The Tungsten–Tungsten Triple Bond. 2. Preparation, Structure, and Dynamical Behavior of Dichlorotetrakis(diethylamido)ditungsten

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Abstract: The mixed chloro(dialkylamido)tungsten(III) compound $W_2Cl_2(NEt_2)_4$ is prepared from the reaction of WCl_4 with deficiencies of $LiNEt_2$ (2–3 equiv). $W_2Cl_2(NEt_2)_4$ is a red, volatile (120°, 10^{-4} cmHg), air-sensitive, diamagnetic crystalline solid. Crystallographic data: space group, $P2_1/n$; unit cell dimensions, $a = 8.166$ (1) Å, $b = 13.299$ (2) Å, $c = 11.444$ (1) Å; $\beta = 100.22$ (1)°; $V = 1223.1$ (3) Å^3; $Z = 2$. Using 1647 reflections having $I > 3\sigma(I)$ the structure was refined to $R_1 = 0.037$ and $R_2 = 0.045$ using anisotropic thermal parameters for all atoms except hydrogen atoms which were not located. The W–W bond length is 2.301 (1) Å, and the W–W–N angles are 102.8 (7)° as compared to 2.293 (2) Å and 103.5 (3)° in $W_2(NMe_2)_6$. The molecule lies on a crystallographic center of symmetry and has, therefore, an anti rotameric conformation. The ^1H NMR spectrum of $W_2Cl_2(NEt_2)_4$ varies considerably with temperature as a result of the temperature-dependent rate of interconversion of proximal and distal ethyl groups. Also, the methylene groups are diastereotopic. The spectra at various temperatures from −20 to +150 °C can be accounted for, and computer-simulated, assuming that only the anti rotamer is present in observable amount. $W_2Cl_2(NEt_2)_4$ reacts with $LiNEt_2$, $LiNMe_2$, and LiMe to give $W_2(NEt_2)_6$, $W_2(NEt_2)_4(NMe_2)_2$, and $W_2Me_2(NEt_2)_4$, respectively.

We have previously reported the preparation, structure, and some properties of the molecules $M_2(NMe_2)_6$, where M = Mo[2] and W,[3] which contain triple bonds between metal atoms. Prior to our work Wilkinson[4] had reported M_2R_6, where M = Mo and W and R is CH_2SiMe_3 which is stable towards β-elimination. It was our conviction that there should be a fairly broad chemistry of molecules containing triple bonds between metal atoms, especially molybdenum and tungsten, and that the above are no more than the first examples of an entire class of compounds of general formula $M_2X_nY_{6-n}$, where M represents Mo or W and X and Y represent a variety of univalent groups such as alkyl, NR_2, OR, halide, etc.

In this paper we offer evidence for this open-ended view of the chemistry of these compounds. We describe in detail the preparation and properties of $W_2Cl_2(NEt_2)_4$ and demonstrate that in this compound the chloro groups can be replaced as in the preparation of $W_2(NEt_2)_4(NR_2)_2$ and $W_2(NEt_2)_4(Me)_2$. Thus we show that the groups X and Y in the general formula can, indeed, be varied.

Results and Discussion

Synthesis. During a synthesis of $W_2(NEt_2)_6$ we noted that crystallization led to a mixture of red and yellow crystals. The yellow crystals closely resembled other crystalline samples of $W_2(NEt_2)_6$. Since the crystals were of good x-ray quality, a portion of this mixture of red and yellow crystals was set aside for x-ray diffraction studies. The remainder of the sample was then recrystallized carefully. The red crystals were fairly readily separated from $W_2(NEt_2)_6$ by taking advantage of the lower solubility of $W_2(NEt_2)_6$ in hexane. Because even recrystallization led to some contamination with $W_2(NEt_2)_6$, a number of large single (or fused) crystals of the red substance were hand picked for further study.

Elemental analysis suggested the empirical formula $W(NEt_2)_2Cl$. In the mass spectrum there is a strong peak corresponding to $W_2(NEt_2)_4Cl_2^+$. Many other ions containing W_2 were observed. The isotopic pattern for $W_2(NEt_2)_4Cl_2^+$ is strikingly different from those of other ditungsten dialkylamides. The observed vs. calculated m/e distribution for $W_2(NEt_2)_4Cl_2$ is shown in Figure 1.

The variable temperature ^1H NMR spectra of $W_2(NEt_2)_4Cl_2$ are significantly different from those of $W_2(NEt_2)_6$ (see later). These observations[5] implied the existence of an anti staggered, ethane-like configuration for the $ClN_2W{\equiv}WN_2Cl$ moiety. An x-ray crystallographic investigation as well as a more thorough NMR study were undertaken to obtain a more detailed knowledge of the structural and dynamical properties of the molecule.

Although compounds M_2L_6, where M = Mo and W, and L = R (alkyl)[4] and NR_2,[2,3] are formed in metathetic reactions involving molybdenum and tungsten halides, the mechanism by which the M–M triple bond is formed is unknown. Since a molecule in which the metal–metal bond is already present but all of the W–Cl linkages are not yet replaced by W–NR_2 linkages could be an intermediate in the preparation of $W_2(NR_2)_6$ species, we were interested in determining the ease of conversion of the W–Cl bonds to W–NR_2 bonds. Hence the reactivity of $W_2(NEt_2)_4Cl_2$ with alkylating and amidating reagents was examined.

