Metal Alkoxides—Models for Metal Oxides. 9.[1] Hydridoditungsten Alkoxides: $W_2(H)(O\text{-}i\text{-}Pr)_8Na\cdot$diglyme and $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$. Further Investigations of the Reaction between $W_2(NMe_2)_6(M{\equiv}M)$ and *i*-PrOH Leading to $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$

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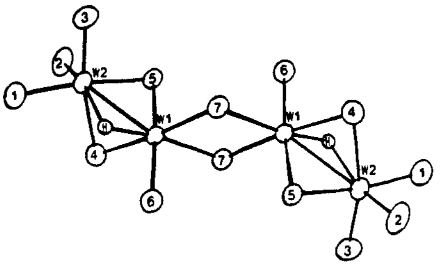
Abstract: Reaction between $W_2(NMe_2)_6(M{\equiv}M)$ and *i*-PrOH ($\gg$6 equiv), which leads to the known compound $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ (*J. Am. Chem. Soc.* **1981**, *103*, 779), is shown to be critically dependent on the presence of the liberated amine. The addition of *i*-PrOH ($\gg$6 equiv) to hydrocarbon solutions of $W_2(O\text{-}t\text{-}Bu)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ does not lead to $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ but rather yields an oligomeric species $[W(O\text{-}i\text{-}Pr)_3]_n$. From the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ in hexane/ROH and NaOR (1 equiv), hexane-insoluble compounds are formed: $NaW_2(H)(OR)_8$, where $R = i\text{-}Pr$ and $CH_2\text{-}t\text{-}Bu$. Extraction into hexane solution by the addition of diglyme (1 equiv) yields $W_2(H)(O\text{-}i\text{-}Pr)_8Na\cdot$diglyme, which has been characterized by NMR studies and a single-crystal X-ray diffraction study. Coordination about each tungsten atom corresponds to a distorted octahedral environment with a central $W_2(\mu\text{-}H)(\mu\text{-}OR)_2$ group: W–W = 2.43 Å. The Na^+ ion is coordinated to three oxygen atoms of the diglyme and two oxygen atoms which form terminal W–OR groups. In tetrahydrofuran solution the Na^+ ion remains associated with the W_2 center, and the compound is best viewed as a mixed-metal alkoxide. $W_2(H)(O\text{-}i\text{-}Pr)_8Na$ reacts with Me_2NH_2I in hexane/*i*-PrOH to give essentially quantitative formation of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$. Addition of NaO-*i*-Pr (2 equiv) to $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ in hexane/*i*-PrOH yields $W_2(H)(O\text{-}i\text{-}Pr)_8Na$. The addition of $MeNH_3I$, dissolved in tetrahydrofuran, to $W_2(H)(OCH_2\text{-}t\text{-}Bu)_8Na$ leads to the formation of the green, hexane-soluble, crystalline compound $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$. This compound contains a distorted confacial bioctahedron, $O_3W(\mu\text{-}H)(\mu\text{-}I)(\mu\text{-}O)WO_2N$, and is closely related to the $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$ molecule having a terminal amine ligand substitute for a μ-OR group and a μ-I ligand in place of a μ-O-*i*-Pr ligand. The key step leading to oxidative-addition of ROH to the $(W{\equiv}W)^{6+}$ moiety is proposed to be a Lewis base promoted conversion of an unbridged d^3–d^3 dimer to a bridged d^3–d^3 dimer and not protonation of the W–W triple bond. These results are compared to previous findings involving the chemistry of M–M multiple bonds. Crystal data for $W_2(H)(O\text{-}i\text{-}Pr)_8Na\cdot$diglyme at −155 °C are the following: a = 24.087 (8) Å, b = 16.540 (5) Å, c = 12.747 (4) Å, β = 125.71 (1)°, Z = 4, d_{calcd} = 1.608 g cm^{-3}, and space group $P2_1/a$; for $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ at −158 °C a = 18.159 (5) Å, b = 10.873 (2) Å, c = 11.599 (3) Å, α = 77.30 (1)°, β = 109.37 (1)°, γ = 96.55 (2)°, Z = 2, d_{calcd} = 1.656 g cm^{-3}, and space group $P\bar{1}$.

Hydride ligands play a prominent role in a number of homogeneous catalytic reactions[2] and presumably play a similarly critical role in heterogeneous catalyzed reactions such as hydrogenation and isomerization of olefins. The compound $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$,[3] which may be viewed as a dimer of a dinuclear compound $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$, is at present the only well-characterized example of a transition-metal hydrido alkoxide[4] and provides us with a possible model for a hydride containing reduced tungsten oxide surface. The essential features of the structure are depicted by I below. The local geometry about each tungsten atom corresponds to a distorted octahedron and the zigzag W_4 atom chain is comprised of two bioctahedral $(W{=}W)^{8+}$ containing units (W=W = 2.45 Å) joined by a common edge W---W = 3.4 Å. Although each tungsten atom is 6-coordinate in the solid-state structure, rapid bridge ⇌ terminal exchange of O-*i*-Pr ligands occurs on the ^1H NMR time scale, even at −80 °C in toluene-d_8. This process scrambles all seven crystallographically different O-*i*-Pr ligands. The molecule behaves as if it is coordinatively unsaturated with respect to Lewis base association reactions, and the hydride ligand is reactive toward olefins. $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ is a catalyst for the conversion of 1-alkenes to *cis*-2-alkenes at ambient temperatures (25–50 °C).



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The initial discovery of the formation of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ in the reaction between $W_2(NMe_2)_6$ and *i*-PrOH led us to expect that other alcoholysis reactions might lead to related hydrido alkoxides of tungsten and that we could develop the chemistry of a class of such compounds. This has not proved to be the case though a variety of tungsten alkoxides have been isolated in these reactions including discrete dinuclear alkoxides and their Lewis base adducts, e.g., $W_2(O\text{-}t\text{-}Bu)_6$[5] and $W_2(OEt)_6(MeNHCH_2CH_2NHMe)$,[6] and cluster compounds of tungsten +4, e.g., $W_4(OR)_{16}$ where R = Me and Et.[7] The particular conditions leading to hydride formation in the reaction between

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[1] Part 8: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Organometallics* **1985**, *4*, 986.

[2] Collman, J. P.; Hegedus, L. A. In "Principles and Applications of Organotransition Metal Chemistry"; University Science Books; Mill Valley, California, 1980.

[3] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Leonelli, J. *J. Am. Chem. Soc.* **1981**, *103*, 779.

[4] To our knowledge the only related compounds claimed in the literature are (i) $Ti_4(OEt)_{13}H$ and (ii) $[Ti(OPh)_2]_3H$. See respectively: (i) Sabo, S.; Gervais, D. *C. R. Seances Acad. Sci., Ser. C* **1980**, *291*, 207. (ii) Flamini, A.; Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 454. There are, of course, other compounds such as $Cp^*_2Zr(H)(OCH_3)$ which contain both hydride and alkoxide ligands together with other ligands ($Cp^* = \eta^5\text{-}C_5Me_5$) but these in no way resemble an oxide-like environment for the metal and the hydride ligand. For $Cp^*_2Zr(H)(OMe)$ see: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733.

[5] Akiyama, M.; Little, D.; Chisholm, M. H.; Haitko, D. A.; Cotton, F. A.; Extine, M. W. *J. Am. Chem. Soc.* **1979**, *101*, 2504.

[6] Chetcuti, M. J.; Chisholm, M. H.; Huffman, J. C.; Leonelli, J. *J. Am. Chem. Soc.* **1983**, *105*, 292.

[7] Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C.; Leonelli, J. *J. Am. Chem. Soc.* **1981**, *103*, 6093.

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$W_2(NMe_2)_6$ and *i*-PrOH became most intriguing. We describe here our further studies of this reaction and our preparation of mixed metal alkoxides $NaW_2(H)(OR)_8$, where R = *i*-Pr and CH_2-*t*-Bu, which have been characterized as either diglyme or tetrahydrofuran adducts. The chemical reactivity of the hydride ligand in these new compounds is under investigation and will be reported subsequently.

