsI plates: 215 (sh), 230 (s), 255 (m), 275 (w), 475 (s), 695 (s), 740 (vs), 805 (m), 890 (w), 940 (w), 1020 (s), 1075 (m), 1150 (w), 1170 (w), 1260 (m), 1300 (w), 1375 (vs), 1455 (vs), 1575 (s).

**W(NMe<sub>2</sub>)<sub>6</sub> + (1) MeLi + (2) CS<sub>2</sub>.** W(NMe<sub>2</sub>)<sub>6</sub> (0.211 g, 0.47 mmol) was dissolved in Et<sub>2</sub>O (35 mL) in a 100-mL airless flask. Methylolithium (0.144 mmol) in Et<sub>2</sub>O (0.08 mL, 2.0 M) was added via syringe. The color darkened slightly from pink-orange to red-orange. CS<sub>2</sub> (0.4 mL, 6.7 mmol) was added. The solution was stirred for 36 h with no apparent change. After the stirring was stopped, a small amount of a fine white precipitate was apparent. (This was presumably LiS<sub>2</sub>CNMe<sub>2</sub>.) The ether was stripped off and the deep red residue was extracted with benzene. An <sup>1</sup>H NMR spectrum showed only a sharp singlet at  $\delta$  3.33 ppm relative to HMDS: W(NMe<sub>2</sub>)<sub>6</sub>.

**W(NMe<sub>2</sub>)<sub>6</sub> + Alkylolithium Reagents.** W(NMe<sub>2</sub>)<sub>6</sub> (0.145 g, 0.33 mmol) was dissolved in hexane (30 mL). A solution of hexane (10 mL), BuLi (0.36 mmol) in hexane (0.15 mL, 2.4 M), and TMEDA (*N,N,N',N'*-tetramethylenediamine) (0.10 mL) was added to the W(NMe<sub>2</sub>)<sub>6</sub> solution. The resulting solution was stirred at room temperature for 24 h. The solvent was stripped and the deep red residue dissolved in benzene. An <sup>1</sup>H NMR spectrum confirmed the presence of W(NMe<sub>2</sub>)<sub>6</sub> as the only NMe<sub>2</sub> containing compound.

In a similar experiment W(NMe<sub>2</sub>)<sub>6</sub> and MeLi (1 equiv) were reacted in ether at room temperature for 12 h. No apparent reaction occurred. The solvent was stripped yielding a red solid which was extracted with benzene. <sup>1</sup>H NMR spectroscopy showed only the

presence of W(NMe<sub>2</sub>)<sub>6</sub> in the benzene-soluble extract.

W(NMe<sub>2</sub>)<sub>6</sub> and LiCH<sub>2</sub>CMe<sub>3</sub> (1 equiv) were similarly reacted in benzene both in an NMR tube and on the bench. No reaction was observed, nor was a reaction observed between *tert*-butyllithium and W(NMe<sub>2</sub>)<sub>6</sub> in benzene even after reflux for 4 h. Crystals of W(NMe<sub>2</sub>)<sub>6</sub> were isolated from this reaction.

**W(NMe<sub>2</sub>)<sub>6</sub> + Amines. (1) With HNEt<sub>2</sub>.** W(NMe<sub>2</sub>)<sub>6</sub> (1.33 g) was placed in a 100-mL round-bottom flask fitted with a condenser and dissolved in benzene (80 mL). HNEt<sub>2</sub> (2.0 mL, 6 equiv) was added and the solution was refluxed for 12 h. The solvent was stripped yielding a red solid. This was redissolved in benzene and a <sup>1</sup>H NMR spectrum was recorded. No reaction had occurred; only W(NMe<sub>2</sub>)<sub>6</sub> was present.

**(2) With NH(CD<sub>3</sub>)<sub>2</sub>.** That W(NMe<sub>2</sub>)<sub>6</sub> and HN(CD<sub>3</sub>)<sub>2</sub> do not react in benzene solution at room temperature has been previously noted.<sup>30</sup>

**(3) With MeNH<sub>2</sub>.** W(NMe<sub>2</sub>)<sub>6</sub> (10 mg, 2.25 × 10<sup>-2</sup> mmol) was dissolved in benzene (0.5 mL) in an NMR tube. H<sub>2</sub>NMe (0.135 mmol) was condensed into the NMR tube using the calibrated vacuum manifold. The NMR tube was sealed with a torch. No reaction was observed by <sup>1</sup>H NMR spectroscopy over a period of 2.5 months.