$W_2(NEt_2)_4Cl_2$ reacted smoothly with $LiNMe_2$ and $LiNEt_2$ to give $W_2(NEt_2)_4(NMe_2)_2$ and $W_2(NEt_2)_6$, respectively. Similarly $W_2(NEt_2)_4Cl_2$ reacted with LiMe to give $W_2(NEt_2)_4Me_2$. We have not as yet investigated other metathetic reactions of $W_2(NEt_2)_4Cl_2$ but it is certainly possible that $W_2(NEt_2)_4Cl_2$ is an intermediate in the synthesis of $W_2(NEt_2)_6$ from reactions of WCl_4 and $LiNEt_2$.

Since our initial isolation of $W_2(NEt_2)_4Cl_2$ was fortuitous we set out to determine the optimum conditions for its formation. We find that the reaction of WCl_4 with $LiNEt_2$ (3 equiv) provides the best yields (17% based on tungsten) free from $W_2(NEt_2)_6$. Similar attempts to prepare $W_2(NMe_2)_4Cl_2$ from reactions of WCl_4 with deficiencies of $LiNMe_2$ were unsuccessful. No $W_2(NMe_2)_4Cl_2$ was ever detected.

Solid-State Structure of $W_2Cl_2(NEt_2)_4$. The compound is composed of discrete molecules of $W_2Cl_2[N(C_2H_5)_2]_4$ in the solid state. Each molecule has rigorous $C_i(\bar{1})$ symmetry since the midpoint of the W–W bond lies on a crystallographic inversion center. A perspective drawing showing the coordination geometry of the tungsten atoms and the atom labeling scheme is presented in Figure 2. The 12 atoms of the asymmetric unit are each uniquely labeled. Atoms related to these by the inversion center receive the same label augmented by a single

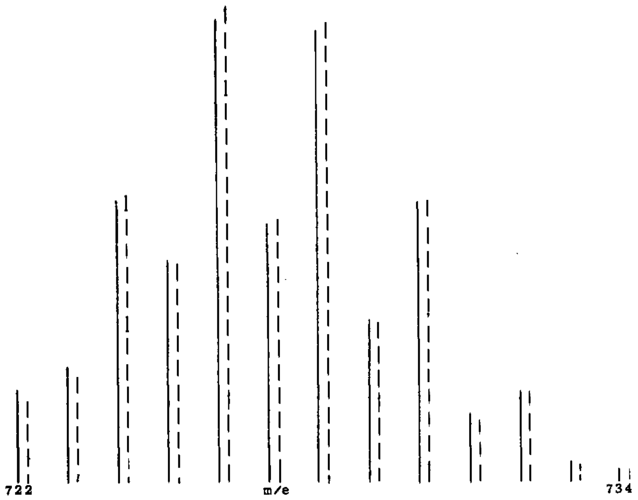

Figure 1. Observed (—) vs. calculated (- - -) m/e for $W_2(NEt_2)_4Cl_2^+$.

Table I. Positional Parameters[a] for $W_2Cl_2(NEt_2)_4$

	x	y	z
W	−0.039 15 (5)	0.066 91 (3)	0.052 56 (3)
Cl	−0.271 4 (4)	0.141 8 (2)	−0.062 7 (3)
N1	−0.077 6 (10)	0.006 2 (6)	0.199 0 (7)
N2	0.157 6 (11)	0.151 0 (7)	0.073 7 (8)
C1	−0.093 3 (17)	0.079 4 (9)	0.294 2 (10)
C2	0.070 7 (21)	0.090 5 (11)	0.383 5 (12)
C3	−0.067 3 (16)	−0.101 1 (9)	0.242 2 (12)
C4	−0.229 7 (19)	−0.134 9 (11)	0.277 9 (13)
C5	0.131 7 (18)	0.250 8 (9)	0.127 9 (12)
C6	0.110 2 (26)	0.334 0 (11)	0.035 7 (16)
C7	0.328 8 (14)	0.133 8 (10)	0.057 0 (11)
C8	0.439 2 (17)	0.103 0 (15)	0.173 9 (15)

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

prime. The final atomic coordinates and anisotropic thermal parameters are listed in Tables I and II, respectively. Figure 3 shows a stereoscopic view of a single molecule in which all atoms are represented by ellipsoids that have shape, orientation, and size consistent with the thermal parameters listed in Table II.

Values for the bond distances and angles are given in Table III. There are no nonbonded intermolecular contacts less than the sum of the van der Waals radii for the corresponding atoms.

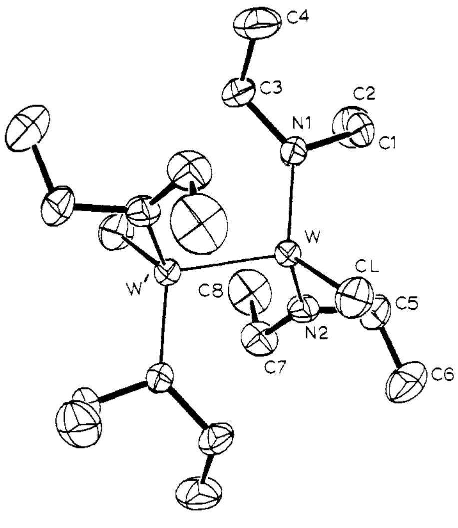

Figure 2. A drawing of the molecular structure of $W_2Cl_2(NEt_2)_4$ in which each atom is represented by its ellipsoid of thermal vibration drawn to enclose 50% of the electron density. The atom labeling scheme is defined. Unlabeled atoms are related by the inversion center to labeled ones and can be designated by the analogous primed labels.

