The Tungsten–Tungsten Triple Bond. 1. Preparation, Properties, and Structural Characterization of Hexakis(dimethylamido)ditungsten(III) and Some Homologues

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Abstract: Metathetic reactions involving a variety of tungsten halides and $LiNMe_2$ lead to $W_2(NMe_2)_6$, $W(NMe_2)_6$, and mixtures of these dimethylamides depending on the tungsten halides used. Pure $W_2(NMe_2)_6$, free from $W(NMe_2)_6$, is prepared from the reaction of WCl_4 with $LiNMe_2$ (4 equiv). The related compounds $W_2(NMeEt)_6$ and $W_2(NEt_2)_6$ are prepared by similar reactions. These tungsten(III) dialkylamides are pale-yellow, diamagnetic crystalline solids and have been characterized by a number of physical techniques including variable temperature ^1H NMR spectroscopy, infrared and Raman spectroscopy, and mass spectroscopy. Two compounds have been studied crystallographically. A substance consisting of $W_2(NMe_2)_6$ molecules and $W(NMe_2)_6$ molecules in a 2:1 ratio crystallizes in the space group $P\bar{3}$, with unit cell dimensions: $a = b = 13.556$ (2), $c = 9.420$ (2) Å; $V = 1499.6$ (5) Å^3. The $W(NMe_2)_6$ molecule occupies the crystallographic position 0, 0, $\frac{1}{2}$ with symmetry $\bar{3}$. The dimensions agree well with those previously determined for the pure $W(NMe_2)_6$ phase. The $W_2(NMe_2)_6$ molecules occupy the $\frac{1}{3}$, $\frac{2}{3}$, z and $\frac{2}{3}$, $\frac{1}{3}$, $\bar{z}$ positions with crystallographic symmetry 3. The W–W distance is 2.294 (1) Å; the mean W–N distance and mean W–W–N angles are, respectively, 1.98 Å and 103.8°. The structure was refined to $R_1 = 0.047$ and $R_2 = 0.061$ using 4531 reflections having $I > 3\sigma(I)$. Crystals consisting entirely of $W_2(NMe_2)_6$ molecules belong to space group $P2_1/c$ (isomorphous with the corresponding Mo compound) with unit cell dimensions of $a = 11.465$ (3) Å, $b = 11.948$ (3) Å, $c = 15.409$ (3) Å, $\beta = 101.84$ (2)°, and $V = 2065.9$ (8) Å^3. There are two crystallographically independent molecules, each having crystallographic symmetry $\bar{1}$ but virtual symmetry which deviates only slightly from $\bar{3}m$ (D_{3d}) and even less from $\bar{3}$ (S_6). In these molecules the W–W distances are 2.290 (2) and 2.294 (2) Å. The mean values of the W–N distance and the W–W–N angles in both molecules are, respectively, 1.97 Å and 103.3°. This structure was refined to $R_1 = 0.055$ and $R_2 = 0.067$ using 1521 reflections having $I > 3\sigma(I)$.

The fact that transition metal atoms have the capacity to form multiple bonds which are discrete, unsupported by bridging ligands and of orders (2, 3) not only equal to those formed by carbon, nitrogen, and oxygen and a few other nontransition elements but uniquely high (namely, of order 4), is a wholly new facet of chemistry which has been recognized only in recent years.[2,3]

Despite the fact that molybdenum and rhenium have provided an abundance of compounds with homonuclear metal to metal bonds of high orders, tungsten has, surprisingly, not displayed similar behavior. Up to this time no compound with a W–W bond of order 4 has been characterized despite the fact that such bonds are found in scores of molybdenum compounds.[3] Moreover, the only compound previously reported which seemed likely to contain an unbridged W–W triple bond is $(Me_3SiCH_2)_6W_2$[4] and this has not been structurally characterized beyond the observation that it is isomorphous to the dimolybdenum analogue which has been shown to have a C_6Mo_2 skeleton with D_{3d} symmetry and an Mo–Mo bond length (2.167 Å), consistent with the presence of a triple bond.

In this paper we describe the first fully characterized molecule containing a triple bond between tungsten atoms and give details of its preparation, chemical and physical properties, and the structure of the molecule in two different crystalline substances.[5]

Results and Discussion

Synthesis. The preparation of $W(NMe_2)_6$ from the reaction of WCl_6 and $LiNMe_2$ (6 equiv) has been reported previously.[6] Although $W(NMe_2)_6$ was characterized[6] by a single-crystal x-ray structural determination, analyses of repeatedly recrystallized samples obtained from these metathetic reactions indicated the presence of reduced tungsten species. Typically, nitrogen to tungsten ratios were in the range 4:1 to 5:1 (see Experimental Section). ^1H NMR spectra of these samples showed two signals at δ 3.33 and 3.30 ppm (rel HMDS) at 30° and above. On cooling the sample the resonance at δ 3.30 ppm initially broadened, collapsed into the baseline (−30°), and gave two resonances at δ 2.35 and 4.28 ppm (rel HMDS) at −40° and below in the integral ratio of one to one. The resonance at δ 3.33 ppm arising from $W(NMe_2)_6$ was invariant with temperature. In the mass spectrum there appeared ions derived from $W(NMe_2)_6$, e.g., WL_6^+, WL_5^+, and WL_4^+, together with ditungsten ions $W_2L_6^+$, $W_2L_5^+$, and $W_2L_4^+$ (L = NMe_2).

These observations suggested that the reaction between WCl_6 and $LiNMe_2$ (6 equiv) had led to a mixture of $W(NMe_2)_6$ and $W_2(NMe_2)_6$ (compare the mass spectrum and variable temperature ^1H NMR spectra of $Mo_2(NMe_2)_6$).[7] All attempts to separate these compounds by fractional sublimation and crystallization failed owing to the similar physical properties of these two compounds. Column chromatography using dehydrated Florisil resulted in extensive decomposition of the sample and $W_2(NMe_2)_6$ was not eluted from the column.

It seemed reasonable to suppose that $W_2(NMe_2)_6$ could be prepared free from $W(NMe_2)_6$ if lower-valent tungsten halides were used instead of WCl_6. However, WCl_3 is not known,[8] though $CrCl_3$ and $MoCl_3$ are. Consequently, we investigated a series of metathetic reactions involving a wide variety of lower-valent tungsten halo species; namely, WBr_5, WCl_2, $WCl_4(THF)_2$, $WCl_4(OEt_2)_2$, [WCl_6 + 3Li-*n*-Bu], $K_3W_2Cl_9$, and $WOCl_4$. Details are given in the Experimental Section.

None of these reactions yielded pure $W_2(NMe_2)_6$. However, there were some rather interesting and surprising results. For example, $WCl_4(THF)_2$, $WCl_4(Et_2O)_2$, and WBr_5 reacted with $LiNMe_2$ to give *pure* $W(NMe_2)_6$ (free from $W_2(NMe_2)_6$) while $K_3W_2Cl_9$, which is the only pure chloro compound of tungsten(III) and is known to contain a strong W–W inter-

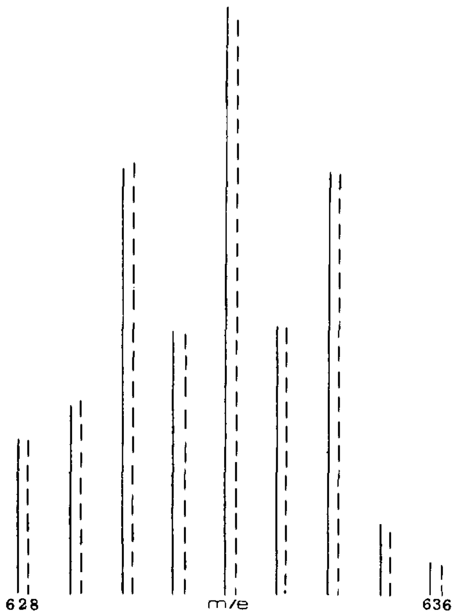

Figure 1. Observed (—) vs. calculated (- - -) *m/e* for $W_2(NMe_2)_6^+$.