Results and Discussion

Syntheses. When the reaction between $W_2(NMe_2)_6$ and *i*-PrOH (≫6 equiv) is carried out at room temperature in a hydrocarbon solvent, typically hexane or toluene, the main product formed at short reaction times, ca. 1 h, is $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$. Indeed this compound can be obtained in crystalline form in >80% yield based on eq 1.

$$W_2(NMe_2)_6 + i\text{-}PrOH(ex) \xrightarrow[\text{hexane, 1 h}]{25\ °C} W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2 + 4HNMe_2 \quad (1)$$

A minor product formed during these reactions at short reaction times is the carbido compound $W_4(C)(O\text{-}i\text{-}Pr)_{12}(NMe)$.[8] This is formed in small quantities, ca. 5–10%, based on tungsten and yields black crystals from hexane/*i*-PrOH. Pure samples of the carbido tungsten cluster are obtained only by careful crystal picking. The carbido compound is unreactive to *i*-PrOH and is not involved in the formation of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$.

The formation of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ in reaction 1 suggested that this was a key intermediate in the reaction leading to $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ and that the reaction followed the sequence (i) rapid alcoholysis and (ii) slow oxidative-addition of *i*-PrOH to the $(W{\equiv}W)^{6+}$ center, as indeed was originally suggested.[3] However, pure samples of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ dissolved in hexane failed to react with added *i*-PrOH at room temperature to give $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$. The major compound formed is $[W(O\text{-}i\text{-}Pr)_3]_n$ which is isolated as large black crystals by crystallization from hexane. $[W(O\text{-}i\text{-}Pr)_3]_n$ is also formed in the alcoholysis reaction shown in eq 2.

$$W_2(O\text{-}t\text{-}Bu)_6 + i\text{-}PrOH(ex) \xrightarrow[\text{hexane, 1 h}]{25\ °C} [W(O\text{-}i\text{-}Pr)_3]_n + 6t\text{-}BuOH \quad (2)$$

If the alcoholysis reaction 2 is carried out in the presence of pyridine, then the pyridine adduct $W_2(O\text{-}i\text{-}Pr)_6(py)_2$[5] is obtained in high yield (>60% by crystallization).

These results implied that $HNMe_2$ played an important role in the formation of the compound $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$. This was further substantiated by the finding that the reaction between $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and *i*-PrOH in hexane yielded $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ when 2–4 equiv of $HNMe_2$, NEt_3, NMe_3, pyridine, or proton-sponge were also added. Similarly the reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and *i*-PrOH in hexane yielded $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ if ca. 4 equiv of $HNMe_2$ or $HNEt_2$ were added, though the addition of only a tertiary amine (NMe_3, NEt_3, proton sponge, or pyridine) did not lead to hydride formation. Thus the presence of an N–H functionality appears crucial to the oxidative addition reaction, as does added base since $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and *i*-PrOH alone do not react to form $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$.

Although $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ can be obtained from the reaction between $[W(O\text{-}i\text{-}Pr)_3]_n$ and *i*-PrOH in hexane with added HNR_2 (4 equiv), the yield of the hydride compound is low. Thus we believe that $[W(O\text{-}i\text{-}Pr)_3]_n$ is not an intermediate in the preparation of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ during the reaction between $W_2(NMe_2)_6$ and *i*-PrOH (≫6 equiv).

When each of $W_2(O\text{-}t\text{-}Bu)_6$, $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$, and $[W(O\text{-}i\text{-}Pr)_3]_n$ is allowed to react in hexane/*i*-PrOH solvent mixtures, ca. 50:50, with NaO-*i*-Pr (1 equiv), a yellow powder is obtained on removal of the solvent. This yellow powder is insoluble in aliphatic or aromatic hydrocarbon solvents but is soluble in THF, dioxane, and *i*-PrOH. If to a suspension of the yellow powder in hexane 1 equiv of diglyme is added, then the yellow powder slowly goes into solution. Crystallization from hexane, by reducing the volume of the solvent, yields $W_2(H)(O\text{-}i\text{-}Pr)_8Na\cdot$diglyme as dark brown crystals.

A similar reaction involving either $W_2(O\text{-}t\text{-}Bu)_6$ or $W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2$ in hexane/*t*-$BuCH_2OH$ with $NaOCH_2$-*t*-Bu (1 equiv) yields a hexane-insoluble compound which is soluble in THF and dioxane. Crystallization from hexane/THF yields $W_2(H)(OCH_2\text{-}t\text{-}Bu)_8Na\cdot2THF$ as dark green crystals.

The hexane-insoluble compounds are formulated as polymeric species $[W_2(H)(OR)_8Na]_x$, where R = *i*-Pr and *t*-$BuCH_2$, formed in the reaction shown in eq 3.

$$W_2(O\text{-}t\text{-}Bu)_6 + NaOR/ROH(excess) \rightarrow NaW_2(H)(OR)_8 + 6t\text{-}BuOH \quad (3)$$

The generality of eq 3 is, however, severely limited, and reactions employing *t*-BuOH, EtOH, and phenol do not yield $NaW_2(H)(OR)_8$ compounds (R = *t*-Bu, Et, and Ph). However, addition of EtOH or *t*-$BuCH_2OH$ to $W_2(H)(O\text{-}i\text{-}Pr)_8Na$ does yield $W_2(H)(OR)_8Na$ where R = *t*-$BuCH_2$ and Et.

The compound $W_2(H)(O\text{-}i\text{-}Pr)_8Na$ reacts with mild proton sources such as $Me_2NH_2^+X^-$ (X = Cl or I) in *i*-PrOH to generate $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ in near quantitative yield, eq 4, and addition of NaO-*i*-Pr (2 equiv) to a hexane/*i*-PrOH solution of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ gives $NaW_2(H)(O\text{-}i\text{-}Pr)_8$, eq 5.

$$NaW_2(H)(O\text{-}i\text{-}Pr)_8 + Me_2NH_2^+X^- \xrightarrow[i\text{-PrOH, 25 °C}]{\text{hexane}} 1/2W_4(H)_2(O\text{-}i\text{-}Pr)_{14} + NaX + Me_2NH \quad (4)$$

$$W_4(H)_2(O\text{-}i\text{-}Pr)_{14} + 2NaO\text{-}i\text{-}Pr \xrightarrow[i\text{-PrOH, 25 °C}]{\text{hexane}} 2NaW_2(H)(O\text{-}i\text{-}Pr)_8 \quad (5)$$

Attempts to prepare $W_4(H)_2(OCH_2\text{-}t\text{-}Bu)_{14}$ by a reaction related to that for the isopropoxide shown in eq 4 failed, though there is evidence from ^1H NMR studies that this compound is initially formed (along with $W_2(H)(Cl)(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)$—an analogue of the monomethylamine adduct formed in reaction 7) but reacts further in an unknown manner. Neither can the compounds $W_4(H)_2(OR)_{14}$, where R = *t*-$BuCH_2$ and Et, be isolated from the alcoholysis reaction shown in eq 6.

$$W_4(H)_2(O\text{-}i\text{-}Pr)_{14} + ROH(ex) \xrightarrow[\text{benzene-}d_6]{25\ °C} W_4(H)_2(OR)_{14} + i\text{-}PrOH \quad (6)$$

$$[R = t\text{-}BuCH_2 \text{ and Et}]$$

The reaction between $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$ and $MeNH_3^+I^-$ in THF (no free alcohol present) yielded the green compound $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ whose formation can be understood in terms of the stoichiometric reaction shown in eq 7.

$$NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8 + 2MeNH_3^+I^- \xrightarrow[\text{THF}]{25\ °C} W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe) + NaI + 2HOCH_2\text{-}t\text{-}Bu + MeNH_2 \quad (7)$$

Physicochemical Properties. The new compounds are all air-sensitive and must be stored and/or worked within dry and oxygen-free atmospheres (N_2) and solvents. Elemental analyses and NMR data are given in the Experimental Section. The compounds $NaW_2H(O\text{-}i\text{-}Pr)_8\cdot$diglyme and $NaW_2H(OCH_2\text{-}t\text{-}Bu)_8\cdot2THF$ are hydrocarbon soluble. The latter compound loses THF under a dynamic vacuum at room temperature. $[W(O\text{-}i\text{-}Pr)_3]_n$ shows a degree of oligomerization ca. 4 in benzene based on a cryoscopic molecular weight determination.