NMR Spectra of $W_2Cl_2(NEt_2)_4$. Proton NMR spectra have been recorded at temperatures from −20 to +150°. All chemical shift values (δ) mentioned in the following discussion are in parts per million, downfield from hexamethyldisiloxane.

At −20° in toluene-d_8 there are two triplets, at δ values of 0.80 and 1.26 which can be assigned to the methyl groups, and two multiplets centered at 2.40 and 4.77 which can be assigned to the methylene groups. For reasons presented earlier[2] we believe that the downfield signals are due to the proximal groups, but an assignment is not essential in the following discussion.

The methylene multiplets in the −20° spectrum can be accounted for by assuming that only the anti rotamer (in which all four NEt_2 groups are equivalent under C_{2h} symmetry) is present. Figure 4 shows the observed and computer-simulated multiplets. The matching is nearly perfect for the proximal multiplet, both with and without methyl decoupling. There are small but noticeable discrepancies for the distal multiplet but we do not consider them significant. For the proximal multiplet the parameters used in the simulated spectra are: δ_A 4.52, δ_B 5.02, δ_X 1.26, $J_{AB} = -13.0$ Hz, $J_{AX} = J_{BX} = 7.0$ Hz. For the distal multiplet they are: δ_A 2.36, δ_B 2.45, δ_X 0.80, $J_{AB} = -13.0$ Hz, $J_{AX} = J_{BX} = 7.0$ Hz. For the spectra obtained with methyl

Table II. Refined Anisotropic Thermal Parameters[a,b] for $W_2Cl_2(NEt_2)_4$

	Values in Å^2						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso}[c]
W	2.30 (2)	2.13 (2)	2.32 (2)	0.01 (2)	0.78 (1)	−0.03 (2)	2.19
Cl	3.8 (1)	4.3 (1)	4.4 (1)	1.2 (1)	0.7 (1)	0.8 (1)	4.0
N1	3.1 (4)	2.2 (4)	2.4 (3)	0.4 (3)	0.6 (3)	0.6 (3)	2.5
N2	3.3 (4)	2.9 (4)	3.4 (4)	−0.8 (3)	1.4 (3)	−0.1 (3)	3.0
C1	5.4 (6)	2.9 (5)	3.1 (5)	0.5 (5)	1.8 (5)	−0.5 (4)	3.4
C2	7.3 (9)	5.5 (8)	3.4 (6)	−1.2 (7)	0.6 (6)	−1.3 (5)	4.9
C3	4.3 (6)	2.6 (5)	4.7 (6)	0.0 (4)	1.9 (5)	0.9 (4)	3.5
C4	5.7 (8)	4.9 (7)	4.8 (6)	−1.9 (6)	1.9 (6)	0.7 (6)	4.6
C5	5.3 (7)	2.4 (5)	5.4 (6)	−0.9 (5)	2.0 (5)	−0.7 (4)	3.8
C6	9.5 (12)	3.3 (6)	7.2 (9)	−0.5 (7)	2.2 (9)	0.6 (6)	5.9
C7	2.5 (5)	4.5 (6)	4.6 (6)	−1.3 (4)	0.9 (4)	−0.5 (5)	3.5
C8	3.2 (5)	8.0 (10)	6.0 (8)	0.0 (6)	−0.6 (6)	−0.6 (7)	5.4

[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} used in refinement as $B_{ij} = 4\,\beta_{ij}/a_i{}^*a_j{}^*$. [c] Isotropic thermal parameters calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

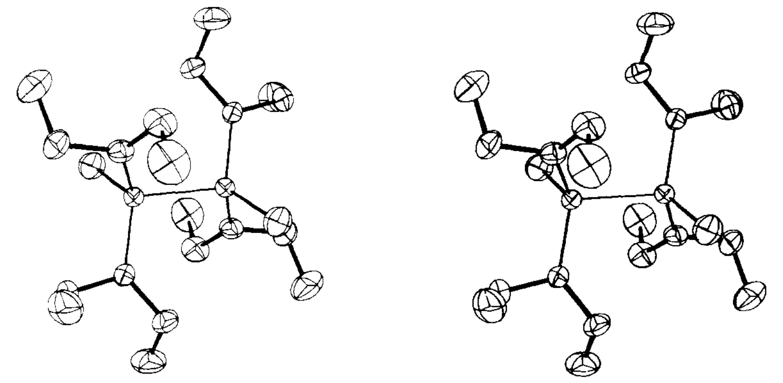

Figure 3. A stereoscopic view of the molecular structure of $W_2Cl_2(NEt_2)_4$ showing clearly the anti rotameric conformation.

Table III. Bond Distances and Angles[a] for $W_2Cl_2(NEt_2)_4$

	Distances, Å	Averages
W-W′	2.3012 (8)	
W-Cl	2.332 (8)	
W-N1	1.935 (8)	1.936
W-N2	1.937 (9)	
N1-C(1)	1.48 (1)	1.49
-C3	1.50 (1)	
N2-C5	1.50 (1)	
-C7	1.46 (1)	
C(1)-C2	1.54 (2)	1.53
C3-C4	1.52 (2)	
C5-C6	1.52 (2)	
C7-C8	1.53 (2)	
	Bond Angles, degrees	
W′-W-Cl	107.93 (9)	
W′-W-N1	103.5 (2)	102.8
W′-W-N2	102.1 (3)	
Cl-W-N1	115.3 (3)	114.4
Cl-W-N2	113.4 (3)	
N1-W-N2	113.0 (4)	
C(1)-N1-C3	112.8 (9)	113.3
C5-N2-C7	113.7 (9)	
N1-C(1)-C2	111.9 (10)	111.5
N1-C3-C4	111.5 (10)	
N2-C5-C6	111.5 (11)	
N2-C7-C8	110.9 (11)	
W-N1-C1	114.3 (4)	
W-N1-C3	132.1 (3)	
W-N2-C5	112.9 (4)	
W-N2-C7	133.2 (3)	

