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Hexakis(dimethylamido)tungsten(VI)

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$W(NMe_2)_6$ has been characterized by a number of physicochemical studies, including single-crystal x-ray diffraction studies, infrared and Raman spectroscopy, NMR spectroscopy, and mass spectroscopy.

Introduction

Homoleptic compounds ML_n where L = R (alkyl),[2,3] NR_2,[4] and OR[5] are now known for all of the group 4–6 transition metals for certain values of *n*. This work arises from our continuing interest in the chemistry of these compounds. We report our characterization of $W(NMe_2)_6$ which is the first compound of formula ML_6 to be characterized for the dialkylamido series (L = NR_2). Preliminary reports of this work have been published.[6,7] Wilkinson and his co-workers[8,9] have recently reported the preparation of WMe_6. The alkoxides $W(OR)_6$ are also known.[10,11] Thus for tungsten there exists a series of homoleptic compounds WL_6, where L = Me, NMe_2, and OR, in addition to a series of dinuclear compounds W_2L_6, where L = CH_2SiMe_3,[12] NR_2,[7] and OBu^t.[13] The latter series contain tungsten-to-tungsten triple bonds unsupported by bridging ligands.

Results and Discussion

Syntheses. Metathetic reactions involving early transition metal halides and $LiNR_2$ (*n* equiv) have in general been successful in the preparation of $M(NR_2)_n$ compounds.[4] With the intent of preparing $W(NMe_2)_6$ we undertook a study of the reaction between WCl_6 and $LiNMe_2$ (6 equiv) in hexane/ether/THF solvent mixtures. From these reactions we obtained $W(NMe_2)_6$ as a red crystalline compound. Although the authenticity of $W(NMe_2)_6$ was verified by a single-crystal x-ray study,[6] subsequent work showed[7] that the bulk samples of $W(NMe_2)_6$ prepared from WCl_6 were always contaminated with $W_2(NMe_2)_6$. It was not possible to separate these two compounds by either fractional crystallization or sublimation because of their very similar physical properties. Further x-ray studies showed[7] that $W_2(NMe_2)_6$ and $W(NMe_2)_6$ cocrystallize. The unit cell contained two molecules of the dinuclear compound and one molecule of the mononuclear species: 2 $W_2(NMe_2)_6$ + 1 $W(NMe_2)_6$. Although physical techniques employing sublimation, crystallization, and chromatography were unsuccessful in separating these two compounds, pure $W(NMe_2)_6$ can be isolated from such mixtures at the expense of destroying the $W_2(NMe_2)_6$.

$W_2(NMe_2)_6$ reacts smoothly at room temperature with *t*-BuOH to give $W_2(OBu^t)_6$ which is very soluble in hydrocarbon solvents.[13] $W(NMe_2)_6$ on the other hand does not react with *t*-BuOH at room temperature.[11] Thus $W(NMe_2)_6$ may be isolated from mixtures of $W(NMe_2)_6$ and $W_2(NMe_2)_6$ by crystallization from *t*-BuOH/benzene solutions.

We have now investigated a number of reactions involving tungsten halides and $LiNMe_2$. The characterized products obtained from these reactions were $W(NMe_2)_6$, $W_2(NMe_2)_6$, or mixtures of the two compounds depending on the choice of the tungsten halide. The products obtained from these reactions were quite unpredictable though reproducible results were obtained.[7] The most efficient syntheses of $W(NMe_2)_6$ which are based on tungsten and are free from $W_2(NMe_2)_6$ have been from (i) WBr_5 and $LiNMe_2$ (5 equiv) and (ii) $WOCl_4$ and $LiNMe_2$ (6 equiv).[7] The dimethylamides were obtained in only low yields in these metathetic reactions and the overall reaction between WCl_n and $LiNMe_2$ (*n* equiv) is clearly complex and at the present time is not understood. These reactions do, however, seem to have some parallel to the work of Wilkinson and his co-workers, who found that WMe_6 could be obtained from the reaction between WCl_6 and MeLi (3 equiv) in the presence of adventitous molecular oxygen.[8,9] We have not wittingly used molecular oxygen, but the finding that we can obtain $W(NMe_2)_6$ from reactions employing WBr_5 or $WCl_4(THF)_2$ clearly indicates that redox processes are involved.