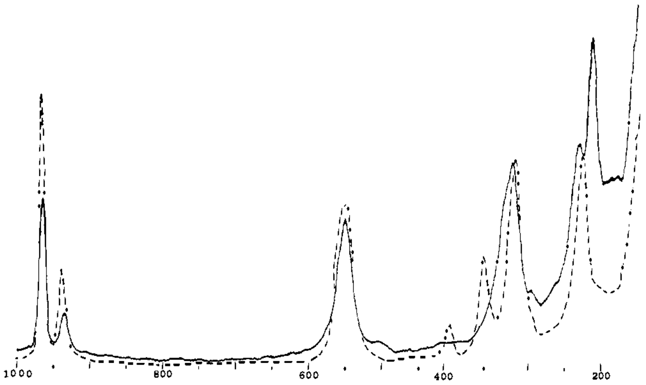

Figure 2. Raman spectrum of a polycrystalline sample of $W_2(NMe_2)_6$ (solid line) compared to $Mo_2(NMe_2)_6$ (broken line) in the range 1000–150 cm^{-1}.

action,[9] was completely inert to $LiNMe_2$ in THF. However, when $WCl_4(Et_2O)_2$ was decomposed at room temperature it gave a black sludge which reacted with $LiNMe_2$ (4 equiv) to give a mixture of $W_2(NMe_2)_6$ and $W(NMe_2)_6$ which was rich in tungsten(III). Furthermore, the yield of tungsten dimethylamides was much higher from this route than from reactions involving WCl_6 and other tungsten halides. Since we were unable to separate $W_2(NMe_2)_6$ from $W(NMe_2)_6$ by classical techniques we resorted to crystallographic analysis of the $W_2(NMe_2)_6$ rich samples prepared in the above manner, with the surprising result (see Crystallographic Section) that both $W_2(NMe_2)_6$ and $W(NMe_2)_6$ are present together in the same unit cell.

Although this study provided structural characterization of the $W_2(NMe_2)_6$ molecule, it was important to obtain pure tungsten(III) dialkylamides since these compounds could act as excellent starting materials for the synthesis of new metalloorganic compounds of tungsten(III).[10] Since $W(NMe_2)_6$ is an extremely sterically congested molecule, it seemed that reactions employing other dialkylamide ligands, which are inherently more bulky, should favor the formation of $W_2(NR_2)_6$ at the expense of $W(NR_2)_6$. This proved to be the case and the reaction of decomposed $WCl_4(OEt_2)_2$ with LiNMeEt and $LiNEt_2$ gave fair yields of the corresponding ditungsten hexadialkylamides and no detectable amounts of $W(NMeEt)_6$ or $W(NEt_2)_6$. Reactions employing more sterically demanding groups, e.g., N-*i*-Pr_2, have so far not provided any characterizable products, not even an analogue to monomeric Cr(N-*i*-$Pr_2)_3$.[11]

During this time we learned[12] that WCl_4 (a compound of unknown structure) could be prepared from the reaction of $W(CO)_6$ with $2WCl_6$ in refluxing chlorobenzene. Consequently, we investigated the reaction between WCl_4 and $LiNMe_2$ (4 equiv) and found that it gave good yields (ca. 40%) based on tungsten of $W_2(NMe_2)_6$—free from $W(NMe_2)_6$. It is therefore possible to prepare pure $W_2(NMe_2)_6$, $W_2(NMeEt)_6$, and $W_2(NEt_2)_6$ in significant quantities.

We have now carried out over 35 reactions between tungsten halides and $LiNMe_2$ and we would hope to be able to make some significant comments on factors favoring formation of $W_2(NMe_2)_6$ relative to $W(NMe_2)_6$. However, this is still not possible, although we can say with some confidence that $W(NMe_2)_6$ is not an intermediate in the synthesis of $W_2(NMe_2)_6$. We believe that $W_2(NMe_2)_6$ is formed by a substitution reaction involving a tungsten cluster while $W(NMe_2)_6$ is readily formed when six NMe_2 ligands coordinate to tungsten—irrespective of the formal valency of tungsten. These reactions may be compared to Wilkinson's syntheses of tungsten alkyls. In the preparation of WMe_6 from WCl_6 and MeLi both reduced tungsten species and the presence of adventitious oxygen are implicated,[13,14] while other more sterically demanding β-elimination stabilized alkyls give W_2R_6.[4,15] In the following paper[16] we demonstrate that a dinuclear species, $W_2Cl_2(NEt_2)_4$, may be an intermediate in the synthesis of $W_2(NEt_2)_6$. Finally, we note that monomeric tungsten(IV) dialkylamides have not been obtained in any of these reactions. This presents a significant departure from the chemistry of chromium and molybdenum.[17]

Physical Properties. The $W_2(NR_2)_6$ compounds, where NR_2 = NMe_2, NMeEt, and NEt_2, are pale yellow, crystalline, diamagnetic solids. They are moisture and oxygen sensitive and progressively turn from pale yellow to green, to brown, to black with exposure to the atmosphere. They are, however, quite thermally stable (<150°) and stable in dry, oxygen-free alkane solvents in which they are appreciably soluble.

A cryoscopic molecular weight determination in benzene confirmed the molecular formula $W_2(NMe_2)_6$ in solution.

These compounds are appreciably volatile at temperatures >100° and 10^{-4} cmHg which allows them to be purified by vacuum sublimation. Their mass spectra show $M_2L_6^+$, $M_2L_5^+$, and $M_2L_4^+$ ions (L = NR_2). The observed vs. computed isotopic pattern for $W_2(NMe_2)_6^+$ is shown in Figure 1. Significantly, *only* dinuclear metal-containing ions were observed. This may be compared with $Cr(NEt_2)_3$ which shows $Cr(NEt_2)_4^+$ but no dinuclear metal-containing ions in the mass spectrometer.

Variable temperature ^1H NMR spectra of $W_2(NR_2)_6$ directly parallel those observed[7] for $Mo_2(NR_2)_6$. ^1H NMR data are given in the Experimental Section. The free energy of activation for proximal and distal alkyl exchange is 11.2 ± 0.2 kcal mol^{-1} for NR_2 = NMe_2 and 13.3 ± 0.4 kcal mol^{-1} for NR_2 = NEt_2, which are slightly lower than those found for $Mo_2(NR_2)_6$. For $W_2(NMeEt)_6$ isomers with proximal methyl groups and distal ethyl groups are favored (see Discussion of the dynamic properties of $Mo_2(NMeEt)_6$ in the preceding paper[7]).

Infrared and Raman spectra of $W_2(NR_2)_6$ (NR_2 = NMe_2, NMeEt, and NEt_2) are reported in the Experimental Section. A comparison of the Raman spectra of polycrystalline samples of $M_2(NMe_2)_6$, where M = Mo and W, is shown in Figure 2.

The infrared spectra of $M_2(NMe_2)_6$, M = Mo and W, in the region 3000–200 cm^{-1} are virtually identical. Similarly the Raman spectra are virtually identical in the range 3000–500

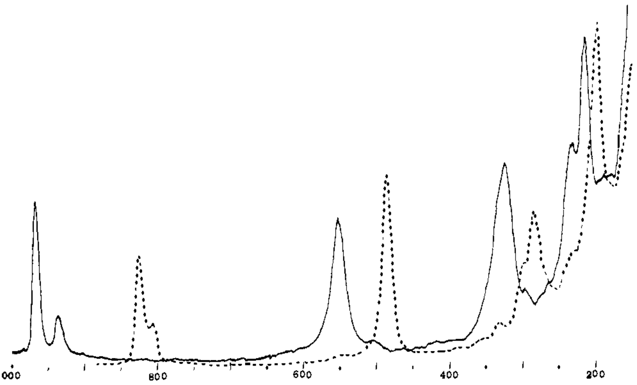

Figure 3. Raman spectrum of polycrystalline $W_2(N(CH_3)_2)_6$ (solid line) compared to $W_2(N(CD_3)_2)_6$ (broken line) in the range 1000-150 cm^{-1}.