Dihedral Angles, degrees

	Plane	Equations of Planes[b] A	B	C	D
I	W′-W-N1	−0.898	−0.157	−0.410	0.000
II	-N2	−0.207	0.472	−0.857	0.000
III	C(1)-N1-C3	−0.972	−0.074	−0.224	0.501
IV	C5-N2-C7	−0.055	0.406	−0.912	−0.003

Dihedral angles, I-III = 12.45; II-IV = 9.99

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

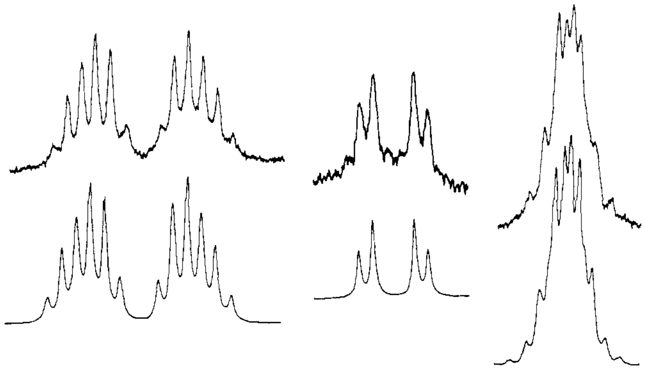

Figure 4. Observed (upper) and computer-simulated (lower) spectra for the methylene groups of $W_2Cl_2(NEt_2)_4$ at −20°, 100 MHz. Parameters used in the simulations are given in the text. At left is the normal proximal (downfield) multiplet; center is the same with the methyl protons decoupled. At right is the normal distal (upfield) multiplet.

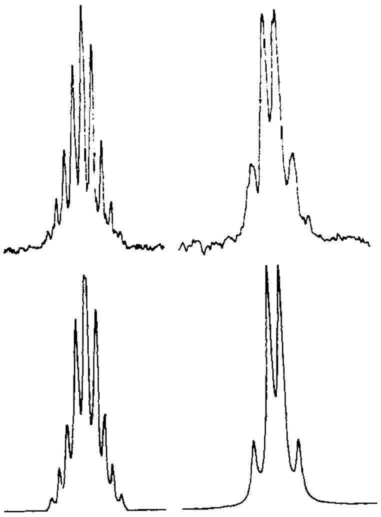

Figure 5. Observed (upper) and computer-simulated (lower) spectra for the methylene groups of $W_2Cl_2(NEt_2)_4$ at +150°, 100 MHz. Spectra at the left are the normal ones; those at the right are with the methyl protons decoupled.

decoupling, $J_{AX} = J_{BX} = 0$ was used, with the other parameters remaining unchanged. Only the decoupled proximal spectrum is shown in Figure 4. The decoupled distal methylene spectrum was equally well simulated.

Figure 5 shows observed and calculated methylene resonances at +150°. The objective here was to see if the observed spectra were consistent with the presence of only one NMR-differentiable methylene group, with chemical shift and coupling parameters equal to, or nearly equal to, the average of the values measured separately for proximal and distal ethyl groups. The values to be averaged at 150° need not be precisely equal to those appropriate to the −20° spectra. Some temperature dependence, mainly in the chemical shifts, would not be unexpected.

The parameters used to compute the multiplets shown in Figure 5 are: $\delta_A{}'$ 3.62, δ_B 3.80, δ_X 1.10, $J_{AB} = -13.0$ Hz, $J_{AX} = J_{BX} = 7.0$ Hz. The coupling constants are exactly equal to

Table IV. Comparison Table of Selected Bond Lengths and Angles for the Related Tungsten and Molybdenum Compounds

	Compound			
Distances, Å	$Mo_2(NMe_2)_6$[a]	$W_2(NMe_2)_6$[b]	$W_2(NMe_2)_6$[a,c]	$W_2Cl_2(NEt_2)_4$
M-M	2.214 (2)	2.294	2.292	2.301
M-N	1.97	1.982	1.97	1.936
N-C	1.48	1.466	1.48	1.49
M-Cl				2.332
	Angles, deg			
M-M-N	103.7	103.8	103.3	102.8
N-M-N	114.6	114.5	114.8	113.0
M-N-C (proximal)	133	132.6	134.	132.6
(distal)	116	116.5	116.	113.6
C-N-C	110	111.0	110.	113.3
M-M-Cl				107.9

[a] Distances and angles are the averages for the two independent molecules of the asymmetric unit. See preceding paper. [b] Values for $W_2(NMe_2)_6$ in the cocrystallized compound $2W_2(NMe_2)_6{\cdot}W(NMe_2)_6$. [c] Values for the pure crystalline compound $W_2(NMe_2)_6$.

those in the low-temperature spectra. The chemical shifts differ from the averages of the low-temperature values by +0.18, +0.07, and +0.07 for A, B, and X, respectively. This suggests that there is a consistent downfield shift for all ethyl proton resonances of about 0.1 ppm from −20 to +150°.