Solid-State and Molecular Structures. $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme. Atomic positional parameters are given in Table I. Selected bond distances and angles are given in Tables II and III, respectively. A view of the molecule showing the atom number scheme is given in Figure 1, and a view of the central $NaW_2(H)O_{11}$ skeleton is given in Figure 2. The hydride ligand, which was not located crystallographically, is represented by an unshaded circle

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[8] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Leonelli, J.; Marchant, N. S.; Smith, C. A.; Taylor, L. *J. Am. Chem. Soc.* **1985**, *107*, 3722.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $NaW_2(H)(O\text{-}i\text{-}Pr)_8$·diglyme

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	1414.8 (2)	2737.9 (3)	5331.5 (4)	14
W(2)	2609.3 (2)	2718.7 (3)	7176.6 (4)	13
O(3)	899 (3)	3614 (4)	4015 (6)	15
C(4)	284 (5)	3509 (7)	2751 (10)	20
C(5)	-139 (6)	4263 (8)	2385 (11)	29
C(6)	453 (6)	3332 (8)	1784 (11)	30
O(7)	816 (3)	2626 (4)	5899 (6)	20
C(8)	102 (5)	2844 (8)	5184 (10)	24
C(9)	-329 (6)	2110 (9)	4542 (11)	38
C(10)	1 (6)	3206 (8)	6181 (11)	33
O(11)	1004 (4)	1897 (5)	4049 (6)	22
C(12)	1175 (5)	1084 (6)	4006 (10)	17
C(13)	536 (6)	582 (7)	3435 (11)	28
C(14)	1446 (6)	1042 (8)	3207 (13)	35
O(15)	1920 (3)	3694 (4)	6653 (6)	19
C(16)	1864 (5)	4553 (7)	6418 (10)	19
C(17)	2463 (5)	4990 (6)	7568 (11)	22
C(18)	1181 (6)	4849 (7)	6100 (12)	29
O(19)	2242 (3)	2972 (4)	5247 (7)	20
C(20)	2351 (6)	3382 (9)	4416 (2)	44
C(21)	2661 (12)	2828 (12)	3986 (19)	91
C(22)	2735 (8)	4115 (0)	4880 (16)	54
O(23)	3349 (3)	3569 (4)	7827 (6)	18
C(24)	4058 (5)	3383 (6)	8593 (10)	17
C(25)	4310 (5)	3146 (7)	7793 (11)	26
C(26)	4433 (6)	4117 (7)	9383 (12)	29
O(27)	2697 (3)	2534 (4)	8778 (6)	18
C(28)	3301 (5)	2480 (7)	10063 (9)	23
C(29)	3490 (6)	3304 (9)	10680 (11)	36
C(30)	3179 (6)	1874 (8)	10803 (10)	28
O(31)	3215 (3)	1873 (4)	7449 (6)	17
C(32)	3167 (5)	1043 (6)	7099 (10)	20
C(33)	3415 (9)	545 (8)	8296 (15)	55
C(34)	3605 (7)	905 (9)	6632 (14)	43
C(35)	1749 (7)	4157 (9)	9467 (14)	45
O(36)	1666 (4)	3314 (5)	9582 (7)	29
C(37)	1235 (7)	3162 (8)	10002 (11)	32
C(38)	1301 (6)	2299 (8)	10337 (11)	32
O(39)	1108 (4)	1845 (5)	9221 (7)	27
C(40)	1145 (7)	996 (8)	9417 (14)	41
C(41)	998 (6)	575 (7)	8235 (13)	33
O(42)	1503 (4)	810 (5)	8065 (7)	30
C(43)	1454 (10)	335 (8)	7066 (16)	55
NA(44)	1579 (2)	2315 (3)	8083 (4)	20

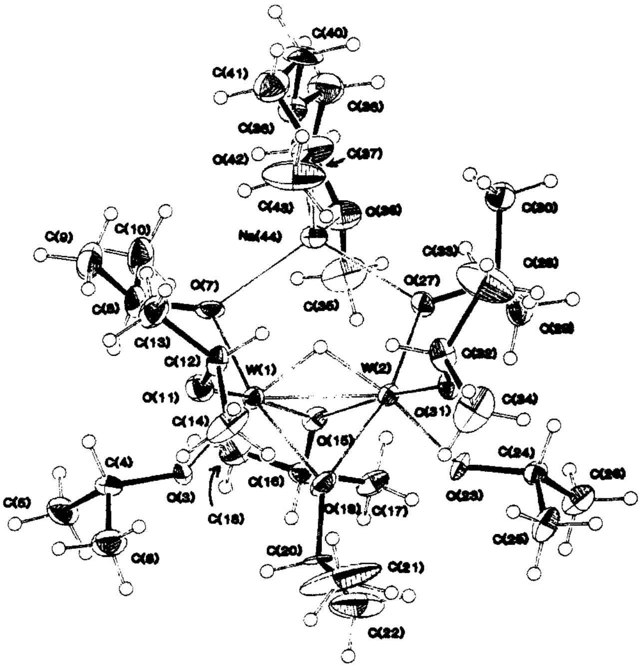

Figure 1. An ORTEP view of the $W_2(H)(O\text{-}i\text{-}Pr)_8Na$·diglyme molecule showing the number scheme used for the atoms.

Table II. Selected Bond Distances (Å) for $NaW_2(H)(O\text{-}i\text{-}Pr)_8$·diglyme

a	b	distance
W(1)	W(2)	2.4313 (11)
W(1)	O(3)	2.007 (6)
W(1)	O(7)	1.964 (6)
W(1	O(11)	1.923 (7)
W(1)	O(15)	2.103 (7)
W(1)	O(19)	2.094 (6)
W(2)	O(15)	2.124 (7)
W(2)	O(19)	2.114 (7)
W(2)	O(23)	2.029 (6)
W(2)	O(27)	1.950 (6)
W(2)	O(31)	1.902 (7)
O(3)	C(4)	1.425 (12)
O(7)	Na(44)	2.328 (8)
O(7)	C(8)	1.444 (12)
O(11)	C(12)	1.418 (12)
O(15)	C(16)	1.442 (12)
O(19)	C(20)	1.405 (13)
O(23)	C(24)	1.420 (11)
O(27)	Na(44)	2.320 (8)
O(27)	C(28)	1.423 (12)
O(31)	C(32)	1.427 (12)
O(36)	Na(44)	2.441 (9)
O(36)	C(35)	1.428 (16)
O(36)	C(37)	1.443 (14)
O(39)	Na(44)	2.434 (8)
O(39)	C(38)	1.425 (14)
O(39)	C(40)	1.420 (14)
O(42)	Na(44)	2.495 (9)
O(24)	C(41)	1.410 (14)
O(42)	C(43)	1.442 (16)

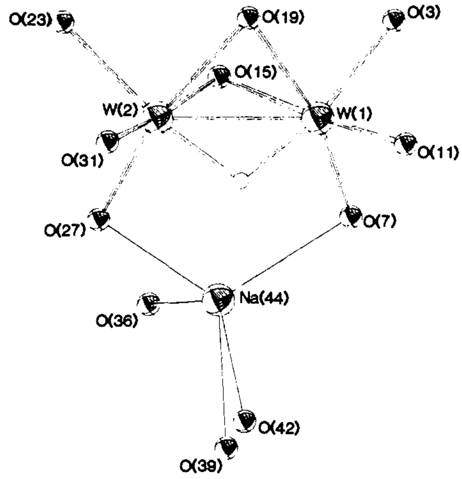

Figure 2. The central $NaW_2(H)O_{11}$ skeleton of the $W_2(H)(O\text{-}i\text{-}Pr)_8Na$·diglyme molecule. The hydride, which was not crystallographically located, is represented by an unshaded circle and has been placed at the centroid of the oxygen atoms O(7), O(11), O(27), and O(31) thereby completing the confacial bioctahedral geometry about the tungsten atoms.

(Figure 2) and has been placed at the centroid of the oxygen atoms O(7), O(11), O(27), and O(31) thereby completing the confacial bioctahedral geometry about the two tungsten atoms.

The molecule can be seen to be related to the $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$ molecule in that the confacial bioctahedral W_2HO_8 skeleton is common to both. The W–W distance, 2.43 Å, is also essentially identical with the short W–W distances (2.45 Å) in $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$. The W–O distances fall into four groups in order of increasing W–O bond length: (i) W–OR terminal ligands trans to μ-OR ligands, 1.91 (1) Å, (ii) Na-μ-OR–W ligands, 1.955 (10) Å, (iii) W–OR terminal ligands trans to W–H, 2.015 (10) Å, and (iv) W_2-μ-OR ligands, 2.11 (2) Å. Of note in this series is the high trans-influence[9] exerted by the hydride ligand and the rel-

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[9] Appleton, T. G.; Clark, H. C.; Manzer, L. M. *Coord. Chem. Rev.* **1973**, *10*, 335.