Table I. Atomic Positional Parameters^{a,b} for $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$

	x	y	z
W(1)	0.333 33	0.666 67	0.205 32 (4)
W(2)	0.333 33	0.666 67	−0.038 16 (4)
W(3)	0.000 00	0.000 00	0.500 00
N(1)	0.171 6 (4)	0.586 0 (5)	0.254 6 (6)
N(2)	0.252 0 (4)	0.504 0 (4)	0.088 4 (6)
N(3)	−0.070 5 (5)	0.069 8 (5)	0.623 6 (8)
C(11)	0.067 8 (6)	0.533 8 (8)	0.167 1 (10)
C(12)	0.144 1 (7)	0.572 2 (8)	0.406 3 (9)
C(21)	0.199 4 (7)	0.399 1 (6)	−0.003 2 (9)
C(22)	0.237 7 (7)	0.477 1 (6)	−0.239 3 (8)
C(31)	−0.056 0 (17)	0.187 2 (15)	0.602 8 (32)
C(32)	−0.145 1 (18)	0.026 8 (23)	0.752 1 (30)
C(33)	−0.189 8 (13)	0.053 1 (16)	0.595 8 (30)
C(34)	−0.028 5 (20)	0.141 3 (20)	0.756 6 (29)

[a] Figures in parentheses are the estimated standard deviations in the least significant digits. [b] Numbers given without esd's are fixed by symmetry.

cm^{-1} but below 500 cm^{-1} there are significant differences as is shown in Figure 2. The presence of a strong polarized band at ca. 320 cm^{-1} for both M = Mo and W clearly precludes assignment of this band to ν_{str}(W–W).

A comparison of the Raman spectra of polycrystalline samples of $W_2(N(CH_3)_2)_6$ and $W_2(N(CD_3)_2)_6$ is shown in Figure 3. The large shifts which accompany deuteration parallel those previously described for $Mo_2(NMe_2)_6$ and demonstrate that W–N and W–W stretching modes are extensively coupled to other vibrational modes of the molecule, including those associated with the CH_3 moieties.

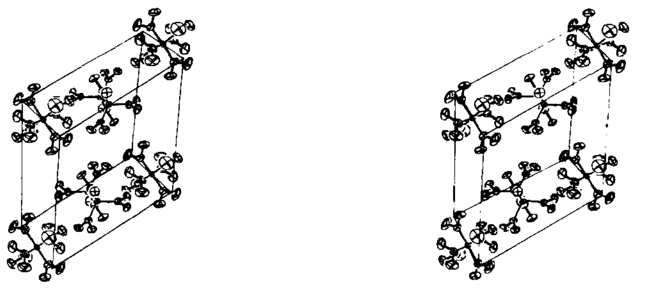

Figure 4. A stereoscopic view of the unit cell of $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$.

Structural Results. $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$. This substance, initially presumed to be simply $W_2(NMe_2)_6$, was found to contain both the dinuclear molecule and the already known[6] $W(NMe_2)_6$ molecule in a ratio of 2:1. The dinuclear molecules lie on the 2d[19] equipoint so that the W–W bonds are collinear with the crystallographic threefold axis. Thus each dinuclear molecule has rigorous crystallographic C_3 symmetry. The mononuclear molecule in each unit cell occupies a position of $S_6(\bar{3})$ crystallographic symmetry, with the tungsten atom located precisely at the point 0, 0, ½. A stereopacking diagram is given in Figure 4. Only one of the two orientations for the methyl groups in the $W(NMe_2)_6$ molecules is shown.

The atomic positional parameters for all atoms are given in Table I and their anisotropically refined thermal parameters are reported in Table II.

The molecular structure of the dinuclear unit as found in this compound is shown in Figure 5 which also defines the labeling scheme used to designate the unique atoms in the molecule. Similarly the $W(NMe_2)_6$ molecule is shown in Figure 6. The bond distances and angles for the $W_2(NMe_2)_6$ molecule in this compound are given in Table III and the bond distances and angles within $W(NMe_2)_6$ are reported in Table IV. The packing diagram shown in Figure 4 shows no unusual features and no short intermolecular contacts were calculated. The only unusual feature for the structure is the twofold disordering of the methyl groups (C(31)-C(34)) bonded to N(3) in $W(NMe_2)_6$. The least-squares planes defined by C(31)-N(3)-C(32) and C(33)-N(3)-C(34) have a dihedral angle of 89.5°.

$W_2(NMe_2)_6$. This substance is isomorphous with its molybdenum analogue.[7] The space group is $P2_1/c$ with four

Table II. Anisotroic Temperature Parameters^{a-c} for $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	2.89 (2)	2.89	2.03 (1)	1.45	0.00	0.00
W(2)	2.84 (2)	2.84	1.86 (1)	1.42	0.00	0.00
W(3)	2.78 (2)	2.78	3.72 (2)	1.39	0.00	0.00
N(1)	3.4 (2)	4.5 (2)	3.3 (2)	1.4 (3)	0.9 (5)	0.7 (4)
N(2)	4.4 (2)	3.1 (2)	3.3 (2)	1.8 (3)	−0.3 (5)	−0.3 (4)
N(3)	4.9 (2)	5.9 (2)	7.9 (4)	2.9 (3)	0.8 (7)	−1.2 (6)
C(11)	3.3 (3)	8.4 (5)	6.2 (5)	1.7 (6)	−0.4 (8)	−0.5 (9)
C(12)	7.2 (4)	8.7 (4)	3.7 (3)	3.8 (6)	2.3 (8)	1.3 (7)
C(21)	6.1 (3)	5.3 (3)	3.4 (3)	2.7 (4)	−0.9 (7)	−1.9 (5)
C(22)	7.0 (4)	3.3 (2)	5.3 (4)	2.1 (4)	0.4 (9)	0.9 (5)
C(31)	9.9 (8)	6.6 (6)	16.3 (22)	5.9 (9)	−0.2 (28)	−1.4 (20)
C(32)	11.2 (9)	14.3 (10)	11.4 (13)	7.0 (16)	7.7 (21)	3.1 (24)
C(33)	5.9 (5)	10.7 (8)	14.2 (18)	6.2 (8)	1.6 (20)	−0.5 (20)
C(34)	8.2 (10)	13.0 (12)	11.2 (13)	3.9 (17)	−2.1 (26)	−8.0 (18)

[a] Figures in parentheses are the estimated standard deviations in the least significant digits. [b] Numbers given without esd's are fixed by symmetry. [c] The B_{ij} in Å^2 is related to the dimensionless β_{ij} employed during refinement as: $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$.

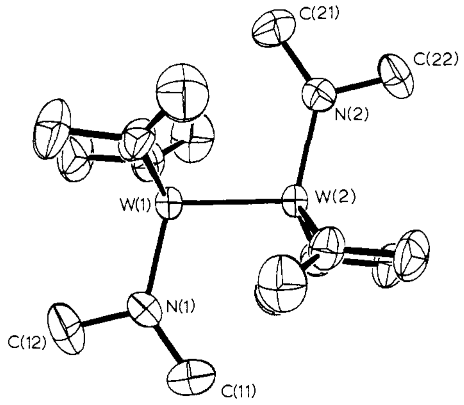

Figure 5. A view of the dinuclear molecule $W_2(NMe_2)_6$ in $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$ showing 50% probability ellipsoids and the atomic labeling scheme.

Table III. Bond Distances and Angles[a] in the $W_2(NMe_2)_6$ Molecule in $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$

	Distances, Å	Averages
W(1)-W(2)	2.294 (1)	
W(1)-n)1)	1.995 (5)	1.982 Å
W(2)-N(2)	1.968 (5)	
N(1)-C(11)	1.471 (9)	
-C(12)	1.465 (9)	1.466 Å
N(2)-C(21)	1.470 (8)	
-C(22)	1.457 (8)	
	Angles, degrees	
W(1)-W(2)-N(2)	103.9 (2)	
W(2)-W(1)-N(1)	103.7 (2)	
N(1)-W(1)-N(1)′	114.5 (4)	
N(2)-W(2)-N(2)′	114.4 (4)	
W(1)-N(1)-C(11)	132.2 (5)	
-C(12)	116.5 (5)	distal = 116.5°
W(2)-N(2)-C(21)	133.0 (4)	proximal = 132.6°
-C(22)	116.4 (4)	
C(11)-N(1)-C(12)	111.4 (6)	
C(21)-N(2)-C(22)	110.6 (5)	

[a] Figures in parentheses are the estimated standard deviations.