It appears that within experimental error, the high temperature spectrum can be attributed simply to the averaging of the proximal and distal resonances which are observable separately at low temperature. There is no positive indication that any other process or species need be considered. Specifically, there is no indication that gauche rotamers are observably populated either at −20° or at +150°. It should be noted that this result does *not* rule out (or in) the possibility that internal rotation about the W≡W bond may occur, nor say anything about the rate or barriers to such rotation, beyond the fact that the energies of the two gauche forms are too high relative to the anti form to allow observable quantities of gauche rotamers to exist. The spectral changes as a function of temperature are reversible. When a sample was held at +150° for 30 min and then rapidly chilled to −20°, the spectrum originally observed at −20° was again seen.

Comparison of Structures. Table IV compares the structural data now available for $Mo_2(NMe_2)_6$, $W_2(NMe_2)_6$, and $W_2Cl_2(NEt_2)_4$. No chemically significant variations occur in any parameter except for the difference of ca. 0.085 Å between the Mo≡Mo bond length and the W≡W bond lengths.

Experimental Section

Materials. WCl_6 was purchased from ROC/RIC and was sealed in glass ampoules (ca. 5-40 g each) under vacuum prior to use. $W(CO)_6$ was obtained from Strem Chemical Co. $ZnEt_2$ (10% solution in benzene) was a gift from the Ethyl Corporation. MeLi (in ether) was purchased from Alfa Inorganics. WCl_4 was prepared from the reaction[6] $2WCl_6 + W(CO)_6 \rightarrow 3WCl_4$ in refluxing chlorobenzene, then stored in glass vials prior to use. $WCl_4(Et_2O)_2$[7] was prepared in situ (100% yield assumed) and used immediately. $LiNMe_2$ was prepared by slowly condensing a stoichiometric amount of $HNMe_2$ (Matheson) into a hexane solution of BuLi (ca. 2.4 M) at −78 °C. $LiNEt_2$ was prepared by adding an equimolar amount of BuLi (2.4 M in hexane) to an ice cold, stirred solution (ether or THF) of diethylamine (Matheson, Coleman and Bell).

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

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

^1H NMR measurements were made on Varian Associates A60 and HA100 instruments equipped with variable temperature probes. Temperatures were calibrated with methanol or ethylene glycol. Unless otherwise noted toluene-d_8 was used as the solvent with hexamethyldisiloxane (HMDS) as the internal reference (δ(HMDS) = δ(TMS) − 0.11). Spectra simulations were carried out on the Nicolet 1080 computer using software provided by the manufacturer.

Mass spectra were obtained using an AEI MS 9 mass spectrometer and the method of direct insertion (100-120 °C).

General Procedures. Due to the highly reactive nature of tungsten halides, $LiNR_2$, $W_2(NEt_2)_4Cl_2$, 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 type techniques.[8] After preparation, samples were stored and handled in a Vacuum Atmospheres Company Dri Lab system.

Solvents (pentane, hexane, ether, THF, 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 not added to ether or THF), then stored over CaH_2 under nitrogen until used.

Decomposed $WCl_4(Et_2O)_2$ + $3LiNEt_2$. $WCl_4(Et_2O)_2$ (82.2 mmol) in ether (250 ml) was allowed to decompose by stirring at 25 °C for 2 h. The solid and solution turned black. $LiNEt_2$ (246 mmol) in hexane (102 ml)/ether (100 ml) was slowly added at 0 °C, with stirring, over 30 min. The slurry turned brown. After stirring for 1 h at 0 °C, the slurry was allowed to warm to room temperature and stirred for 8 h. The solvent was removed under reduced pressure (30-40 °C); the residue was thoroughly dried (1 h, 60 °C, 10^{-3} Torr), and then extracted with warm hexane (200 ml). The solvent was removed from the filtrate (ca. 50 °C) and the residue was dried (8 h, 80-100 °C, 10^{-3} Torr), then extracted with warm hexane (150 ml). The filtrate was concentrated to about 50 ml (at 50 °C) then cooled to −20 °C. The light brown solid was filtered off and dried. The yield was about 4 g (13% based on tungsten). The product was carefully recrystallized from hexane, whereby fairly large crystals and clumps of crystals (ca. 1-10 mg each) were obtained. We noted that there were pale yellow crystals (as expected for $W_2(NEt_2)_6$) and bright red crystals (presumably a new and unexpected compound). These two compounds were separated mechanically in the drybox. NMR, ir, and mass spectra indicated that the yellow compound was indeed $W_2(NEt_2)_6$ (see previous paper) while the red compound was found to be $W_2(NEt_2)_4Cl_2$. Anal. Calcd for $W_2(NEt_2)_4Cl_2$: C, 26.52; H, 5.57; N, 7.60; Cl, 9.41. Found: C, 26.43; H, 5.55; N, 7.71; Cl, 9.75. $W_2(NEt_2)_4Cl_2$ has a peak in its mass spectrum corresponding to $W_2(NEt_2)_4Cl_2^+$ (see Figure 1). Its ir spectrum has bands at 232 w, 302 m, 333 sh, 350 s, 505 m, 533 s, 588 s, 790 s, 880 s, 886 sh, 914 m, 1000 s, 1046 s, 1067 s, 1085 m, 1094 sh, 1145 s, 1188 s, 1273 cm^{-1} m.

^1H NMR data (60 MHz in toluene-d_8): T = −32 °C, $\delta(NCH_2CH_3)$ 2.43 (quartet) and 4.85 ppm (multiplet), $\delta(NCH_2CH_3)$ 0.83 and 1.28 ppm (triplet), J_{H-H} = 7 Hz; T = 116 °C, $\delta(NCH_2CH_3)$ 3.72 (multiplet) and 1.10 ppm (triplet), the spectrum was unchanged at 170 °C (in mesitylene). δ in parts per million relative to HMDS.