Table III. Selected Bond Angles (deg) for $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme

a	b	c	angle
W(2)	W(1)	O(3)	128.63 (18)
W(2)	W(1)	O(7)	110.56 (20)
W(2)	W(1)	O(11)	122.97 (21)
W(2)	W(1)	O(15)	55.28 (19)
W(2)	W(1)	O(19)	55.10 (19)
O(3)	W(1)	O(7)	98.42 (27)
O(3)	W(1)	O(11)	92.93 (27)
O(3)	W(1)	O(15)	85.01 (27)
O(3)	W(1)	O(19)	88.12 (27)
O(7)	W(1)	O(11)	96.9 (3)
O(7)	W(1)	O(15)	88.98 (28)
O(7)	W(1)	O(19)	164.22 (28)
O(11)	W(1)	O(15)	173.97 (27)
O(11)	W(1)	O(19)	97.05 (28)
O(15)	W(1)	O(19)	77.24 (26)
W(1)	W(2)	O(15)	54.50 (18)
W(1)	W(2)	O(19)	54.31 (17)
W(1)	W(2)	O(23)	130.35 (19)
W(1)	W(2)	O(27)	111.03 (19)
W(1)	W(2)	O(31)	122.35 (20)
O(15)	W(2)	O(19)	76.36 (26)
O(15)	W(2)	O(23)	86.61 (27)
O(15)	W(2)	O(27)	92.02 (27)
O(15)	W(2)	O(31)	172.72 (27)
O(19)	W(2)	O(23)	90.53 (26)
O(19)	W(2)	O(27)	164.88 (26)
O(19)	W(2)	O(31)	96.49 (27)
O(23)	W(2)	O(27)	98.51 (28)
O(23)	W(2)	O(31)	92.15 (27)
O(27)	W(2)	O(31)	95.3 (3)
W(1)	O(3)	C(4)	125.8 (6)
W(1)	O(7)	Na(44)	103.0 (3)
W(1)	O(7)	C(8)	127.1 (6)
Na(44)	O(7)	C(8)	128.9 (6)
W(1)	O(11)	C(12)	134.6 (6)
W(1)	O(15)	W(2)	70.22 (23)
W(1)	O(15)	C(16)	129.4 (6)
W(2)	O(15)	C(16)	140.8 (6)
W(1)	O(19)	W(2)	70.59 (21)
W(1)	O(19)	C(20)	136.9 (7)
W(2)	O(19)	C(20)	146.8 (7)
W(2)	O(23)	C(24)	123.2 (6)
W(2)	O(27)	Na(44)	103.4 (3)
W(2)	O(27)	C(28)	128.9 (6)
Na(44)	O(27)	C(28)	127.5 (6)
W(2)	O(31)	C(32)	137.4 (6)
Na(44)	O(36)	C(35)	122.3 (7)
Na(44)	O(36)	C(37)	114.9 (7)
C(35)	O(36)	C(37)	112.5 (9)
Na(44)	O(39)	C(38)	115.7 (7)
Na(44)	O(39)	C(40)	114.6 (7)
C(38)	O(39)	C(40)	113.2 (10)
Na(44)	O(42)	C(41)	109.8 (7)
Na(44)	O(42)	C(43)	121.3 (7)
C(41)	O(42)	C(43)	110.6 (10)
O(7)	Na(44)	O(27)	110.66 (27)
O(7)	Na(44)	O(36)	115.7 (3)
O(7)	Na(44)	O(39)	117.76 (28)
O(7)	Na(44)	O(42)	101.9 (3)
O(27)	Na(44)	O(36)	92.5 (3)
O(27)	Na(44)	O(39)	131.6 (3)
O(27)	Na(44)	O(42)	102.8 (3)
O(36)	Na(44)	O(39)	66.8 (3)
O(36)	Na(44)	O(42)	130.9 (3)
O(39)	Na(44)	O(42)	68.3 (3)

atively small lengthening that occurs when the OR ligands are bonded to both W and Na.

In Figure 3, a view looking down the W–W bond vector is shown. This view of the molecule also shows that the coordination environment about the Na atom may be described in terms of a distorted trigonal bipyramid. The central oxygen atom of the diglyme ligand, O(39), and the two alkoxide oxygen atoms, O(7) and O(27), lie in the trigonal plane and the terminal oxygen atoms of the diglyme, O(36) and O(42) which form the axial positions

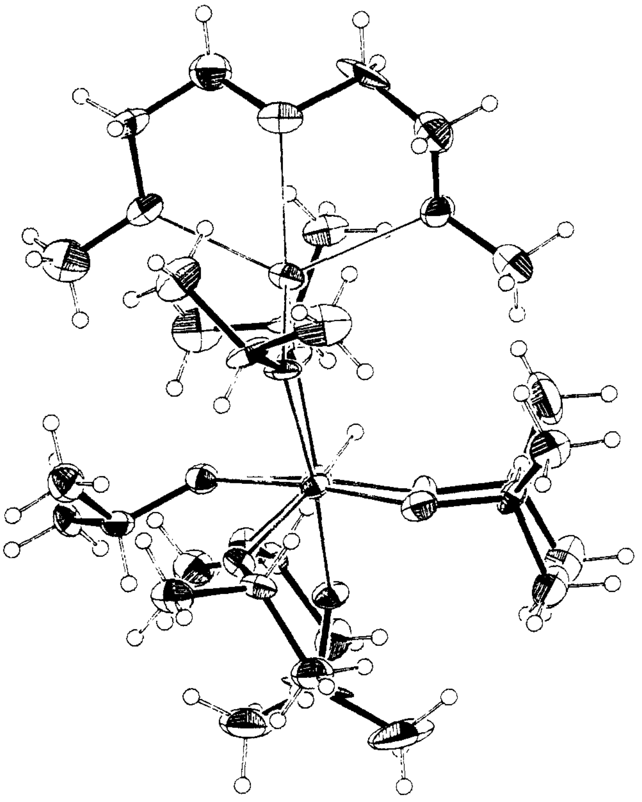

Figure 3. A view of the $W_2(H)(O\text{-}i\text{-}Pr)_8Na\cdot$diglyme molecule looking down the W–W bond vector showing the distorted trigonal-bipyramidal geometry about the Na^+ ion.

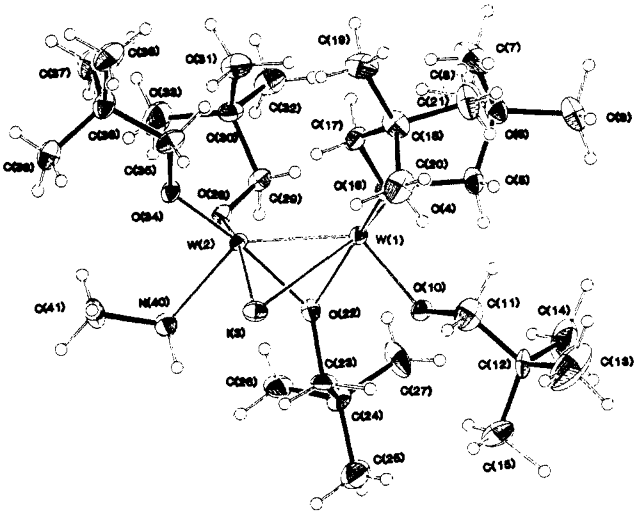

Figure 4. An ORTEP view of the $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ molecule showing the number scheme used for the atoms.

of the top, are by the nature of the ligand pulled toward each other: O(36)–Na–O(42) = 130°. It is also interesting to note that the Na–O bond distances to the OR ligands, 2.32 (1) Å, are much shorter than those distance to the diglyme oxygen atoms which span a range from 2.43 to 2.50 Å. A closely related environment for a Na^+ ion was recently reported by Floriani and co-workers[10] for a tetranuclear sodium–vanadium compound containing a V(III)–V(III) double bond: $V_2(salophen)_2Na_2\cdot 6THF$, where salophen is the *N,N'-O*-phenylenebis(salicylideneiminato)dianion.

$W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$. Atomic positional parameters are given in Table IV, and selected bond distances and angles are reported in Tables V and VI, respectively. A view of the molecule giving the atom number scheme is given in Figure 4, and a view of the central $W_2(H)(I)O_6N$ skeleton is given in Figure

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[10] Gambarotta, S.; Mazzanti, M.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1116.