Shortland and Wilkinson reported[8] that WMe_6 reacted with $HNMe_2$ to give $W(NMe_2)_6$ and that reaction with $HN(i\text{-}Pr)_2$ gave the corresponding tungsten dialkylamide. We have been unable to verify this claim.

Attempts to prepare $W(NR_2)_6$ compounds where R is other than methyl failed. This is not altogether surprising since such species would be exceedingly crowded. For example, although it is possible to fit five NEt_2 ligands around a third-row transition metal, e.g.,[4] as in $Ta(NEt_2)_5$, molecular models suggest it would not be possible to fit six NEt_2 ligands.

Reactions involving WCl_6 and $LiNEt_2$ (6 equiv) gave a mixture of products including $W_2(NEt_2)_6$.[7] Volatile mononuclear species were also formed and a pale yellow distillable liquid (60 °C (10^{-4} cmHg)) which we formulate as $W(NEt)_2(NEt_2)_2$ has been partially characterized from these reactions (see later). Formation of the nitrene or imido ligand has precedent in the chemistry of tantalum.[14] Reactions involving $TaCl_5$ and $LiNR_2$ (5 equiv) gave $Ta(NR)(NR_2)_3$ compounds when R = Et, Pr^n, Bu^n.[14] The mechanism of the formation of the nitrene ligand in these reactions is not known. However, an interesting parallel is found in metal alkyl chemistry, for while it has been possible to synthesize $TaMe_5$, more sterically demanding alkyl ligands give rise to carbene complexes, e.g.,[15] $Ta(CHR)(CH_2R)_3$ where R = CMe_3.

Characterization. $W(NMe_2)_6$ is a red crystalline compound of considerable thermal stability. It readily sublimes under high vacuum (100 °C (10^{-4} cm Hg)) and decomposes under nitrogen without melting at temperatures above 200 °C. It is only slightly soluble in hexane, benzene, and other hydrocarbon solvents. Its solubility in benzene at 25 °C is ca. 1 g/100 mL. Crystals of $W(NMe_2)_6$ are remarkably hydrolytically stable compared to those of other metal dimethylamides. Indeed crystalline $W(NMe_2)_6$ decomposes only over a period of hours in the atmosphere. In solution $W(NMe_2)_6$ is more sensitive toward hydrolysis. A cryoscopic molecular weight determination comfirmed its monomeric nature in benzene: calcd, 448; found, 428 ± 20. The ^1H NMR spectrum of $W(NMe_2)_6$ recorded in toluene-d_8 showed a single resonance at δ 3.33 ppm (relative to hexamethyldisiloxane) which was independent of temperature in the range of +80 to −80 °C. The ^{13}C NMR spectrum also showed a single resonance, δ 53.2 ppm (relative to TMS). These NMR observations are entirely consistent with the structure of $W(NMe_2)_6$ found in the crystalline state.

Molecular Structure and Bonding. The molecular structure of $W(NMe_2)_6$ has now been determined by two independent single-crystal x-ray studies: (i) on a crystal of pure $W(NMe_2)_6$[6] and (ii) on a crystal containing two dinuclear

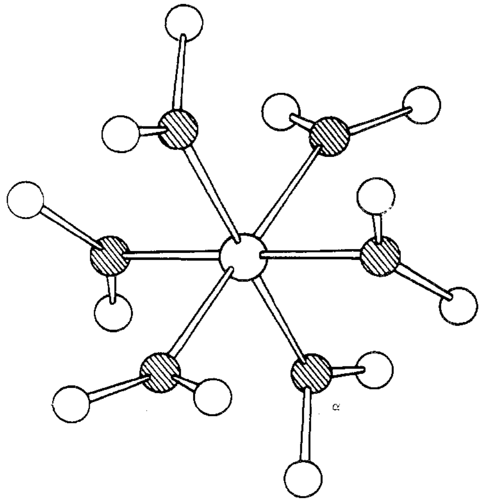

Figure 1. Molecular structure of $W(NMe_2)_6$ deduced from single-crystal x-ray studies. W–N = 2.017 (6) Å,[7] 2.032 (25) Å;[6] N–C = 1.515 (15) Å;[7] α = 104 (1)°.[6,7] The molecule has T_h symmetry.