Preparation of $W_2(NEt_2)_4Cl_2$ from WCl_4. $LiNEt_2$ (60.9 mmol) in hexane (25 ml)/THF (60 ml) was added over 40 min to WCl_4 (6.63 g, 20.3 mmol) in THF (125 ml) with stirring, at 25 °C. The dark reddish brown slurry was stirred for 17 h; then the solvent was removed under reduced pressure. The residue was thoroughly dried (60°, 10^{-3} Torr), then extracted with warm hexane (150 ml). The solvent was removed from the filtrate and the product was sublimed from the residue (130–150 °C, 10^{-3} Torr). The residue was extracted with hexane (75 ml), the solvent was removed from the filtrate and additional product was sublimed from this residue (130–150 °C, 10^{-3} Torr). The sublimates were combined and recrystallized from hexane, yielding 1.2 g (17% based on tungsten) of $W_2(NEt_2)_4Cl_2$.

WCl_4 + 2$LiNMe_2$; Attempted Preparation of $W_2(NMe_2)_4Cl_2$. $LiNMe_2$ (20.4 mmol) in hexane (20 ml)/THF (50 ml) was added to WCl_4 (3.32 g) in THF (50 ml) with stirring, at 25 °C, over 40 min. The solution turned reddish brown. After stirring for 60 min the solvent was removed under reduced pressure and the residue was thoroughly dried (50 °C, 10^{-3} Torr), then extracted with warm hexane (40 ml at 50 °C).

The only hexane soluble product was a trace (ca. <0.1 g) of $W_2(NMe_2)_6$.

$W_2(NEt_2)_4Cl_2$ + $LiNEt_2$. $LiNEt_2$ (3.90 mmol) in ether (20 ml) was added to $W_2(NEt_2)_4Cl_2$ (0.944 g, 1.30 mmol) in ether (50 ml) with stirring, at 25 °C, over 10 min. The red solution turned cloudy and yellowish over about 15 min. After stirring for 2 h the solvent was removed under reduced pressure and the residue was extracted with warm hexane (60 ml). The filtrate was concentrated to about 20 ml at 50 °C, then cooled slowly to −20 °C. The yellow, crystalline $W_2(NEt_2)_6$, 0.529 g (50% yield based on tungsten), was filtered off and dried.

Preparation of $W_2(NEt_2)_4(NMe_2)_2$. $W_2(NEt_2)_4Cl_2$ (0.322 g, 0.44 mmol) was added to $LiNMe_2$ (1.33 mmol) in ether (30 ml) at room temperature, with stirring. The solution rapidly turned yellow. After stirring for 10 h the solvent was removed under reduced pressure and the residue was extracted with warm hexane (30 ml). The solvent was removed from the filtrate and $W_2(NEt_2)_4(NMe_2)_2$ was sublimed (130–150 °C, 10^{-3} Torr) from the residue. The yield was 0.25 g (75% based on tungsten). Anal. Calcd for $W_2(NEt_2)_4(NMe_2)_2$: C, 32.27; H, 7.04; N, 11.29. Found: C, 33.00; H, 7.62; N, 11.47. Its ir spectrum had bands at 326 s, 340 sh, 430 w, 492 sh, 500 s, 555 s, 583 s, 650 w, 676 w, 778 sh, 792 s, 873 s, 878 sh, 904 m, 951 vs, 1000 vs, 1041 s, 1045 sh, 1063 m, 1089 m, 1125 m, 1148 s, 1184 s, 1246 s, 1257 sh, 1275 m, 1310 w, 1329 m, 1345 cm^{-1} s. ^1H NMR data (60 MHz, in toluene-d_8): $T = -60$ °C, δ(NMe) 2.39 and 4.33 ppm (singlet), δ(NCH_2CH_3) 2.47 and 4.84 ppm (quartet), and 0.92 and 1.28 ppm (triplet); $J_{H-H} = 7$ Hz; $T = 50$ °C, δ(NMe) 3.35 ppm (singlet), δ(NCH_2CH_3) 3.65 ppm (quartet) and 1.10 ppm (triplet), δ in parts per million relative to HMDS.

Preparation of $W_2(NEt_2)_4Me_2$. MeLi (1.2 mmol) in ether (2 ml) was added to $W_2(NEt_2)_4Cl_2$ (0.351 g, 0.483 mmol) in ether (20 ml) at room temperature with stirring. The solution rapidly turned cloudy. After stirring for 1 h the solvent was removed under reduced pressure and the residue was extracted with hexane (40 ml). The orange filtrate was concentrated to about 10 ml and cooled to −20 °C. The red crystals were filtered off and dried. The yield was 0.2 g (54% based on tungsten). Anal. Calcd for $W_2(NEt_2)_4Me_2$: C, 31.50; H, 6.76; N, 8.16. Found: C, 31.26; H, 6.58; N, 8.12. The mass spectrum had a strong peak due to $W_2(NEt_2)_4Me_2^+$ and numerous other W_2-containing ions. Its ir spectrum (400–1350 cm^{-1}) had bands at 495 s, 518 s, 590 s, 658 w, 788 s, 876 s, 884 sh, 909 m, 1004 vs, 1044 m, 1064 m, 1088 m, 1095 sh, 1149 s, 1187 s, 1276 m, 1310 m, 1331 w, 1347 cm^{-1} s. ^1H NMR data (60 MHz, in toluene-d_8): $T = -40$ °C, δ(Me) 1.21 and 1.30 ppm (singlet), δ(NCH_2CH_3) 4.85 and 2.40 ppm (multiplet), δ(NCH_2CH_3) 0.85 and 1.27 ppm (triplet), $^3J_{H-H} = 7$ Hz; $T = +80°$, δ(NCH_2CH_3 3.53 ppm (multiplet), δ(NCH_2CH_3) 1.06 ppm (triplet). δ in parts per million relative to HMDS.