**(4) With NH<sub>3</sub>.** W(NMe<sub>2</sub>)<sub>6</sub> (10 mg, 2.25 × 10<sup>-2</sup> mmol) was dissolved in benzene (0.5 mL) in an NMR tube. Anhydrous NH<sub>3</sub> (1 mmol) was condensed into the NMR tube using a calibrated vacuum line. The NMR tube was sealed with a torch. A slow reaction occurred leading to a white precipitate. The disappearance of W(NMe<sub>2</sub>)<sub>6</sub> with concomitant formation of Me<sub>2</sub>NH was seen in the <sup>1</sup>H NMR spectrum. The reaction was not pursued beyond these observations.

**Miscellaneous Reactions. Sealed-Tube Reactions.** W(NMe<sub>2</sub>)<sub>6</sub> (ca. 10 mg, 2.25 × 10<sup>-2</sup> mmol) was dissolved in benzene (ca. 0.5 mL) in each of a number of NMR tubes. These samples were then reacted with each of the following: allene, ethylene, 1,3-butadiene, cyclopentadiene, and phenylacetylene. In all instances no reaction was found to occur. With hexafluorobut-2-yne a reaction did occur. In the presence of a large excess of the acetylene the solution turned to a gel within 24 h at room temperature. The reaction was repeated on a larger scale. The solution was filtered using a fine frit. A red benzene solution of W(NMe<sub>2</sub>)<sub>6</sub> and a finely divided white precipitate were obtained. The white solids were washed with benzene and dried under high vacuum. Anal. Calcd for (CF<sub>3</sub>CCCCF<sub>3</sub>)<sub>n</sub>: C, 29.63; H, 0.00; N, 0.00; F, 70.37. Found: C, 27.97; H, 0.00; N, <23 ppm; F, 72.31. (Analysis was obtained from Schwarzkopf, Woodside, N.Y.)

**With CO, H<sub>2</sub>, NO, and O<sub>2</sub>.** On the bench top, a benzene solution of W(NMe<sub>2</sub>)<sub>6</sub> was stirred at room temperature for 12 h under an atmosphere of each of the above. In each case no reaction was apparent and W(NMe<sub>2</sub>)<sub>6</sub> was recovered.

**With (i) Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>-</sup> and (ii) MeSO<sub>3</sub>CF<sub>3</sub>.** W(NMe<sub>2</sub>)<sub>6</sub> was reacted with both Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>-</sup> (1 equiv) and MeSO<sub>3</sub>CF<sub>3</sub> (1 equiv) in dichloromethane. A reaction was apparent in both instances but no pure tungsten compound was isolated. The products of the reactions were brown gums which were insoluble in benzene and alkane solvents. Attempts to obtain crystals from CH<sub>2</sub>Cl<sub>2</sub>/ether solutions failed.

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**Registry No.** W(OMe)<sub>6</sub>, 35869-33-1; W(OEt)<sub>6</sub>, 62571-53-3; W(O-*n*-Pr)<sub>6</sub>, 62571-52-2; W(O-*i*-Pr)<sub>6</sub>, 52321-90-1; W(O(allyl))<sub>6</sub>, 62571-51-1; WO(O-*t*-Bu)<sub>4</sub>, 58832-09-0; W(NMe<sub>2</sub>)<sub>3</sub>(OMe)<sub>3</sub>, 62571-50-0; W(NMe<sub>2</sub>)<sub>6</sub>, 26382-63-8; (CF<sub>3</sub>)<sub>3</sub>COH<sub>2</sub>N(Me)<sub>2</sub>, 62506-17-6; W(S<sub>2</sub>CNMe<sub>2</sub>)<sub>4</sub>, 61069-37-2; W(SMe)<sub>3</sub>, 42592-21-2; W(SPh)<sub>3</sub>HNMe<sub>2</sub>, 62571-43-1; (CF<sub>3</sub>CCCCF<sub>3</sub>)<sub>n</sub>, 26984-91-8; W(NMe<sub>2</sub>)<sub>3</sub>(O<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub>, 53392-65-7; <sup>13</sup>C, 14762-74-4; W(OMe)<sub>5</sub>(O<sub>2</sub>CNMe<sub>2</sub>), 62601-23-4.