molecules, $W_2(NMe_2)_6$, and one mononuclear molecule, $W(NMe_2)_6$, per unit cell.[7] The geometry of the $W(NC_2)_6$ moiety is shown in Figure 1. The $W(NC_2)_6$ moiety thus belongs to the symmetry point group T_h, which is a symmetry point group shared by few other molecules.[16]

The CNC angles, ca. 103°, are significantly smaller than those found in other $M{-}NMe_2$ containing compounds. For example, the CNC angles in $W_2(NMe_2)_6$[7] and $Ti(NMe_2)_2(O_2CNMe_2)_2$[17] are 111 and 112°, respectively. The small CNC angle in $W(NMe_2)_6$ probably reflects the severe steric congestion in the molecule.

The planarity of the trans $C_2N{-}W{-}NC_2$ units suggests delocalized nitrogen to tungsten (p_π–d_π) π bonding. If we assume that σ interactions are more important than π interactions, then the bonding in $W(NMe_2)_6$ may be depicted schematically by the molecular orbital diagram shown in Figure 2. Tungsten attains a share of 18 valence-shell electrons and the W–N bond order may approach 1.5. Structural evidence in support of nitrogen to tungsten π bonding in $W_2Me_2(NEt_2)_4$ has been presented.[18]

Support for the bonding scheme described in Figure 2 may be seen in the He I photoelectron spectrum of $W(NMe_2)_6$ recently reported by Lappert and co-workers.[19] The first band in the PE spectrum occurred at 6.74 eV and was assigned to ionization from the T_u nonbonding π molecular orbital. The second band at 7.92 eV was attributed to ionization from the π bonding T_g molecular orbital.

The red color of $W(NMe_2)_6$ is due to a tailing into the visible region of the electronic spectrum of an intense band at 30 000–33 000 cm^{-1}. According to the molecular orbital diagram shown in Figure 2 this may be assigned to the transition $t_g^* \leftarrow t_u$, which is equivalent to a single electron transfer from a nitrogen p_π orbital to a tungsten d orbital (d_{xy}, d_{xz}, or d_{yz}) on a simple crystal field basis.

Mass Spectrum. $W(NMe_2)_6$ gives a weak molecular ion, $W(NMe_2)_6^+$ in the mass spectrometer, and a base peak corresponding to $W(NMe_2)_5^+$. This is typical of WL_6 compounds (L = Me,[8] OMe[11]). Table I reports mass spectral data for $W(NMe_2)_6$ together with a number of prominent metastable reactions. The prominent mode of fragmentation involves loss of $\cdot NMe_2$, $HNMe_2$, and $\cdot Me$, which is charac-