Table IV. Fractional Coordinates and Isotopic Thermal Parameters for the $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	7237.7 (2)	1042.3 (3)	8731.4 (3)	12
W(2)	7125.4 (2)	253.1 (3)	10821.9 (3)	11
I(3)	5883.9 (3)	-1067 (1)	9182 (1)	17
O(4)	8099 (3)	2181 (5)	8846 (5)	20
C(5)	8245 (5)	2923 (9)	7734 (8)	23
C(6)	9125 (5)	3095 (8)	7908 (8)	20
C(7)	9463 (7)	1819 (10)	8153 (13)	42
C(8)	9506 (6)	3792 (10)	8972 (10)	32
C(9)	9180 (6)	3908 (10)	6669 (10)	31
O(10)	6436 (3)	1853 (5)	7230 (5)	17
C(11)	6227 (6)	1551 (9)	6024 (9)	28
C(12)	5823 (6)	2615 (8)	5041 (8)	22
C(13)	5594 (10)	2198 (14)	3783 (11)	67
C(14)	6367 (8)	3779 (12)	4999 (12)	52
C(15)	5090 (6)	2986 (12)	5222 (10)	38
O(16)	7444 (3)	-104 (5)	7882 (5)	18
C(17)	7812 (5)	-1270 (8)	8304 (8)	19
C(18)	7760 (5)	-1889 (8)	7218 (9)	20
C(19)	8199 (6)	-3120 (8)	7756 (10)	26
C(20)	6911 (6)	-2153 (9)	6505 (9)	29
C(21)	8150 (6)	-1020 (10)	6326 (9)	31
O(22)	6576 (3)	1761 (5)	9540 (5)	15
C(23)	5845 (5)	2391 (8)	9041 (9)	20
C(24)	5969 (5)	3714 (8)	9306 (8)	20
C(25)	5168 (6)	4321 (10)	8671 (10)	34
C(26)	6211 (5)	3693 (9)	10689 (9)	24
C(27)	6572 (7)	4456 (9)	8762 (11)	33
O(28)	7746 (3)	1292 (5)	11960 (5)	16
C(29)	8382 (5)	2196 (8)	11916 (8)	17
C(30)	9147 (5)	1734 (8)	12841 (8)	19
C(31)	9407 (5)	928 (8)	12489 (10)	26
C(32)	9752 (5)	2829 (9)	12840 (9)	26
C(33)	9065 (6)	1323 (11)	14143 (9)	36
O(34)	7416 (3)	-1361 (5)	11800 (5)	15
C(35)	7755 (5)	-2397 (8)	11637 (8)	21
C(36)	8055 (5)	-3331 (8)	12838 (8)	20
C(37)	8739 (6)	-2762 (9)	13767 (9)	29
C(38)	8343 (6)	-4459 (9)	12525 (9)	29
C(39)	7405 (6)	-3786 (9)	13377 (10)	31
N(40)	6252 (4)	375 (6)	11789 (7)	18
C(41)	6222 (6)	-668 (10)	12827 (10)	33

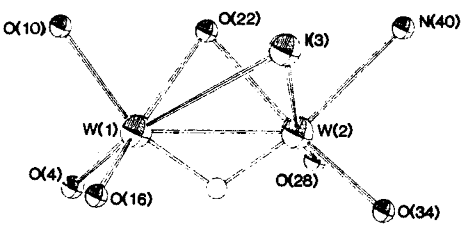

Figure 5. An ORTEP view of the W_2HIO_6N skeleton of the $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ molecule. The hydride ligand, which was not located crystallographically, is represented by an unshaded circle at the centroid of the oxygen atoms O(4), O(16), O(28), and O(34), thereby completing pseudo-octahedral geometry for each tungsten atom.

Table V. Selected Bond Distances (Å) for the $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ Molecule

a	b	distance
W(1)	W(2)	2.4557 (9)
W(1)	I(3)	3.2577 (11)
W(1)	O(4)	1.868 (6)
W(1)	O(10)	1.966 (5)
W(1)	O(16)	1.885 (6)
W(1)	O(22)	2.053 (6)
W(2)	I(3)	2.8944 (10)
W(2)	O(22)	2.052 (5)
W(2)	O(28)	1.914 (5)
W(2)	O(34)	1.894 (5)
W(2)	N(40)	2.254 (7)
O(4)	C(5)	1.451 (11)
O(10)	C(11)	1.425 (11)
O(16)	C(17)	1.414 (10)
O(22)	C(23)	1.446 (10)
O(28)	C(29)	1.437 (10)
O(34)	C(35)	1.417 (10)
N(40)	C(41)	1.473 (12)

Table VI. Selected Bond Angles (deg) for the $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ Molecule

a	b	c	angle
W(2)	W(1)	I(3)	58.895 (22)
W(2)	W(1)	O(4)	108.97 (17)
W(2)	W(1)	O(10)	127.72 (16)
W(2)	W(1)	O(16)	118.87 (17)
W(2)	W(1)	O(22)	53.24 (15)
I(3)	W(1)	O(4)	167.69 (17)
I(3)	W(1)	O(10)	87.10 (17)
I(3)	W(1)	O(16)	83.88 (17)
I(3)	W(1)	O(22)	71.29 (15)
O(4)	W(1)	O(10)	103.35 (24)
O(4)	W(1)	O(16)	101.94 (24)
O(4)	W(1)	O(22)	103.74 (23)
O(10)	W(1)	O(16)	92.25 (23)
O(10)	W(1)	O(22)	80.08 (22)
O(16)	W(1)	O(22)	1549.25 (23)
W(1)	W(2)	O(22)	53.28 (15)
W(1)	W(2)	O(28)	110.87 (17)
W(1)	W(2)	O(34)	124.91 (16)
W(1)	W(2)	N(40)	136.07 (19)
O(22)	W(2)	O(28)	93.18 (22)
O(22)	W(2)	O(34)	166.07 (22)
O(22)	W(2)	N(40)	85.14 (24)
O(28)	W(2)	O(34)	99.77 (23)
O(28)	W(2)	N(40)	81.69 (26)
O(34)	W(2)	N(40)	91.67 (25)
W(1)	I(3)	W(2)	46.589 (22)
W(1)	O(4)	C(5)	120.9 (5)
W(1)	O(10)	C(11)	125.9 (5)
W(1)	O(16)	C(17)	132.4 (5)
W(1)	O(22)	W(2)	73.48 (18)
W(1)	O(22)	C(23)	133.0 (5)
W(2)	O(22)	C(23)	142.5 (5)
W(2)	O(28)	C(29)	132.4 (5)
W(2)	O(34)	C(35)	134.2 (5)
W(2)	N(40)	C(41)	116.7 (6)

5. The hydride ligand, which was not located crystallographically, is represented by an unshaded circle at the centroid of the oxygen atoms O(4), O(16), O(28), and O(34), thereby completing pseudooctahedral geometry for each tunsten atom. The $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ molecule is also seen to be related to the $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$ structure having a terminal amine ligand substitute for a μ-OR ligand that spans the two $(W{=}W)^{8+}$ units and a μ-I in place of a μ-OR spanning the $(W{=}W)^{8+}$ unit.

The W-O distances fall in the expected range for W-OR terminal and W-μ-OR ligands,[11] and again the trans-influence[9] of the hydride ligand is seen to yield a long W-O distance for the terminal W-OR group in the trans-position. Conversely, the terminal W-OR group trans to the μ-I ligand is very short. The W-I distances are very asymmetric, W(1)-I = 3.26 (1) Å vs. W(2)-I = 2.89 (1) Å. Since the bridging iodo ligand is trans to terminal W-OR ligands at each tungsten, this asymmetry presumably reflects an internal charge compensation that the presence of the neutral donor ligand, H_2NMe, at W(2) produces, i.e., the effective oxidation states of W(1) and W(2) are the same if the bridging iodide is mostly associated with W(2) viz W(2)-I → W(1).