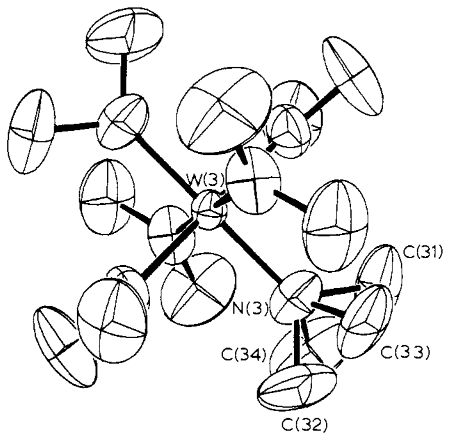

Figure 6. A view of the $W(NMe_2)_6$ molecule in $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$ showing 50% probability ellipsoids and the atomic labeling scheme. For purposes of clarity the disorder (C(31)-C(34)) observed for the methyl groups is shown on oly one of the six NMe_2 groups.

molecules in the unit cell. The placement of the molecules is not, however, the usual one for $Z = 4$ in this space group, such that one entire molecule constitutes the asymmetric unit and the centers of inversion lie between molecules. In this case there are two independent pairs of molecules occupying the two nonequivalent twofold equipoints[19] at inversion centers, viz., at 0, 0, 0 and 0, ½, ½ (molecule I) and ½, ½, 0 and ½, 0, ½ (molecule II). The asymmetric unit consists of one-half of each of two nonequivalent molecules. The atomic positional parameters are given in Table V and the anisotropic thermal parameters are given in Table VI. The molecular structure of molecule I is shown in Figure 7 along with the labeling scheme. A figure for molecule II is not given since the two molecules, I and II, are essentially identical. The labeling scheme for molecule II is derived from that used for I by replacing the first digit in parentheses, which is always a 1 for molecule I by a 2. Thus, N(13) of molecule I corresponds to N(23) of molecule II. Bond distances and angles for both molecules are given in Table VII.

Comparison with Other Structures. The molecular structure parameters for $W_2(NMe_2)_6$ have been determined in three independent molecules, two in pure $W_2(NMe_2)_6$ and another

Table IV. Bond Distances and Angles[a] in the $W(NMe_2)_6$ Molecule in $2W_2(NMe_2) \cdot W(NMe_2)_6$

	Distances, Å	Averages		
W(3)-N(3)	2.017 (6)			
N(3)-C(31)	1.515 (20)			
C(32)	1.496 (20)	1.515 Å		
C(33)	1.539 (20)			
C(34)	1.510 (20)			
	Bond angles, deg			Bond angles, deg
N(3)-W(3)-N(3)′	90.0 (9)		C(31)-N(3)-C(32)	102.8 (13)
W(3)-N(3)-C(31)	125.1 (10)		(33)	73.0 (13)
C(32)	132.1 (10)		(34)	67.9 (14)
C(33)	122.8 (10)		C(32)-N(3)-C(33)	68.0 (12)
C(34)	131.7 (11)		(34)	62.8 (13)
			C(33)-W(3)-C(34)	105.4 (14)

Dihedral Angles, deg

	Plane	Equation of Planes[b]			
		A	*B*	*C*	*D*
I	W(2)-W(1)-N(1)	1.001	1.000	0.000	6.783
II	W(1)-W(2)-N(2)	0.866	−0.499	0.000	0.002
III	C(11)-N(1)-C(12)	−0.003	0.999	0.000	6.774
IV	C(21)-N(2)-C(22)	0.867	−0.499	−0.004	0.003

[a] Figures in parentheses are the estimated standard deviations. [b] These equations are of the form $AX + BY + CZ = D$. Dihedral angle, I-III = 0.24; dihedral angle, II-IV = 0.23.

Table V. Atomic Positional Parameters[a] for $W_2(NMe_2)_6$

	x	y	z
W(1)	−0.006 98 (9)	0.426 11 (9)	0.451 91 (7)
W(2)	0.457 08 (9)	0.053 12 (9)	0.439 91 (7)
N(11)	0.073 (2)	0.480 (2)	0.360 (1)
N(12)	0.076 (2)	0.304 (2)	0.529 (2)
N(13)	−0.179 (2)	0.406 (2)	0.413 (2)
N(21)	0.566 (2)	0.031 (2)	0.356 (1)
N(22)	0.455 (2)	0.205 (2)	0.489 (2)
N(23)	0.300 (2)	−0.016 (2)	0.401 (1)
1C(11)	0.132 (3)	0.588 (4)	0.343 (3)
2C(11)	0.078 (4)	0.399 (3)	0.288 (2)
1C(12)	0.139 (3)	0.298 (4)	0.619 (2)
2C(12)	0.080 (3)	0.198 (3)	0.481 (2)
1C(13)	−0.283 (3)	0.463 (4)	0.438 (3)
2C(13)	−0.215 (3)	0.306 (3)	0.355 (3)
1C(21)	0.676 (3)	−0.030 (4)	0.359 (2)
2C(21)	0.534 (3)	0.096 (3)	0.270 (2)
1C(22)	0.502 (4)	0.254 (13)	0.575 (2)
2C(22)	0.399 (4)	0.292 (3)	0.431 (2)
1C(23)	0.233 (4)	−0.105 (3)	0.432 (3)
2C(23)	0.218 (3)	0.037 (3)	0.324 (2)

[a] Figures in parentheses are the estimated standard deviations in the least significant digits.

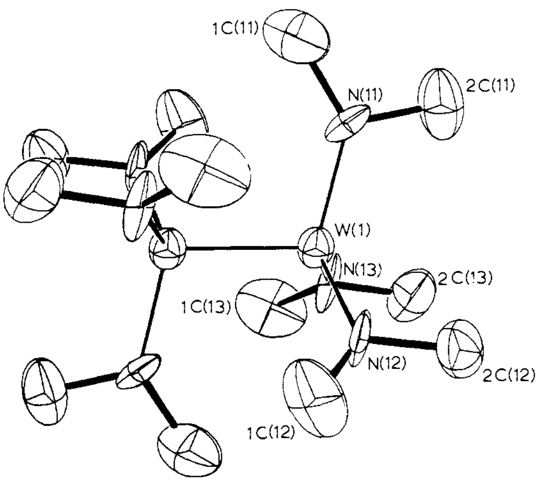

Figure 7. A view of the $W_2(NMe_2)_6$ molecule as found in pure $W_2(NMe_2)_6$ showing 40% probability ellipsoids and the atomic labeling scheme.

in $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$. Agreement between the three sets of parameters is excellent. The pure $W_2(NMe_2)_6$ is isomorphous with the molybdenum compound and, aside from the expected difference in M-M bond distances, there are no meaningful differences in the two molecular structures. The increase in the M-M distance from $Mo_2(NMe_2)_6$ to $W_2(NMe_2)_6$ is approximately 0.08 Å, corresponding to an increase of 0.04 Å in the metal radius. This seems a reasonable difference for these elements which occur shortly after the lanthanide contraction. It is interesting, however, that no such difference is observed in the metal-nitrogen distances. This might be taken to imply that there is slightly more nitrogen-to-metal π bonding in the tungsten compound. Aside from this small quantitative difference, the electronic structure of $W_2(NMe_2)_6$ must be very similar to that of the molybdenum analogue, which we have already discussed.[7]

The compound $W_2(CH_2SiMe_3)_6$[4] presumably contains a W-W triple bond but detailed comparison is impossible since its structure has not been determined. We are not aware of any other report of a tungsten compound in which a W-W triple bond, unsupported by bridging groups is thought to exist. In the $W_2Cl_9^{3-}$ ion a triple interaction between the two metal atoms, consisting of a σ and two π components has been proposed several times in the literature.[20,21] However, due to the vastly different nature of the structure, a comparison of the W-W distance[9] (2.41 Å) in $W_2Cl_9^{3-}$ with that in $W_2(NMe_2)_6$ is not useful.