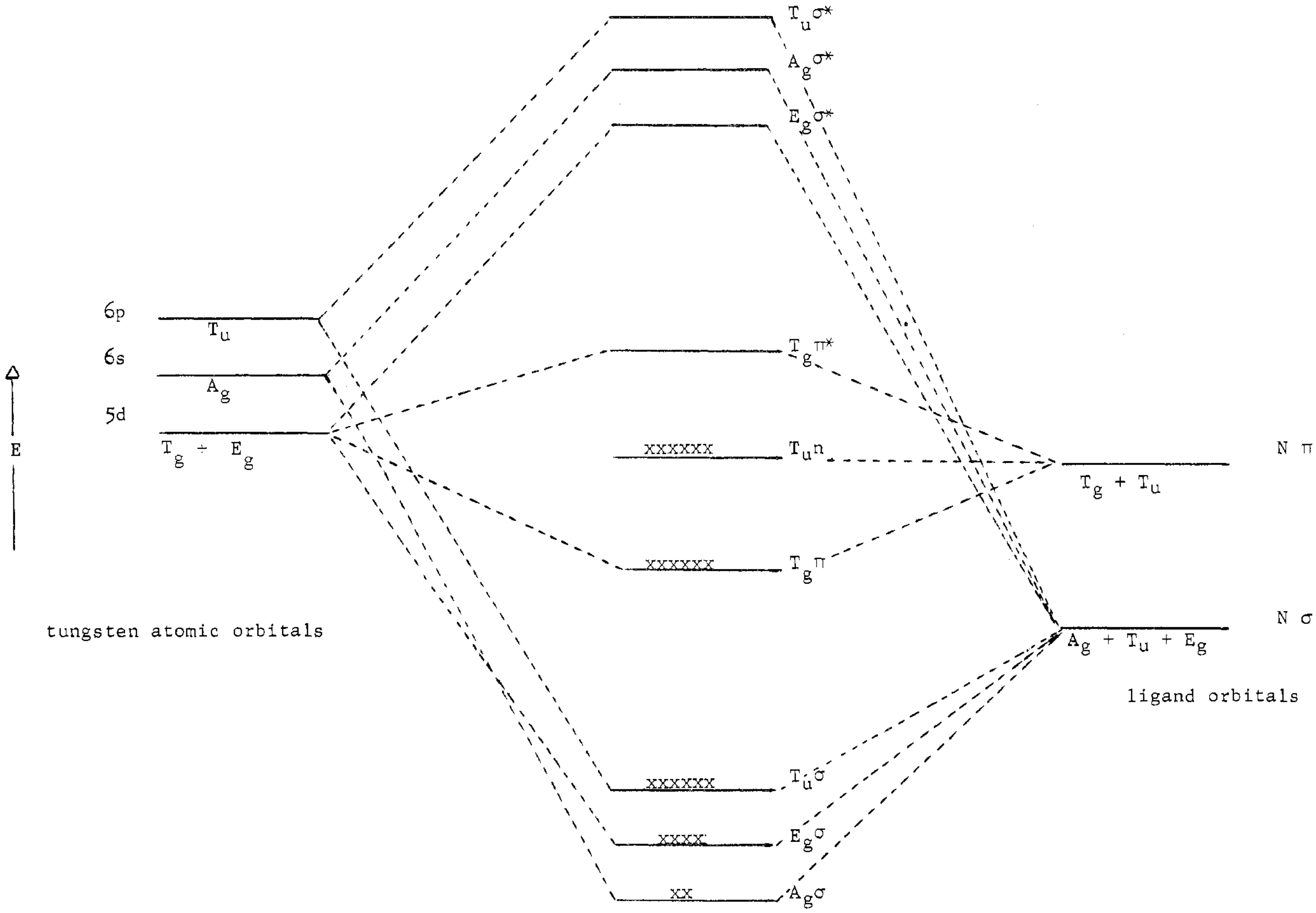

Figure 2. Schematic molecular orbital energy level diagram for $W(NMe_2)_6$.

Table I. Mass Spectral Data for $W(NMe_2)_6$ Obtained at 90 °C, 1.8×10^{-6} cmHg, and 70 eV