NMR Studies. (1) ^1H NMR. The ^1H NMR spectra of $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme and $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8\cdot 2THF$ in toluene-d_8 reveal fluxional molecules showing only one time-averaged OR group at room temperature, but the hydride ligand appears as a sharp singlet at ca. 9 ppm flanked by satellites due to coupling to ^{183}W, $I = ^1/_2$, natural abundance = 14.5%. The relative intensities of the satellites to the central hydride signal indicate the $W_2(\mu\text{-}H)$ moiety is present. The hydride portion of

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(11) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

Table VII. Summary of Crystal Data

empirical formula	$W_2C_{30}H_{71}O_{11}Na$	$W_2C_{31}H_{72}NO_6I$
color of crystal	black	black
crystal dimensions (mm)	0.08 × 0.10 × 0.18	0.12 × 0.11 × 0.11
space group	$P2_1/a$	$P\bar{1}$
cell dimensions		
temp (°C)	−155	−158
a (Å)	24.087 (8)	18.159 (5)
b (Å)	16.540 (5)	10.873 (2)
c (Å)	12.747 (4)	11.599 (3)
α		77.30 (1)
β	125.71 (1)	109.37 (1)
γ		96.55 (2)
Z (molecules/cell)	4	2
volume, Å^3	4123.69	2105.41
calculated density (g/cm^3)	1.608	1.656
wavelength (Å)	0.71069	0.71069
molecular weight	998.57	1049.52
linear absorption coefficient (cm^{-1})	57.395	63.363
detector to sample distance (cm)	22.5	22.5
sample to source distance (cm)	23.5	23.5
take-off angle (deg)	2.0	2.0
av ω scan width at half-height (deg)	0.25	0.25
scan speed (deg/min)	4.0	4.0
scan width (deg + dispersion)	2.0	2.0
individual background (s)	6	5
aperture size (mm)	3.0 <<tmc 4.0	3.0 × 4.0
2θ range (deg)	6–45	6–45
total no. of reflections collected	6422	6034
no. of unique intensties	5418	5520
no. of $F > 3.00\sigma(F)$	4151	4684
$R(F)$	0.0396	0.0321
$R_w(F)$	0.0414	0.0339
goodness of fit for the last cycle	0.915	0.744
maximum δ/σ for last cycle	0.05	0.05

the spectrum is temperature-independent but at low temperatures alkoxide scrambling becomes slow on the NMR time scale. The low-temperature limiting spectra indicate the presence of a molecular plane of symmetry and are consistent with expectations based on the molecular structure of $NaW_2(H)(O\text{-}i\text{-}Pr)_8$·diglyme found in the solid state. See Figure 6.

The ^1H NMR spectrum for $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ recorded in toluene-d_8 is also consistent with the structure found in the solid state which has no elements of symmetry. At low temperature there are six well-resolved AB quartets for the methylene protons of the six different $OCH_2\text{-}t\text{-}Bu$ ligands. At room temperature there is evidence for the onset of some dynamic process involving alkoxide group exchange but this does not involve reversible dissociation of the H_2NMe ligand since its resonances remain unchanged. Note that the NH_2 protons are diastereotopic. Also, the hydride signal shows coupling to two different ^{183}W nuclei, $J_{^{183}W\text{-}^1H}$ = 95 and 148 Hz. See Figure 7. These very different coupling constants presumably reflect an asymmetric hydride bridge and the different amount of W 6s orbital contribution used in the W–H bond involving the two tungsten atoms. Note W(2)–H is trans to H_2NMe, and W(1)–H is trans to a OR ligand.

(2) ^{23}Na NMR. The ^{23}Na NMR signals of $NaW_2(H)(O\text{-}i\text{-}Pr)_8$·diglyme and $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$·2THF in toluene-$d_8$ show single resonances with line widths of ca. 400 and 1000 Hz, respectively. These line widths are comparable to signals previously seen for Na^+ ions complexed to crown-ethers or compounds in which the anion effectively competes with the solvent in the Na^+ coordination sphere.[12] These broad line widths may be contrasted with line widths of ca. 10 and 40 Hz for NaCl in H_2O and $NaBPh_4$ in THF, respectively. The ^{23}Na line width observed for $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$·2THF dissolved in THF is ca. 250 Hz, down from 1000 Hz in toluene. The broad ^{23}Na signals are entirely consistent with the view that these $NaW_2H(OR)_8$ compounds may be regarded as mixed-metal alkoxides or tight ion pairs creating an asymmetric environment about the Na atom. When a sample of $NaW_2H(O\text{-}i\text{-}Pr)_8$ and $NaO\text{-}i\text{-}Pr$ was dissolved in THF, two ^{23}Na signals were observed corresponding to the signals associated with the two isopropoxide compounds. Clearly Na ion exchange is slow on the NMR time scale if it occurs at all. Attempts at cation exchange employing PPN^+ and R_4N^+ were unsuccessful.

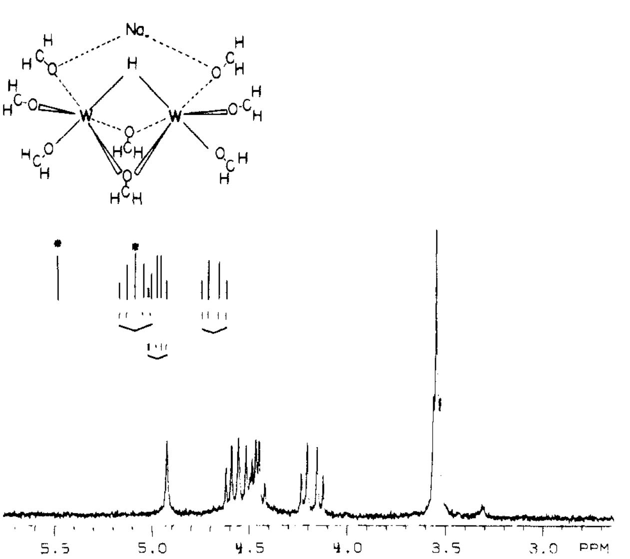

Figure 6. The methylene region of the low-temperature (−45 °C) limiting ^1H NMR spectrum (in toluene-d_8) of $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$·2THF. A mirror plane bisecting the W–W double bond, containing the Na atom and the bridging atoms, renders the terminal alkoxides pairwise equivalent with diastereotopic methylene protons. This gives rise to three AB quartets. The bridging neopentoxides are inequivalent but not diastereotopic, therefore two singlets are observed. The latter are denoted by an asterisk in the line spectrum shown in the inset which represents the observed spectrum in the region 4.0 to 5.0 ppm.

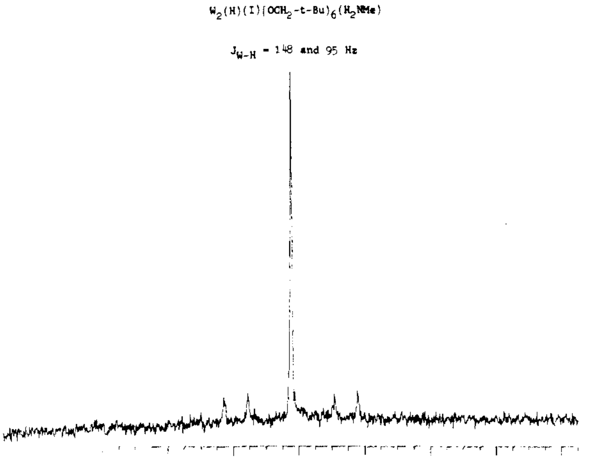

Figure 7. The hydride resonance in the ^1H NMR spectrum (in toluene-d_8) of $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ showing the coupling to two inequivalent ^{183}W nuclei.

Mechanistic Considerations Concerning the Oxidative-Addition of RO–H to the $(W{\equiv}W)^{6+}$ Center. Oxidative-addition of HX molecules (X = a halide or carboxylate) to quadruple bonds between molybdenum[13,14] and tungsten atoms[15] has been known

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[12] Lazlo, P. *Angew. Chem., Int. Ed. Engl.* **19788**, *17*, 254.

[13] Bino, A.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 332.

[14] Bino, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1979**, *101*, 4150.

[15] Cotton, F. A.; Mott, G. N. *J. Am. Chem. Soc.* **1982**, *104*, 5978.

for some years. Addition of HCl and HI across the Mo–Mo triple bond in $Cp_2Mo_2(CO)_4$ has also been noted.[16] There has only been one attempt at a mechanistic study of this type of reaction and that is the work of Haim and Miller,[17] who examined the kinetics of the reaction shown in eq 8.

$$Mo_2Cl_8^{4-}(\text{M≣M}) + HCl \rightarrow Cl_3Mo(\mu\text{-H})(\mu\text{-Cl})_2MoCl_3^{3-} + Cl^- \quad (8)$$

The reaction shown in eq 8 occurs with concentrated HCl (6–12 M was used in the study) which contrasts with the relatively mild acid, *i*-PrOH, which adds across the $(W{\equiv}W)^{6+}$ unit in the formation of the hydrido-containing $(W{=}W)^{8+}$ alkoxides in this study.