Experimental Section

Materials. WCl_6, $WOCl_4$, and WBr_5 were purchased from ROC/RIC. WCl_2 was purchased from VAR/LAC/OID Chemical Co. Metal halides were divided into small portions (ca. 5-40 g) and sealed in glass ampoules under vacuum for storage prior to their use. $W(CO)_6$ was obtained from Strem Chemicals, Inc. $ZnEt_2$ was a gift from the Ethyl Corp. (10% solution in benzene). $K_3W_2Cl_9$[22] was prepared shortly before use. $WCl_4(THF)_2$[23] and $WCl_4(Et_2O)_2$[23] were prepared in situ (100% yields assumed) and used immediately. $LiNMe_2$ was prepared by slowly condensing a stoichiometric amount of $HNMe_2$ into a hexane solution of BuLi (ca. 2.0 M at −78 °C). All other LiNRR′ were prepared by adding an equimolar amount of BuLi (ca. 2.0 M in hexane) to an ice cold, stirred solution (THF or ether) of the amine. $HNMe_2$ was obtained from Matheson, HNMeEt from the

Table VI. Anisotropic Temperature Parameters[a,b] for $W_2(NMe_2)_6$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	3.08 (6)	2.83 (6)	2.76 (6)	0.14 (4)	0.25 (4)	−0.17 (4)
W(2)	3.16 (6)	3.66 (6)	2.40 (6)	0.46 (4)	−0.12 (4)	0.07 (4)
N(11)	3.9 (9)	1.7 (9)	4.3 (8)	−0.6 (8)	0.2 (9)	1.1 (8)
N(12)	5.7 (9)	1.4 (9)	4.8 (9)	0.5 (9)	0.9 (9)	−1.6 (9)
N(13)	4.1 (9)	1.4 (10)	5.9 (10)	2.1 (9)	−1.0 (9)	−1.3 (9)
N(21)	6.7 (10)	6.7 (11)	1.3 (9)	−0.7 (10)	1.8 (9)	1.9 (9)
N(22)	4.9 (9)	4.7 (10)	5.8 (9)	3.0 (10)	2.4 (10)	0.5 (10)
N(23)	1.7 (9)	6.3 (10)	3.2 (9)	−0.5 (9)	−1.5 (9)	−0.8 (9)
1C(11)	6.7 (19)	9.4 (19)	5.5 (18)	−0.8 (18)	2.2 (15)	0.5 (17)
2C(11)	7.8 (18)	6.4 (18)	4.3 (16)	1.9 (16)	−0.6 (15)	−1.6 (14)
1C(12)	7.3 (19)	10.5 (19)	3.1 (16)	1.7 (19)	−1.8 (14)	−1.3 (15)
2C(12)	7.3 (18)	4.8 (16)	4.5 (16)	2.1 (14)	1.2 (13)	−0.1 (13)
1C(13)	1.3 (13)	13.3 (19)	9.0 (19)	−0.7 (17)	1.0 (14)	0.9 (18)
2C(13)	7.4 (17)	4.5 (15)	6.9 (18)	−0.4 (14)	0.7 (16)	−0.1 (14)
1C(21)	2.9 (18)	11.6 (19)	5.6 (17)	4.4 (16)	1.6 (14)	0.6 (15)
2C(21)	6.8 (19)	8.1 (18)	3.0 (14)	−0.1 (16)	1.5 (15)	2.1 (13)
1C(22)	10.6 (14)	8.4 (18)	1.6 (13)	−2.5 (17)	1.7 (14)	−2.1 (13)
2C(22)	10.1 (19)	4.7 (16)	4.7 (17)	1.3 (18)	0.0 (15)	1.2 (14)
1C(23)	2.8 (18)	7.3 (18)	8.1 (18)	−1.4 (15)	−1.6 (15)	−0.8 (14)
2C(23)	4.5 (17)	4.6 (15)	5.2 (16)	−1.3 (13)	−1.9 (13)	1.9 (13)

[a] Figures in parentheses are the estimated standard deviations in the least significant digits. [b] The B_{ij} in Å^2 is related to the dimensionless β_{ij} employed during refinement as: $B_{ij} = 4\beta_{ij}/a_i^* a_j^*$.

Table VII. Bond Distances and Angles[a] in $W_2(NMe_2)_6$

Molecule I		Molecule II		Average
		Distances, Å		
W-W′	2.290 (2)		2.294 (2)	
W-N(11)	1.95 (2)	N(21)	1.99 (2)	1.97
-N(12)	1.99 (2)	N(22)	1.97 (3)	
-N(13)	1.96 (2)	N(23)	1.96 (2)	
N(11)-1C(11)	1.51 (4)	N(21)-1C(21)	1.45 (4)	1.48
-2C(11)	1.47 (4)	-2C(21)	1.53 (4)	
N(12)-1C(12)	1.44 (4)	N(22)-1C(22)	1.45 (4)	
2C(12)	1.48 (4)	-2C(22)	1.44 (4)	
N(13)-1C(13)	1.50 (4)	N(23)-1C(23)	1.46 (4)	
2C(13)	1.49 (4)	-2C(23)	1.48 (3)	
		Bond Angles, deg		
W(1)′-W(1)-N(11)	103.7 (6)	W(2)′-W(2)-N(21)	103.2 (7)	103.3
-N(12)	102.7 (6)	-N(22)	103.5 (8)	
-N(13)	103.1 (6)	-N(23)	103.5 (7)	
N(11)-W(1)-N(12)	115.9 (10)	N(21)-W(2)-N(22)	115.7 (10)	114.9
-N(13)	114.2 (10)	-N(23)	113.8 (10)	
N(12)-W(1)-N(13)	114.8 (10)	N(22)-W(2)-N(23)	114.8 (10)	
W(1)-N(11)-1C(11)	134 (2)	W(2)-N(21)-1C(21)	135 (2)	
-2C(11)	115 (2)	hs0556-2C(21)	116 (2)	
-N(12)-1C(12)	134 (2)	-N(22)-1C(22)	134 (2)	proximal = 134
-2C(12)	113 (2)	-2C(22)	118 (2)	distal = 116
-N(13)-1C(13)	132 (2)	-N(23)-1C(23)	136 (2)	
-2C(13)	115 (2)	-2C(23)	117 (2)	
1C(11)-N(11)-2C(11)	110 (3)	1C(21)-N(21)-2C(21)	109 (2)	110
1C(12)-N(12)-2C(12)	113 (3)	1C(22)-N(22)-2C(22)	108 (3)	
1C(13)-N(13)-2C(13)	113 (3)	1C(23)-N(23)-2C(23)	107 (2)	

Dihedral Angles, deg

	Plane	Equations of planes[b] A	B	C	D
I	W(1)′-W(1)-N(11)	−0.782	0.356	−0.511	−0.491
II	-N(12)	0.934	0.269	−0.234	−1.639
III	-N(13)	0.157	0.635	−0.757	−2.164
IV	W(2)′-W(2)-N(21)	−0.68	−0.790	−0.397	−4.934
V	-N(22)	0.964	0.179	−0.196	2.523
VI	-N(23)	0.512	−0.614	−0.601	−2.402
VII	1C(11)-N(11)-2C(11)	−0.783	0.345	−0.517	−0.587
VIII	1C(12)-N(12)-2C(12)	0.913	0.300	−0.277	−1.846
IX	1C(13)-N(13)-2C(13)	0.071	0.578	−0.813	−2.499
X	1C(21)-N(21)-2C(21)	−0.442	−0.785	−0.434	−4.991
XI	1C(22)-N(22)-2C(22)	0.945	0.175	−0.276	1.855
XII	1C(23)-N(23)-2C(23)	0.453	−0.638	−0.622	−2.655

Dihedral angle: I-VII = 0.74, II-VIII = 3.29, III-IX = 6.70, IV-X = 2.63, V-XI = 4.70, VI-XII = 3.86

[a] Figures in parentheses on the estimated standard deviations. [b] These equations are of the form $AX + BY + CZ = D$.

Ames Laboratory, $HNEt_2$ and HN-*i*-Pr_2 from Matheson Coleman and Bell. $HN(CD_3)_2$ was purchased from Merck, Sharp and Dohme.

WCl_4 was prepared from the reaction[12] $2WCl_6 + W(CO)_6$ in refluxing chlorobenzene, and stored in glass vials prior to use.

Physical and Analytical Measurements. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, using drybox sampling techniques.

Molecular weight determinations were made under a purified nitrogen atmosphere in an all-glass cryoscopic apparatus incorporating a thermister bridge.[24]

Infrared spectra were obtained from Nujol mulls between CsI plates using a Beckman IR-12 spectrophotometer.

Raman spectra were obtained on a spectrophotometer equipped with a Coherent Radiation Model CR5 Ar^+ laser, a Spex Model 1401 double monochrometer, and a cooled ITT FW-130 startracker photomultiplier tube using the Ar^+ 5145 Å exciting line. Spectra of solid samples were obtained from capillary tubes sealed under N_2; solution spectra were obtained in THF using the Spex rotating quartz cell adapted for air sensitive work.

^1H NMR spectra were obtained from Varian A60 and HA-100 instruments equipped with variable temperature probes. Temperatures were calibrated with methanol (low temperature) or ethylene glycol (high temperature).

Toluene-d_8 was used as the NMR solvent and hexamethyldisiloxane (HMDS) was used as the internal reference ($\delta_{HMDS} = \delta_{Me_4Si} - 0.11$).