m/e (^{184}W)	Ion	Abundance
448	$W(NMe_2)_6^{+\cdot}$	5
404	$W(NMe_2)_5^+$	100
360	$W(NMe_2)_4^{+\cdot}$	46
359	$W(NMe_2)_3NCH_2Me^+$	21
345	$W(NMe_2)_3NMe^+$	88
316	$W(NMe_2)_3^+$	75
302	$W(NMe_2)_2HNMe^+$	26
300	$W(NMe_2)_2NCH_2^+$	16
298	$W(NMe_2)_2NC^+$	16
296	$W(NCH_2Me)_2NC^+$	39
286	$WNMe_2(NMe)_2^+$	5
284	$WNMe_2NMeNCH^+$	5
282	$WNMe_2(NCH_2)_2^+$	5
273	$WNMe(HNMe)_2^+$	10
269	$WNMe(NCH_2)_2^{+\cdot}$	10
267	$W(NCH_2)_2NCH^{+\cdot}$	10
259	$WNMe_2H_2NMe^+$	10
257	$WNMe_2NMe^+$	13
255	$WNMe_2NCH^+$	13
253	$WNCH_2MeCN^+$	7
243	$WNMeHNMe^+$	10
239	$WNMeCN^+$	5
228	$WNMe_2^+$	5
214	$WHNMe^+$	Trace
202	$W(NMe_2)_5^{2+}$	0.5
197	WNC^+	Trace
196	$WC^{+\cdot}$	Trace
180	$W(NMe_2)_4^{2+}$	33
172	$W(NMe_2)_3NCH_2^{2+}$	3
165	$W(NMe_2)_2(NMe)_2^{2+}$	2
158.5	$WH(NMe_2)_3^{2+}$	2
157.5	$W(NMe_2)_2NCH_2Me^{2+\cdot}$	3
156.5	$W(NMe_2)_2NCMe^{2+}$	3
155.5	$W(NMe_2)_2NCH^{2+}$	3
154.5	$WNMe_2NCH_2MeNC^{2+}$	2
149.5	$W(NMe_2)_2NCH^{2+}$	5
148.5	$WNMe_2NCH_2MeNC^{2+}$	10
147.5	$WNMe_2NCMeNC^{2+}$	5
141.5	$WNMe_2NMeNC^{2+}$	2
139.5	$WNCMeNCH_2NC^{2+}$	2
133.5	$WNMeNCH_2NC^{2+}$	2

Metastable Reactions

1. $W(NMe_2)_6^{+\cdot} \xrightarrow[m = 364.3]{-Me_2N\cdot} W(NMe_2)_5^+$

2. $W(NMe_2)_5^+ \xrightarrow[m = 320.8]{-Me_2N\cdot} W(NMe_2)_4^{+\cdot}$

3. $W(NMe_2)_5^+ \xrightarrow[m = 319.0]{-Me_2NH} W(NMe_2)_3NCH_2Me^+$

4. $W(NMe_2)_4^{+\cdot} \xrightarrow[m = 330.6]{-Me\cdot} W(NMe_2)_3NMe^+$

5. $W(NMe)_4^{+\cdot} \xrightarrow[m = 277.4]{-Me_2N\cdot} W(NMe_2)_3^+$

6. $W(NMe_2)_3NMe^+ \xrightarrow[m = 260.9]{-Me_2NH} W(NMe_2)_2NCH_2^+$

7. $W(NMe_2)_2HNMe^+ \xrightarrow[m = 298.0]{-H_2} W(NMe_2)_2NCH_2^+$

8. $W(NMe_2)_2NCH_2^+ \xrightarrow[m = 296.0]{-H_2} W(NMe_2)_2NC^+$

9. $W(NMe_2)_2NC^+ \xrightarrow[m = 246.4]{-HCN} WNMe_2NCH_2Me^+$

teristic of the behavior of early transition metal dimethylamides in the mass spectrometer.

Vibrational Spectra. Infrared spectral studies have been reported for a number of metal dimethylamides and assignments have been suggested.[20-22] These earlier studies should form a basis for an assignment of the vibrational spectra of $W(NMe_2)_6$. However such assignments do not appear justifiable in the light of the following observations.

Table II. Vibrational Data for $W[N(CH_3)_2]_6$ and $W[N(CD_3)_2]_6$ in the Region below 1000 cm^{-1}

Infrared[a]		Raman[b]	
H_{36}	D_{36}	H_{36}	D_{36}
322 m	285 m		
		335 s (d)	300 s (d)
364 s	333 s		
		357 s (p)	317 s (p)
420 w	379 w		
		559 vs (p)	482 vs (p)
545 vs	466 vs		
		959 vs (d)	824 (d)
942 vvs	812 vvs		
		985 s (p)	830 (p)

[a] Nujol mull; CsI plates. [b] THF as solvent; spinning cell.