X-Ray Crystallography. Crystal Selection and Data Collection. The crystal used for data collection was selected from a crystalline sample containing red-orange crystals of $W_2Cl_2(NEt_2)_4$ and yellow crystals known to be $W_2(NEt_2)_6$. A large evenly shaped crystal, approximating a 0.5 mm cube, was ground to a sphere 0.345 mm in diameter and sealed in a thin-walled glass capillary under nitrogen. Although these crystals did not appear to be as oxygen sensitive in the solid state as those containing $W_2(NMe_2)_6$, all steps involving crystal selection, grinding, and mounting were done in a nitrogen filled glove bag. Since the procedures for crystal examination and data collection have been previously described,[9] only deviations from these procedures will be reported. The crystal was found to have monoclinic, $2/m$, Laue symmetry. A small shell of data showed the systematically absent reflections $0k0$ ($k \neq 2n$) and $h0l$ ($h + l \neq 2n$), indicating the uniquely determined space group $P2_1/n$ (a nonstandard setting of $P2_1/c$).[10] The crystal appeared to be of excellent quality having average peak widths at half-height less than 0.20° for several intense reflections. The final lattice constants and orientation matrix used for the calculation of the setting angles in data collection were determined by least-squares refinement of the diffraction geometry for 15 high-angle reflections in the range, $24.0° < 2\theta$ Mo K$\alpha < 36.0°$, chosen to give a good sampling of diffractometer settings and crystal indices. The refined lattice parameters are: $a = 8.166$ (1) Å, $b = 13.299$ (2) Å, $c = 11.444$ (1) Å, $\beta = 100.22$ (1)°, and $V = 1223.1$ (3) Å^3. The observed volume is consistent with that expected for $Z = 2$ requiring the molecules to lie on inversion centers.

The data were collected with a Syntex P$\bar{1}$ autodiffractometer equipped with a graphite-crystal monochromator using Mo Kα radiation. Variable scan rates from 3.0 to 24.0°/min were used for symmetric scans from 0.9° below to 0.9° above the calculated Mo Kα_1–Mo Kα_2 doublet. A total of 2173 reflections having $0.0° < 2\theta$ Mo K$\alpha < 50.0°$ were recorded. A spherical absorption correction ($\mu = 101.6$ cm^{-1}) was applied to all data. The four standard reflections measured every 150 reflections during data collection showed no significant fluctuations or trends and the 2173 data were reduced to a set of relative $|F_o|^2$ after corrections for Lorentz and polarization effects. Those 1645 reflections having $I > 3\sigma(I)$ were retained as observed and used in the final structure refinement.[11]

Structural Solution and Refinement. The atomic coordinates for the tungsten atom were derived from a three-dimensional Patterson synthesis and refined in two cycles of least-squares refinement to give discrepancy indices

$$R_1 = \Sigma||F_o| - |F_c||/|F_o| = 0.219$$

$$R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2)^{1/2} = 0.317$$

The least-squares refinement minimizes the function $\Sigma w(|F_o| - |F_c|)^2$. In the initial stages of refinement all reflections were given unit weights.

The atomic scattering factors used in all refinements were those of Cromer and Waber.[12] Anomalous dispersion effects were included in the calculated scattering factors for tungsten and chlorine.[13] A difference Fourier synthesis at this point clearly revealed the remaining 11 atoms of the asymmetric unit. The 12 atoms were refined employing isotropic thermal parameters for all atoms to give residuals of $R_1 = 0.067$ and $R_2 = 0.077$. All atoms were refined to convergence in three cycles of least-squares refinement using anisotropic temperature factors to give $R_1 = 0.037$ and $R_2 = 0.047$. Empirical weights ($\omega = 1/\sigma^2$) were then calculated from the equation

$$\sigma = \sum_0^3 A_n|F_o|^n = 5.83 - 1.31 \times 10^{-2}F_o + 5.63 \times 10^{-5}F_o^2 - 1.71 \times 10^{-8}F_o^3$$

The A_n are coefficients derived from the least-squares fitting of the curve $||F_o| - |F_c|| = \Sigma_0^3 A_n|F_o|^n$ where the F_c values were calculated from the fully refined model using unit weighting. The final cycles of full-matrix least-squares refinement utilized these weights and anisotropic thermal parameters to give final values of $R_1 = 0.037$ and $R_2 = 0.045$. In the final cycle the extinction coefficient was also refined to a value of 1.043×10^{-6} During the final cycle of refinement no parameter shifted by more than 0.01σ where σ is the estimated standard deviation of that parameter. A final difference Fourier map showed no feature of structural significance other than possible positions for some of the hydrogen atoms. No significant differences were observed between the refined parameters which utilized unit weights and those utilizing the empirical weights.

A table of observed and calculated structure factors for the data used in the final refinement is available elsewhere.[14]

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Supplementary Material Available: A table of structure factors (7 pages). Ordering information is given on any current masthead page.