Mass spectra were obtained on a AEI MS 9 by the method of direct insertion with probe temperatures 100-120 °C.

General Procedures. Due to the highly reactive nature of tungsten halides, $LiNR_2$, $W_2(NR_2)_6$, and related compounds, all preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere or in vacuo using standard Schlenk techniques.[25] Solvents (pentane, hexane, THF, ether, benzene, and toluene) were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, sodium, and phenyl ether (Ph_2O was added to ether or THF), then stored over CaH_2 under nitrogen until used. After preparation samples were stored and handled in a Vacuum Atmospheres Company Dri Lab system.

WCl_6 + $LiNMe_2$. WCl_6 (47.3 g, 119 mmol) was added to $LiNMe_2$ (663 mmol in hexane (425 ml)/toluene (200 ml)) with stirring, at 0 °C, over 15 min. No reaction occurred. Ether (50 ml) was added (*Caution:* the reaction can become quite exothermic if too much ether is added.) The reaction mixture started to turn brown. After 30 min additional ether (50 ml) was added and the mixture was stirred for 12 h. About 100 ml of solvent was removed under reduced pressure, the reaction mixture was filtered, and the solvent was removed from the filtrate under reduced pressure. The residue was thoroughly dried

(40 °C (10^{-3} Torr)), then extracted with warm hexane (200 ml). The solvent was removed from the filtrate and the residue was dried thoroughly (10 h, 30 °C, 10^{-3} Torr), then extracted with warm hexane (100 ml). The solution was concentrated to ca. 50 ml at 50 °C then cooled to −20 °C. The resulting solid was filtered off, washed twice with hexane (ca. 20 ml), and then dried. The red solid was recrystallized twice by extracting it through a coarse fritted filter with refluxing pentane: yield 4.61 g. Anal. Found: C, 26.50; H, 6.66; N, 15.76.

The product was recrystallized from toluene. Anal. Found: C, 26.87; H, 6.54; N, 15.28; W, 50.81. These data agree moderately well with figures calculated for a 1:1 mixture of $W(NMe_2)_6$ and $W_2(NMe_2)_6$: C, 26.68; H, 6.72; N, 15.56; W, 51.05.

Similar results were obtained by (i) dissolving the $LiNMe_2$ in THF/hexane prior to the addition of the WCl_6, (ii) adding the $LiNMe_2$ as an ether slurry to WCl_6 (in ether). Note that when carrying out the inverse addition THF cannot be used as a solvent since it readily reacts with WCl_6.

The composition of a $W_2(NMe_2)_6/W(NMe_2)_6$ mixture is easily determined via ^1H NMR. At probe temperature (40 °C) there are two singlets at δ 3.33 ($W(NMe_2)_6$) and 3.30 ppm ($W_2(NMe_2)_6$). At lower temperatures (ca. −50 °C) there are three singlets, at δ 3.33 ppm ($W(NMe_2)_6$) and δ 4.24 and 2.36 ppm ($W_2(NMe_2)_6$), where δ is in parts per million relative to HMDS.

WBr_5 + $LiNMe_2$. WBr_5 (11.1 g, 19 mmol) was added over 15 min, with stirring, at 0 °C, to $LiNMe_2$ (96 mmol in hexane (50 ml)/THF (150 ml)). The solution turned orange, then reddish brown as the addition proceeded. After stirring for 2 h the solution was warmed to ca. 50 °C, the solvent was removed under reduced pressure, and the residue was thoroughly dried (25 °C, 24 h, 10^{-4} Torr), then extracted with warm hexane (225 ml at 50 °C). The filtrate was concentrated to ca. 40 ml in vacuo at 50 °C, then cooled to −20 °C. The red solid was filtered off, washed with hexane (ca. 5 ml) and dried: yield 1.33 g (16% based on W) of pure $W(NMe_2)_6$ (via NMR).

$WOCl_4$ + $LiNMe_2$. $LiNMe_2$ (138 mmol, in hexane (70 ml)/THF (200 ml)) was added to $WOCl_4$ (11.8 g, 34.5 mmol in 150 ml of ether) with stirring, at 0 °C, over 75 min. The solution turned brown. After stirring for 2 h the solvent was removed under reduced pressure and the residue was dried (5 h at 25 °C, 10^{-3} Torr) then extracted with hexane (175 ml). The filtrate was concentrated to ca. 40 ml at 50 °C then cooled to −20 °C. The red solid was filtered off and dried. The yield was ca. 1 g (6%) of almost pure (ca. 95%) $W(NMe_2)_6$. NMR, ir, and mass spectroscopy indicated there was no $W_2(NMe_2)_6$ present.

WCl_2 + $LiNMe_2$. WCl_2 (8.5 g, 33.4 mmol) was added to $LiNMe_2$ (67 mmol) in hexane (30 ml)/THF (200 ml) at 0 °C, with stirring, over 15 min. The dark brown solution was stirred at 25 °C for 1 h then refluxed for 3 h. The solvent was removed under reduced pressure. The residue was dried overnight (25 °C, 10^{-3} Torr) and then extracted with hexane (200 ml). The solvent was removed from the filtrate and the residue was extracted with pentane (150 ml). The solvent was removed and the residue was purified via sublimation (100–130 °C, 10^{-3} Torr). The red sublimate (ca. 0.1 g) was a mixture of $W(NMe_2)_6$ and $W_2(NMe_2)_6$ (via NMR).

$K_3W_2Cl_9$ + $LiNMe_2$. $K_3W_2Cl_9$ (5.8 g, 7.21 mmol) was added to $LiNMe_2$ (22 mmol in hexane (10 ml)/THF (150 ml)) with stirring, at 25 °C. No visible reaction occurred over 6 days. After 2 weeks the solvent was removed and the residue was extracted with hexane (150 ml). There were no hexane soluble products.

$LiNMe_2$ + "Reduced" WCl_6. BuLi (77 mmol, 2.0 M) in hexane was added to WCl_6 (15.3 g, 38.4 mmol) in ether (150 ml) with stirring, at −78 °C, over 30 min. There was a dark solid and a brown solution. The slurry was cooled in an ice-salt bath and additional BuLi (38 mmol, 2.0 M) in hexane was added, with stirring. $LiNMe_2$ (154 mmol) in hexane (77 ml)/THF (200 ml) was added to the slurry, at 0 °C, with stirring, over 30 min. The slurry turned black. It was stirred for 5 h at 0 °C, then the solvent was removed under reduced pressure and the residue was thoroughly dried (10 h, 25 °C, 10^{-3} Torr). The residue was extracted with hexane (200 ml). The filtrate was concentrated to ca. 40 ml and cooled to −20 °C. The red solid was filtered off, washed with two small portions of hexane (ca. 10 ml), and dried. The yield was 0.71 g (4% based on W) of almost pure $W(NMe_2)_6$ (via NMR).

$WCl_4(THF)_2$ + $LiNMe_2$. $LiNMe_2$ (139 mmol) in hexane (70 ml)/THF (200 ml) was added to $WCl_4(THF)_2$ (ca. 35 mmol) with stirring, at ca. −40 °C, over a period of 45 min. The slurry turned reddish brown. After stirring 5 h at −50 °C, the solution was filtered off and the solvent was removed under reduced pressure. The residue was dried (12 h, 25 °C, 10^{-3} Torr) and then extracted with hexane (200 ml). The filtrate was concentrated to ca. 30 ml and cooled to −20 °C. The red solid was filtered off and dried. NMR and ir showed that the product was pure $W(NMe_2)_6$. The yield was 0.82 g (5% based in W). This reaction was repeated successfully.

Preparation of Decomposed $WCl_4(Et_2O)_2$. A slurry of $WCl_4(Et_2O)_2$, (66 mmol) in ether (ca. 250 ml), was stirred at room temperature for ca. 2 h. The solid and solution turned black. $LiNR_2$ was then added to the slurry under the appropriate conditions (see following reactions).

Decomposed $WCl_4(Et_2O)_2$ + $LiNMe_2$. $LiNMe_2$ (267 mmol) in hexane (134 ml)/THF (400 ml) was added to decomposed $WCl_4(Et_2O)_2$ (88.9 mmol in ca. 250 ml of ether) with stirring, at 0 °C over 90 min. The solution turned deep brown. The solution was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure at 30 °C. The residue was thoroughly dried (50 °C, 10^{-3} Torr) then extracted with hexane (400 ml). The filtrate was concentrated to ca. 75 ml and then cooled to −20 °C. The red solid was filtered off and dried. The yield was 8.6 g (27% based on tungsten) of ca. 1:2 $W(NMe_2)_6/W_2(NMe_2)_6$ (via NMR).