From our studies of the reaction between $W_2(NMe_2)_6$ and *i*-PrOH in hexane or toluene solutions, we find that the liberated dimethylamine plays a critical role in the oxidative-addition process. Firstly, it is involved as a ligand in the initially formed alcoholysis product $W_2(O\text{-}i\text{-Pr})_6(HNMe_2)_2$. Secondly, the reaction still requires further base ($HNMe_2$, NMe_3, NEt_3, or proton sponge) which leads us to suggest that the N–H bond of a coordinated amine is deprotonated by the excess base. This would generate an amide ligand, NMe_2^-, capable of acting as a four-electron donor and promoting bridge formation, eq 9,

$$W_2(O\text{-}i\text{-Pr})_6(HNMe_2)_2 + B\!: \xrightarrow[\text{hexane}/i\text{-PrOH}]{25\ ^\circ\text{C}} BH^+[W_2(O\text{-}i\text{-Pr})_6(NMe_2)L_2]^- \quad (9)$$

where L may be either $HNMe_2$ or *i*-PrOH.

This step is then followed by oxidative-addition of either an N–H or O–H bond to the bridged d^3–d^3 dimer with subsequent rapid alcoholysis of the amide ligand and proton transfer from the acid BH^+. This can be depicted by the sequence shown in eq 10.

$$\text{(i)}\quad W_2(O\text{-}i\text{-Pr})_6(NMe_2)(HO\text{-}i\text{-Pr})_2^- \rightarrow W_2(H)(O\text{-}i\text{-Pr})_7(NMe_2)^- + HO\text{-}i\text{-Pr}$$

$$\text{(ii)}\quad W_2(H)(O\text{-}i\text{-Pr})_7(NMe_2)^- + HO\text{-}i\text{-Pr} \rightarrow W_2(H)(O\text{-}i\text{-Pr})_8^- + HNMe_2$$

$$\text{(iii)}\quad W_2(H)(O\text{-}i\text{-Pr})_8^- + BH^+ \rightarrow W_2(H)(O\text{-}i\text{-Pr})_7(HO\text{-}i\text{-Pr}) + B \quad (10)$$

The alcoholate $W_2(H)(O\text{-}i\text{-Pr})_7(HO\text{-}i\text{-Pr})$ formed in step iii of eq 10 would be in equilibrium with $W_4(H)_2(O\text{-}i\text{-Pr})_{14}$ in the presence of alcohol solvent.

A number of the steps and intermediates in this proposed reaction sequence find parallels in the reactions leading to $W_4(H)_2(O\text{-}i\text{-Pr})_{14}$ starting from $W_2(O\text{-}t\text{-Bu})_6$, namely the reactions shown in eq 3, 4, and 5. Also it should be noted that Rothwell and co-workers[18] in their study of the reactions between $Mo_2(NMe_2)_6$ and substituted phenols have isolated and structurally characterized an amine salt, eq 11.

$$Mo_2(NMe_2)_6 + ArOH \rightarrow [Mo_2(OAr)_7(HNMe_2)_2]^- Me_2NH_2^+ \quad (11)$$

In reaction 11 an unbridged d^3–d^3 dimer is converted to a bridged d^3–d^3 dimer, of the form $X_3M(\mu\text{-}X)_3MX_3$. This is our proposed key step in the reaction sequence, eq 9, which precedes the oxidative-addition step.

Why should oxidative-addition of an O–H (or N–H) bond proceed via a bridged d^3–d^3 dimer relative to an unbridged dimer. We believe that a simple explanation can be gleaned from the orbital energetics of the d^3–d^3 systems. In the unbridged d^3–d^3 dimers of formula $X_3M{\equiv}MX_3$ or $LX_3M{\equiv}MX_3L$, the M–M triple bond of configuration $\sigma^2\pi^4$ has a large HOMO–LUMO gap and the M–M bonds are relatively stable. The first and second IP's from π and σ, M–M bonds, respectively, occur at ca. 6 and 7 eV.[19,20] In the bridged d^3–d^3 dimers of formula $X_3M(\mu\text{-}X)_3MX_3$ the metal–metal bonding is weaker, in part due to the lengthening of the M–M distance which accompanies bridge formation and also because, now in the bridge form, there is extensive mixing of M–M and M–L bonding orbitals. In particular π-donor ligands weaken and raise the energy of the M–M bonding π orbitals and many of the dimolybdenum bridged d^3–d^3 dimers are paramagnetic.[18] Thus we believe that the energy of activation for oxidative-addition is reduced by the conversion of the unbridged d^3–d^3 dimer to the bridged form. Thermodynamically the oxidative-addition is favored for W–W multiple bonds relative to Mo–Mo multiple bonds and this is now a commonly accepted aspect of multiple M–M bond chemistry.[21,22] This surely underscores why alcoholysis reactions involving $W_2(NMe_2)_6$ commonly lead to oxidation to W(4+), whereas the analogous reactions involving $Mo_2(NMe_2)_6$ retain oxidation state 3+ for molybdenum. The reader may note that the present reaction, oxidative-addition to a dinuclear metal center, is just the microscopic reverse of reductive elimination from a dinuclear metal center, a reaction in name which has caught considerable attention with respect to mechanistic detail.[23–27]

Concluding Remarks. Our further studies of the reaction between $W_2(NMe_2)_6$ and *i*-PrOH have revealed that the oxidative-addition of *i*-PrOH to the $(W{\equiv}W)^{6+}$ center is base promoted. A simple protonation of the $M{\equiv}M$ bond is clearly not operative, and stronger acids such as $(CF_3)_2CHOH$ and *t*-BuCOOH have been shown to react with $W_2(O\text{-}t\text{-Bu})_6$ to give only products of *t*-BuO substitution.[28] That is not to say, however, that protonation of the $M{\equiv}M$ is not a possible pathway for oxidative-addition to the $(W{\equiv}W)^{6+}$ center in other reactions. One can envisage a mechanistic parallel with additions to alkynes which may be promoted by either nucleophilic or electrophilic attack.[29] Further studies aimed at converting the unbridged to bridged d^3–d^3 dimers and investigations of the reactivity of the latter are clearly warranted. The high-yield synthesis of the $NaW_2(H)(OR)_8$ compounds (R = *i*-Pr and *t*-$BuCH_2$) by the reaction shown in eq 3 provides entry into a new class of compounds which by analogy with mixed metal main group hydrido alkoxides, e.g.,[30] $NaAl(H)(OR)_3$, may find use as reagents in organic syntheses. Further studies on the reactivities of the new compounds $NaW_2(H)(OR)_8$ are in progress.

Experimental Section

Reagents and General Techniques. General procedures and the preparations of $W_2(NMe_2)_6$, $W_2(O\text{-}i\text{-Pr})_6(HNMe_2)_2$, $W_2(OCH_2\text{-}t\text{-Bu})_6(HNMe_2)_2$, $W_2(O\text{-}t\text{-Bu})_6$, and $W_4(H)_2(O\text{-}i\text{-Pr})_{14}$ have been previously described.[3,5] Dry and oxygen-free solvents were used in all experiments. All manipulations were carried out under inert atmospheres with standard Schlenk techniques.

^1H NMR spectra were recorded on a Nicolet NT-360 360-MHz spectrometer in toluene-d_8, benzene-d_6, or dioxane-d_8. Chemical shifts are reported relative to Me_4Si calculated from the chemical shifts of the residual protons of the solvent employed. ^{23}Na NMR spectra were

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recorded on the Nicolet NT-360 spectrometer at 95.5 MHz, with a saturated solution of NaCl in H_2O as an external standard.

Elemental analyses were performed by Bernhardt Analytical Laboratories of West Germany.

Reaction of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ with *i*-PrOH. $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (200 mg, 0.25 mmol) was dissolved in hexane (5 mL). *i*-PrOH (5 mL) was introduced via a syringe. The resulting brown solution was stirred at ambient temperature for ca. 8 h after which time the solvent was removed in vacuo. The brown-black solids thus obtained showed no evidence of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ by ^1H NMR spectroscopy but rather a complex mixture containing $[W(O\text{-}i\text{-}Pr)_3]_n$ (discussed below).

Reaction of $W_2(O\text{-}t\text{-}Bu)_6$ with *i*-PrOH. $W_2(O\text{-}t\text{-}Bu)_6$ (250 mg, 0.31 mmol) was dissolved in hexane (10 mL). *i*-PrOH (5 mL) was added. An immediate color change from deep red to brown was observed. After the solution was stirred at ambient temperature for ca. 8 h, the solvent was removed in vacuo. Again, the brown-black solids obtained showed no evidence of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ by ^1H NMR spectroscopy and contained $[W(O\text{-}i\text{-}Pr)_3]_n$.