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X-Ray and Neutron Diffraction Studies on $HW_2(CO)_8(NO)(P(OCH_3)_3)$. A Compound with a Slightly Asymmetric Hydrogen Bridge Bond[1]

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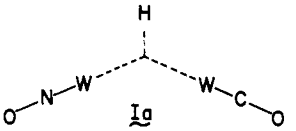
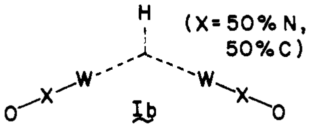
Abstract: The molecular structure of $HW_2(CO)_8(NO)(P(OCH_3)_3)$, prepared by treating $HW_2(CO)_9(NO)$ with trimethyl phosphite, was studied with x-ray and neutron diffraction techniques. The presence of the bulky $P(OCH_3)_3$ ligand eliminated the packing disorder problems which occurred in the earlier neutron diffraction analysis of $HW_2(CO)_9(NO)$, and allowed the detailed geometry of the WHW region to be examined closely for possible asymmetric features. The structure of $HW_2(CO)_8(NO)(P(OCH_3)_3)$ consists of $W(CO)_5$ and $W(CO)_3(NO)(P(OCH_3)_3)$ fragments joined by a single WHW three-center bond. The nitrosyl ligand was located at an axial position, thereby confirming earlier results on $HW_2(CO)_9(NO)$. In the present neutron diffraction study the WHW bond was found to be slightly asymmetric, the difference between the two W-H distances being 0.035 (10) Å. The hydrogen atom is closer to the $W(CO)_5$ group than to the $W(CO)_3(NO)(P(OCH_3)_3)$ group, as expected since the $W(CO)_5$ unit is the more electron-deficient half of the molecule. The rest of the structure is very similar to that of $HW_2(CO)_9(NO)$: the molecule has a bent backbone with staggered equatorial ligands, and the hydrogen atom is significantly removed from the point of intersection of the axial W-C and W-N vectors. Other details of the WHW region: W-H = 1.859 (6) and 1.894 (6) Å, $W \cdots W$ = 3.381 (2) Å, W-H-W = 129.4 (3)°, H-W-W = 25.5 (2)° and 25.0 (2)°. Crystallographic details for $HW_2(CO)_8(NO)(P(OCH_3)_3)$: unit cell $P\bar{1}$; $a = 10.012$ (7), $b = 11.261$ (8), $c = 9.062$ (6) Å; $\alpha = 90.84$ (5), $\beta = 90.52$ (6), $\gamma = 76.35$ (4)°; $V = 992.7$ Å^3, $Z = 2$. Final agreement factors for data with $I > 3\sigma$: $R = 0.050$ for 2481 x-ray reflections and $R = 0.089$ for 2385 neutron reflections. In comparing compounds having bent W-H-W bonds (such as $HW_2(CO)_9(NO)$, $HW_2(CO)_8(NO)(P(OCH_3)_3)$, $[(Ph_3P)_2N]^+[HW_2(CO)_{10}]^-$) with those having linear W-H-W bonds (such as $[Et_4N]^+[HW_2(CO)_{10}]^-$), it is found that the W-W overlap distance remains constant rather than the W-W or W-H bond distances.

Our recent neutron diffraction analysis of $HW_2(CO)_9(NO)$[4] indicated the presence in this compound of a central three-center W-H-W bond in which the hydrogen atom is displaced off the extrapolated intersection of the lines through the axial ligands (Ia). Since the two tungsten atoms are situated in different environments, we were hopeful of finding a noticeable degree of asymmetry in the W-H-W bond. However, a 50-50% nitrosyl-carbonyl packing disorder (Ib) gave rise to a hydrogen position symmetrically disposed about the normal to the $W \cdots W$ bond. It was not possible to decide if this observed symmetry was intrinsic to the $HW_2(CO)_9(NO)$ molecule or if the symmetry was a consequence of the packing disorder.



Ia



Ib

The isoelectronic molecule $HW_2(CO)_8(NO)(P(OCH_3)_3)$ was therefore prepared with the expectation that the axial carbonyl-nitrosyl disorder would be prevented by the presence of the bulky $P(OCH_3)_3$ ligand on one of the tungsten atoms. The structural results for this compound would then allow an improved assessment of the bonding for a bridging hydrogen atom in an asymmetric environment.

Experimental Section

Preparation of $HW_2(CO)_8(NO)(P(OCH_3)_3)$. All manipulations were performed under nitrogen and all solvents were thoroughly purged with nitrogen before use. $HW_2(CO)_9NO$ (1.497 g, 2.3 mmol), prepared by published methods,[4,5] was dissolved in 300 ml of hexane and $P(OCH_3)_3$ (0.35 ml, 2.8 mmol) was added. This solution was stirred under nitrogen for 40 h and the solvent removed under vacuum; the resultant orange-yellow powder was dissolved in a minimum volume of 5% CH_2Cl_2-95% C_6H_{14} mixture and chromatographed on a 5 × 22 cm column of silica gel packed in hexane. Three bands were developed: first a small light yellow band, then a long dark yellow band, and finally a short bright orange band. The solvent was removed from the fractions and the dark yellow band recrystallized from hexane to give $HW_2(CO)_8(NO)(P(OCH_3)_3)$ (40% yield). Anal. Calcd for $HW_2(CO)_8(NO)(P(OCH_3)_3)$: C, 17.69; H, 1.34; N, 1.87. Found: C, 17.70; H, 1.53; N, 1.86.