Preparation of $W_2(NMeEt)_6$. LiNMeEt (197 mmol) in hexane (80 ml)/THF (150 ml) was added to decomposed $WCl_4(Et_2O)_2$ (65.5 mmol in ca. 300 ml of ether) with stirring, at 0 °C over about 1 h. The solution turned reddish brown. The ice bath was allowed to melt and the reaction mixture was stirred 11 h. The solvent was removed under reduced pressure at 30 °C and the residue was dried thoroughly (60 °C, 10^{-3} Torr, 6 h), and then extracted with 200 ml of warm hexane. The solvent was removed from the filtrate and the residue was sublimed (110–140 °C, 10^{-3} Torr). The sublimate was recrystallized from hexane. The yield was 10.0 g (43% based on W). Anal. Calcd for $W_2(NMeEt)_6$: C, 30.18; H, 6.75; N, 11.73. Found: C, 30.21; H, 6.60; N, 11.16.

The infrared spectrum showed bands at 245 w, 316 w, 337 m, 430 s, 573 vs, 790 m, 865 vs, 985 vs, 995 sh, 1048 m, 1978 m, 1110 m, 1152 s, 1202 vs, 1300 s, and 1337 cm^{-1} s.

The Raman spectrum showed bands at 187 w, 223 m (p), 325 s (p), 427 w, 575 s (p), 871 s, 1000 s, 1046 m, 1077 m, 1153 w, 1207 s, 1315 m, 1357 w, 1381 m, 1423 s, and 1459 cm^{-1} s.

^1H NMR data: T = 40 °C: $\delta(NMe)$ 3.82 ppm (singlet) and $\delta(NCH_2CH_3)$ 3.10 (quartet) and 1.02 ppm (triplet) J_{H-H} = 7 Hz; T = −80 °C, $\delta(NMe)$ 4.28 (ca. 90%) and 2.26 (ca. 10%) ppm (singlet) and $\delta(NCH_2CH_3)$ 2.38 (ca. 90%) and 4.75 (ca. 10%) ppm (quartet) and 0.95 ppm (triplet) J_{H-H} = 7 Hz, δ in parts per million relative to HMDS.

Preparation of $W_2(NMe_2)_6$. A slurry of WCl_4 (16.8 g, 51.4 mmol) in ether (100 ml) was cooled to 0 °C in an ice bath. $LiNMe_2$ (206 mmol in hexane (90 ml)/THF (150 ml)) was added with stirring over 15 min. The slurry turned light brown. The ice bath was allowed to melt when the addition was complete and the reaction mixture was stirred overnight (ca. 10 h). It was refluxed for 2 h; then the solvent was removed under reduced pressure at 30-50 °C. The residue was dried thoroughly (50 °C, 10^{-3} Torr) and then extracted with 200 ml of hot hexane (ca. 60 °C). The filtrate was concentrated to ca. 50 ml at ca. 50 °C, then cooled to −20 °C. The brown solid was filtered off and dried, then purified via sublimation (120-140 °C, 10^{-3} Torr). The yield was 7.4 g (46% based on W). Anal. Calcd for $W_2(NMe_2)_6$: C, 22.81; H, 5.70; N, 13.30. Found: C, 22.74; H, 5.60; N, 13.17.

Infrared bands appear at 237 w, 319 m, 344 s, 550 vs, 940 vvs, 964 s, 1043 m, 1125 m, 1149 s, and 1243 cm^{-1} vs; Raman bands at 213 s (p), 230 sh (dp), 323 s (p), 550 s (p), 935 m, 964 s, 1045 w, 1081 w, 1119 w, 1149 w, and 1243 cm^{-1} w.

In the mass spectrometer a parent ion (base peak) corresponding to $W_2(NMe_2)_6^+$ and peaks due to $W_2(NMe_2)_5^+$ and $W_2(NMe_2)_4^+$ were observed.

^1H NMR spectra show a singlet at probe temperature (40 °C), δ 3.30 ppm and two singlets at low temperature (−50 °C), δ 4.24 and 2.36 ppm, δ in parts per million relative to HMDS. The coalescence temperature (T_c) is −35.3 °C at 60 MHz.

Preparation of $W_2(N(CD_3)_2)_6$. $W_2(N(CD_3)_2)_6$ was prepared as above except using $LiN(CD_3)_2$. Parent ion corresponding to $W_2(N(CD_3)_2)_6^+$ was found in the mass spectrum.

The infrared spectrum showed bands at 311 m, 485 vs, 812 vs, 823 vs, 904 s, 953 m, 1030 s, 1050 s, 1067 s, 1119 vs, 1130 vs, and 1163 cm^{-1} vs; Raman spectrum showed bands at 195 vs, 228 w sh, 284 s, 298 w sh, 485 s, 805 m, 823 s, 1020 m sh, 1052 s, 1086 s, 1125 w, and 1163 cm^{-1} s.

Preparation of $W_2(NEt_2)_6$. WCl_4 (8.62 g, 26.4 mmol) was added to $LiNEt_2$ (106 mmol in hexane (46 ml)/ether (77 ml)) at 0 °C, with stirring, over 15 min. The slurry turned light brown. It was warmed to room temperature and stirred for 10 h. The solution was reddish brown with pale solids. The solvent was removed under reduced pressure and the residue was thoroughly dried (3 h, 60 °C, 10^{-3} Torr). The residue was extracted with warm hexane (150 ml). The solvent was removed from the filtrate and $W_2(NEt_2)_6$ was sublimed (120–150 °C, 10^{-3} Torr) from the residue, yielding 2.0 g (19% based on W) of $W_2(NEt_2)_6$. Anal. Calcd for $W_2(NEt_2)_6$: C, 36.01; H, 7.56; N, 10.50. Found C, 36.14; H, 7.60; N, 10.37.

The infrared spectrum shows bands at 290 w, 315 m, 506 s, 582 s, 778 m, 792 s, 877 s, 905 m, 972 w, 998 vs, 1041 m, 1063 m, 1088 m, 1146 s, 1183 s, 1207 w, 1272 w, 1308 w, 1325 m, and 1341 cm^{-1} s.

The mass spectrum shows a strong peak corresponding to the molecular ion, $W_2(NEt_2)_6^+$.

^1H NMR data in toluene-d_8: $T = 75$ °C, δ 3.65 (quartet), 1.11 ppm (triplet); $T = -60$ °C, δ 4.87 and 2.37 ppm (quartets), δ 1.30 and 0.97 ppm (triplets), $J_{H-H} = 7$ Hz; δ in parts per million relative to HMDS.

The coalescence temperature (T_c) is 9.5 °C at 60 MHz (methylene protons).

LiN-*i*-Pr_2 + Decomposed $WCl_4(Et_2O)_2$. LiN-*i*-Pr_2 (277 mmol) in hexane (110 ml)/THF (100 ml) was added to decomposed $WCL_4(Et_2O)_2$ (69 mmol) in ether (200 ml) with stirring, at 25 °C, over 30 min. The solution turned brown. After stirring for 3 h the solvent was removed under reduced pressure, the residue was dried under vacuum (10 h, 60 °C, 10^{-3} Torr) then extracted with warm hexane (200 ml). The solvent was removed from the filtrate and a sublimation of the residue was attempted. Nothing sublimed (≤ 160 °C, 10^{-3} Torr). The residue was extracted with warm hexane (75 ml) and the solvent was removed from the filtrate. The residue was a dark black solid. No tungsten containing fragments were observed in the mass spectrum. The residue was submitted for elemental analysis. Anal. Found: C, 34.34; H, 6.13; N, 6.96; Cl, 3.1 ± 0.5.

X-Ray Data Collection for $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$. Because of the unstable nature of the crystals in air, all operations involving crystal selection and mounting were conducted in a nitrogen filled glove bag. An approximately cubic crystal, 0.6 mm on an edge, was cut from a larger, dark reddish orange single crystal and ground to a sphere 0.40 mm in diameter. This crystal, used for data collection, was sealed in a thin-walled glass capillary under nitrogen. Procedures used for crystal characterization and data collection have been previously described.[26] The crystal was shown to be of good quality from ω-scans which had peak widths at half-height of less than 0.22° for several intense reflections. Preliminary lattice constants and axial photographs indicated that the crystal belonged to the trigonal system and had $\bar{3}$ Laue symmetry. A small shell of data was collected and it revealed no systematically absent reflections; the space group was therefore tentatively assumed to be $P\bar{3}$ ($C_{3i}{}^1$, No. 147).[19] The choice of the centrosymmetric space group was supported at all stages of the subsequent structure solution and refinement.