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## The Molybdenum–Molybdenum Triple Bond. 2.<sup>1</sup> Hexakis(alkoxy)dimolybdenum Compounds: Preparation, Properties, and Structural Characterization of $Mo_2(OCH_2CMe_3)_6$

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$Mo_2(NMe_2)_6$  reacts with alcohols and trialkylsilanols, ROH, to give alkoxides and trialkylsiloxides, respectively, of empirical formula  $Mo_2(OR)_6$ . Bulky RO groups, e.g., those with R =  $PhMe_2C$ ,  $Me_3C$ ,  $Me_2CH$ ,  $Me_3CCH_2$ ,  $Me_3Si$ , and  $Et_3Si$ , give dinuclear compounds  $Mo_2(OR)_6$ , which, on the basis of physicochemical studies, including vibrational spectroscopy, variable-temperature <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and mass spectroscopy, are formulated as compounds containing molybdenum-to-molybdenum triple bonds unsupported by bridging alkoxy ligands. This claim is supported by a single-crystal x-ray diffraction study on the neopentoxide. For  $Mo_2(OCH_2CMe_3)_6$  the space group is  $P2_1/n$  with  $a = 18.160$  (10) Å,  $b = 11.051$  (7) Å,  $c = 9.956$  (6) Å,  $\beta = 104.30$  (4)°,  $V = 1936$  (2) Å<sup>3</sup>, and  $Z = 2$ . The central  $Mo_2O_6$  skeleton has virtual  $D_{3d}$  symmetry, i.e., ethanelike geometry. The Mo–Mo distance is 2.222 (2) Å and the mean Mo–O distance is 1.88 (2) Å. The deviation from  $D_{3d}$  symmetry within the  $Mo_2O_6$  core resides principally in the three crystallographically independent Mo–O angles: two are effectively identical (105.4 and 105.5°) while the third is smaller (98.3°). In hydrocarbon solvents  $Mo_2(OCH_2CMe_3)_6$  is unstable and slowly and irreversibly oligomerizes to an insoluble form of the alkoxide,  $[Mo(OCH_2CMe_3)_3]_n$ . The less sterically demanding ethoxy and methoxy ligands also give rise to polymeric alkoxides. The ethoxide is diamagnetic and tetrameric,  $Mo_4(OEt)_{12}$ , in benzene solution. In the mass spectrometer polynuclear and mononuclear ions are observed; the most abundant ions are  $Mo_4(OEt)_{12}^+$ ,  $Mo_3(OEt)_9^+$ ,  $Mo_2(OEt)_6^+$ , and  $Mo(OEt)_3^+$ . The dinuclear alkoxides  $Mo_2(OR)_6$ , where R =  $SiMe_3$  and  $CH_2CMe_3$ , react with amines to give adducts  $Mo_2(OR)_6 \cdot 2L$ . The chemistry of the dinuclear alkoxides of molybdenum is compared with that of the related  $M_2L_6$  compounds, where M = Mo or W and L = R (alkyl) or  $NR_2$ , and with related organo derivatives of trivalent chromium.

### Introduction

Metal alkoxides tend to undergo the minimum degree of oligomerization consistent with the attainment of the favored coordination number of the metal.<sup>3</sup> Thus for titanium tetraethoxide a tetrameric structure allows each titanium atom to achieve six-coordination by sharing of  $TiO_6$  octahedra.<sup>4</sup> However, bulky alkoxy ligands may prevent the attainment of the favored coordination number of the metal: titanium tetra-*tert*-butoxide is monomeric. A similar situation is found in the chemistry of the alkoxides of trivalent chromium.

$Cr(OR)_3$  compounds, where R = Me, Et, and *n*-Pr, are polymeric and, on the basis of magnetic susceptibility data and diffuse-reflectance spectra, are believed to have all chromium atoms in  $CrO_6$  units.<sup>3,5</sup> Bulky *tert*-alkoxy ligands do not allow trivalent chromium to attain its favored six-coordination. For example, the polymeric compound  $LiCr(O-t-Bu)_4$  provides a rare example of a trivalent chromium ion in a four-coordinated pseudotetrahedral environment.<sup>6</sup>

In this paper we describe a general preparation of alkoxides of trivalent molybdenum. For the first time in the chemistry