Table II contains infrared and Raman data, including polarization measurements, for $W[N(CH_3)_2]_6$ and $W[N(CD_3)_2]_6$ in the range below 1000 cm^{-1}. For a molecule with a center of inversion the selection rules predict that no band should be both infrared and Raman active. For $W(NMe_2)_6$ this situation is met. For the WN_6 octahedral moiety we expect six normal modes: ν_1 (A_{1g}), ν_2 (E_g), and ν_5 (T_{2g}) are Raman active; ν_3 (T_{1u}) and ν_4 (T_{1u}) are infrared active. The strong infrared-active band at 545 cm^{-1} could readily be assigned to ν_3, the antisymmetric W–N stretching mode. However, on deuteration this band shifts to 466 cm^{-1}. A shift of 79 cm^{-1} cannot be attributed to mass effects on $\nu_{str}[W-N(CH_3)_2]$ and $\nu_{str}[W-N(CD_3)_2]$. Similarly in the Raman spectrum the very strong polarized band at 559 cm^{-1} might readily be assigned to ν_1, the totally symmetric W–N stretching vibration, if it were not known that on deuteration this band shifted to 482 cm^{-1}. Again a shift of 77 cm^{-1} is not reconcilable with the assignment of this band to a simple W–N stretching mode.

The shifts which accompany deuteration parallel those previously described[7] for $M_2(NMe_2)_6$, where M = Mo and W, and demonstrate that W–N stretching modes are extensively coupled to other vibrational modes associated with the CH_3/CD_3 moieties. Simple vibrational assignments for $W(NMe_2)_6$ are clearly not possible.

Diethylamido Derivatives. From the reaction between WCl_6 and $LiNEt_2$ (6 equiv) we failed to isolate any pure compound. Mass spectral analysis indicated the presence of $W_2(NEt_2)_6$[7] in the residues which remained after vacuum distillation of an orange liquid. The orange liquid gave a very complicated ^1H NMR spectrum and the distillate is clearly composed of two or more compounds. The most volatile fraction of this distillate (60 °C (10^{-4} cmHg)) is an exceedingly air-sensitive pale yellow liquid which darkens with prolonged contact with glass. The ^1H NMR spectrum of this fraction was quite simple and consisted of two ethyl resonances in the integral ratio 2:1. In the ^{13}C NMR spectrum two types of ethyl carbon resonances are found. We suggest that this fraction contains the nitrene compound $W(NEt)_2(NEt_2)_2$. Such a compound has precedent in the chemistry of tantalum, e.g., in the formation of $Ta(NEt)(NEt_2)_3$.[14,20]

Experimental Section

Physical and Analytical Measurements. General procedures and the preparation of pure $W(NMe_2)_6$ from the reactions (i) between WBr_5 and $LiNMe_2$ (5 equiv) and (ii) between $WOCl_4$ and $LiNMe_2$ (6 equiv) have been described previously.[7]

From $W(NMe_2)_6$ and $W_2(NMe_2)_6$ Mixtures. A mixture of $W(NMe_2)_6$ and $W_2(NMe_2)_6$, ca. 2 g, prepared from the reaction between WCl_6 and $LiNMe_2$ was dissolved in the *t*-BuOH/benzene azeotrope

(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 3×10^{-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; δ 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; δ 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; δ 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, δ 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 $WO(O\text{-}t\text{-}Bu)_4$. 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 alkyllithium 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),[2,3] NR_2,[4] and OR,[5] 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 σ bonds within a series of closely related compounds. For tungsten there exist two known series: WL_6, where L = Me,[6] NMe_2,[7,8] and OMe,[7] and W_2L_6, where L = CH_2SiMe_3,[9,10] NR_2,[11] and O-*t*-Bu.[12] This work arises from our continuing interest in the chemistry of these compounds.[13] 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.[6]

Results and Discussion

Aminolysis. A characteristic of metal dialkylamides is their