The final lattice parameters and the orientation matrix used for data collection were obtained from the least-squares refinement of the diffraction geometry for 15 high-angle reflections in the range $20.0° < 2\theta \text{Mo K}\alpha < 35.0$, chosen to give a good sampling of diffractometer settings and crystal indices. Final lattice parameters are: $a = b = 13.556$ (2) Å, $c = 9.420$ (2) Å, and $V = 1499.6$ (5) Å^3. The observed volume agreed satisfactorily with that anticipated for $Z = 3$ on the assumption, which was being made at this point, that the crystal contained only $W_2(NMe_2)_6$ molecules. With the assumption of three identical molecules, the molecules were required to occupy special positions of crystallographic inversion symmetry.

Data were collected at 22 ± 2 °C using a Syntex $P\bar{1}$ autodiffractometer, with graphite-monochromatized Mo Kα radiation and the θ–2θ scan technique. Scans were recorded using variable scan rates from 4 to 24° per min, depending upon the intensity of the reflection, and scan ranges from Mo Kα_1 − 0.8° to Mo Kα_2 + 0.8°. A total of 5555 unique data having 2θ Mo Kα < 50.0° were measured from which the 4531 reflections having $I > \sigma(I)^{26}$ were retained as observed and used in the subsequent structure solution and refinement. Four standard reflections, measured every 150 reflections, showed no significant change during data collection. In view of the high linear absorption coefficient,[27] $\mu = 81.25$ cm^{-1}, a spherical absorption correction[28] was applied to the data. After corrections for Lorentz and polarization effects the intensities were reduced to a set of relative $|F_o|^2$ values for use in structure refinement.[28]

Solution and Refinement of the Structure of $2W_2(NMe_2)_6 \cdot W(NMe_2)_6$. Initial attempts at the structure solution, assuming the crystal contained only $W_2(NMe_2)_6$ molecules with the center of the W–W bond occupying a crystallographic inversion center, failed to yield a satisfactory solution for the three-dimensional Patterson function. After a great deal of frustration, satisfactory agreement with the calculated Patterson function was obtained by placing dinuclear molecules, $W_2(NMe_2)_6$, on the doubly degenerate crystallographic threefold axis at $\frac{1}{3}, \frac{2}{3}, z$ and $\frac{2}{3}, \frac{1}{3}, \bar{z}$ (the W–W vector lying along the z axis) and a single monomeric species, $W(NMe_2)_6$, on the crystallographic $\bar{3}$ position at 0, 0, $\frac{1}{2}$. This solution was satisfactorily consistent with there being essentially three molecules within the unit cell. The z positional parameter for the two tungsten atoms on the threefold axis and the isotropic temperature parameters for three tungsten atoms were refined in two cycles of least-squares refinement to discrepancy indices of

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.119$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.190$$

The function minimized during the least-squares refinement[28] is $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor, w, is equal to $4F_o{}^2/\sigma(F_o{}^2)^2$. Atomic scattering factors used in all stages of the structure refinement were those of Cromer and Waber.[29] Anomalous dispersion effects were included in the calculation of the scattering factors for tungsten.[30] A difference fourier map at this point revealed the positions for all of the remaining atoms of the dinuclear species and the nitrogen atom of the monomer. These ten atoms were first refined isotropically, and then, employing anisotropic thermal parameters for all atoms, giving values of 0.069 and 0.097 for R_1 and R_2, respectively. A difference fourier synthesis at this point revealed the positions of the methyl carbon atoms for the mononuclear molecule. This molecule was observed to be disordered so that the two planes formed by C(31)–N(3)–C(32) and C(33)–N(3)–C(34) had essentially a 90° dihedral angle, as shown in Figure 6. A 50:50 disorder was assumed in the final cycles of refinement. The structure was refined to convergence in four cycles of full-matrix least-squares refinement yielding final discrepancy values $R_1 = 0.047$ and $R_2 = 0.061$ for the 14 atoms of the asymmetric unit employing anisotropic thermal parameters for all atoms. During the final cycle of refinement no parameter shifted by more than 0.15 times the estimated standard deviation of that parameter. A final difference Fourier map was essentially flat with the most prominent peak lying along the line between the two tungsten atoms of the dinuclear molecule. While some of the other peaks were in positions one might expect for hydrogen atoms, no attempt was made to include them in the structure refinement.

X-Ray Data Collection for $W_2(NMe_2)_6$. Because of the similarity of the two compounds, only deviations from the procedures used for the preceding compound need be detailed. The greenish brown crystals of pure $W_2(NMe_2)_6$ were found to be much less stable in the solid state than those for the compound containing both $W_2(NMe_2)_6$ and $W(NMe_2)_6$. Data collection was commenced on four different crystals before one was found to be sealed sufficiently well to allow data collection. The crystal used for the final data collection was ground to a sphere 0.42 mm in diameter and sealed in a thin-walled glass capillary. ω-Scans for several intense reflections had peak-widths at half heights less than 0.24°. Preliminary crystal examination and lattice constants showed the crystal to be isomorphous, as one would expect, with the previously reported compound $Mo_2(NMe_2)_6$,[7] space group $P2_1/c$.

Lattice parameters and an orientation matrix were obtained from 15 reflections, $19.0° < 2\theta$ Mo Kα < 33.0°. The unit cell dimensions are: $a = 11.465$ (3) Å, $b = 11.948$ (3) Å, $c = 15.409$ (3) Å, $\beta = 101.84$ (2)°, and $V = 2065.9$ (8) Å^3. A total of 2381 data having 2θ(Mo Kα) ≤ 43.0 were collected using the θ–2θ scan technique and scans extending from 1.0° below Mo Kα_1 to 1.0° above Mo Kα_2. Variable scan rates from 4 to 24°/min were employed. Collection of a second shell of data from $43.0 < 2\theta$(Mo Kα) < 50.0° was started but terminated when the intensities of the four standard reflections, being measured every 200 reflections, showed a sharp drop in intensity. A spherical absorption correction was applied to the data ($\mu = 117.9$ cm^{-1}),[27] and the intensities were reduced to a set of relative $|F_o|^2$ after corrections for Lorentz and polarization effects.[28] A total of 1521 reflections having $I > 3\sigma(I)$ and 2θ(Mo Kα) $\geq 43.0°$, which is the equivalent of one-half of a Cu sphere of data, were used in the subsequent structure refinement.[28]

Solution and Refinement of $W_2(NMe_2)_6$. Since the compound is isomorphous in the solid state with $Mo_2(NMe_2)_6$, the positions for the 20 atoms in the asymmetric unit were taken as those for the corresponding molybdenum compound. The positional and isotropic thermal parameters for the 20 atoms were refined to $R_1 = 0.079$ and $R_2 = 0.088$ using unit weights for all reflections. The positional and anisotropic temperature factors were then refined to discrepancy values of $R_1 = 0.055$ and $R_2 = 0.062$. An examination of the data at this point showed the presence of extinction effects and the value for the extinction coefficient was refined to a final value of 0.1759×10^{-6}.

Empirical weights ($w = 1/\sigma^2$) were calculated from the equation:

$$\sigma = \sum_0^3 A_n|F_o|^n = 5.83 - 1.31 \times 10^{-2}F_o + 6.1 \times 10^{-5}F_o^2 - 7.0 \times 10^{-7}F_o^3$$

The coefficients A_n were derived from least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 A_n|F_o|^n$$

where the F_c values were calculated from the fully refined model using unit weighting. Final cycles of full-matrix least-squares refinement utilized these empirical weights to give final values of 0.055 and 0.067 for R_1 and R_2, respectively. During the final cycle of refinement no parameter shifted by more than 0.05σ. No significant differences were observed between the final parameters from least-squares refinement cycles which utilized the empirical weights and those which utilized unit weights. A final difference Fourier map revealed no features of structural significance.

Tables of observed and calculated structure factor amplitudes for both structures are available as explained below in the paragraph on supplementary material.

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Supplementary Material Available: Tables of structure factors for both structures (27 pages). Ordering information is given on any current masthead page.

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