Reactions of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ with *i*-PrOH in the Presence of Added Amine. $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (250 mg, 0.31 mmol) was reacted with an excess of *i*-PrOH (5 mL) in the presence of 2–4 equiv of various amines in hexane (5 mL) at ambient temperature for ca. 12 h. The solvent was then removed in vacuo, and the brown solids were taken up in hexane and cooled to 0 °C. Crystalline $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ was isolated in 30–40% yield. $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ was easily identified by its distinctive ^1H NMR spectrum.[3] The following amines have been employed: $HNMe_2$, NMe_3 (passed through a drying tube and introduced to the reaction mixture from a calibrated vacuum manifold), NEt_3, pyridine, and proton sponge (1,8-bis(dimethylamino)naphthalene, purchased from Aldrich, used without further purification).

Reactions of $W_2(O\text{-}t\text{-}Bu)_6$ with *i*-PrOH in the Presence of Added Amine. (1) Formation of $W_2(O\text{-}i\text{-}Pr)_6L_2$ Compounds. $W_2(O\text{-}t\text{-}Bu)_6$ (250 mg, 0.31 mmol) was dissolved in hexane (10 mL). $HNMe_2$ (6.5 equiv; 2.0 mmol) was condensed in via a calibrated vacuum manifold, followed by the addition of *i*-PrOH (5 mL) at 0 °C. The color of the solution changed immediately from deep red to brown. From this reaction mixture at 0 °C, brown cubes of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were isolated in ca. 60% yield. By ^1H NMR spectroscopy, the mother liquor was shown to contain both $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and $[W(O\text{-}i\text{-}Pr)_3]_n$.

Similarly, black crystalline $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ was obtained from the reaction of $W_2(O\text{-}t\text{-}Bu)_6$ (200 mg, 0.25 mmol) in hexane (10 mL) and pyridine (1–2 mL) with *i*-PrOH (5 mL) at 0 °C, again in ca. 60% yield. $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and $[W(O\text{-}i\text{-}Pr)_3]_n$ were identified in the filtrate by ^1H NMR spectroscopy.

(2) Formation of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$. $W_2(O\text{-}t\text{-}Bu)_6$ (250 mg, 0.31 mmol) was dissolved in hexane (10 mL). HNR_2 (6 equiv) ($HNEt_2$ was added via a syringe; $HNMe_2$ was introduced from a vacuum manifold) was added, followed by *i*-PrOH (5 mL). The solution was stirred at ambient temperature for ca. 12 h. Solvent was removed in vacuo. Crystallization from hexane yielded $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ in ca. 30% yield. Again, ^1H NMR spectroscopy showed that the mother liquor contained $[W(O\text{-}i\text{-}Pr)_3]_n$ as well as $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$.

(3) Formation and Characterization of $[W(O\text{-}i\text{-}Pr)_3]_n$. $W_2(O\text{-}t\text{-}Bu)_6$ (250 mg, 0.31 mmol) was dissolved in hexane (10 mL). A tertiary amine (6 equiv) (NMe_3, NEt_3, or proton sponge) was introduced, followed by the addition of *i*-PrOH (5 mL). After ca. 12 h at ambient temperature (or at 0 °C), the solvent was removed in vacuo, and the solids were dissolved in hexane. Long black rods, $[W(O\text{-}i\text{-}Pr)_3]_n$, were isolated in ca. 60% yield (based on tungsten). ^1H NMR at 360 MHz, 22 °C in toluene-d_8: δ ($OCHMe_2$) 1.2–1.6 (6 H, br, overlapping resonances); δ ($OCHMe_2$) 4.2–6.1 (1 H, 3 br resonances and one sharp septet). Mass spectrum, a base peak at 722 *m/e* was observed and can be attributed to $[W_2(O\text{-}i\text{-}Pr)_6]^+$. Anal. Calcd for $Wo_3C_9H_{21}$: C, 29.9; H, 5.9; N, 0.0. Found: C, 29.78; H, 5.78; N, 0.12.

Reaction of $[W(O\text{-}i\text{-}Pr)_3]_n$ with *i*-PrOH and HNR_2. $[W(O\text{-}i\text{-}Pr)_3]_n$ (250 mg, 0.7 mmol of tungsten) was reacted with an excess of HNR_2 (10 equiv) ($HNMe_2$ was condensed in from a vacuum manifold, and $HNEt_2$ was added via a syringe) and *i*-PrOH (5 mL) in hexane (5 mL). After the solution was stirred at ambient temperature for ca. 12 h, the solvent was removed in vacuo. The brown solids were dissolved in hexane and cooled to 0 °C. Crystalline $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ was isolated in <30% yield and identified by ^1H NMR spectroscopy.

Syntheses and Characterization of $NaW_2(H)(OR)_8$. $NaW_2(H)(O\text{-}i\text{-}Pr)_8$. (1) $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (200 mg, 0.25 mmol) was reacted with 1 equiv of NaO-*i*-Pr (20 mg, 0.24 mmol) and *i*-PrOH (5 mL) in hexane (10 mL). After the solution was stirred for ca. 12 h at ambient temperature, the solvent was removed in vacuo, and the resulting hydrocarbon-insoluble yellow powder (formed in >50% yield) was washed with hexane. The yellow compound, formulated as $[NaW_2(H)(O\text{-}i\text{-}Pr)_8]_x$, is soluble in *i*-PrOH. THF, and dioxane and is believed to be a polymeric species. ^1H NMR at 360 MHz, 22 °C in dioxane-d_8: δ ($OCHMe_2$) 1.22 (48 H, br); δ ($OCHMe_2$) 4.79 (8 H, br); δ ($W_2\mu\text{-}H$) 8.78 (1 H, s with satellites, $J_{^{183}W-^1H}$ = 111 Hz). ^{32}Na NMR at 95.5 MHz, 22 °C in THF (NaCl in H_2O as external standard): δ ($NaW_2(H)(O\text{-}i\text{-}Pr)_8$) 0 ($\nu_{1/2}$ = 200 Hz). ^{23}Na NMR of a solution of $NaW_2(H)(O\text{-}i\text{-}Pr)_8$ and NaO-*i*-Pr in THF: δ ($NaW_2(H)(O\text{-}i\text{-}Pr)_8$) 0; δ (NaO-*i*-Pr) 13.

(2) $W_2(O\text{-}t\text{-}Bu)_6$ (100 mg, 0.12 mmol), 1 equiv of NaO-*i*-Pr (10 mg, 0.12 mmol) and excess *i*-PrOH (4 mL) were reacted in hexane (8 mL) for ca. 12 h at ambient temperature. $[NaW_2(H)(O\text{-}i\text{-}Pr)_8]_x$ was isolated in <30% yield on removal of solvent followed by washing with hexane.

(3) $[W(O\text{-}i\text{-}Pr)_3]_n$ (200 mg, 0.55 mmol of W) was reacted with NaO-*i*-Pr (25 mg, 0.30 mmol) and *i*-PrOH (5 mL) in hexane (10 mL) at ambient temperature for ca. 12 h. After removal of solvent and washing with hexane, $[NaW_2(H)(O\text{-}i\text{-}Pr)_8]_x$ was isolated in ca. 20% yield.

$NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme. $[NaW_2(H)(O\text{-}i\text{-}Pr)_8]_x$ (100 mg, 0.12 mmol) was suspended in hexane (10 mL). An excess of diglyme (0.1 mL, 0.7 mmol) was introduced. The suspension was stirred for 1–2 h at ambient temperature until all the yellow solid had gone into solution. On reducing the volume and cooling to 0 °C, brown crystalline $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme was isolated (50 mg, 0.05 mmol, 42% yield). ^1H NMR at 360 MHz, 22 °C in toluene-d_8: δ ($OCHMe_2$) 1.55 (48 H, d); δ ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$) 3.1–3.2 (14 H, s and overlapping multiplets); δ ($OCHMe_2$) 5.18 (8 H, septet); δ ($W_2\mu\text{-}H$) 9.04 (1 H, s, with satellites, $J_{^{183}W-^1H}$ = 112 Hz). ^{23}Na NMR at 95.5 MHz, 22 °C in toluene-d_8: δ ($NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme) −4 ($\nu_{1/2}$ = 400 Hz). Anal. Calcd for $NaW_2O_{11}C_{30}H_{71}$: C, 36.08; H, 7.17. Found: C, 35.83; H, 7.01.

$NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$. (1) $W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2$ (200 mg, 0.20 mmol) was reacted with $NaOCH_2\text{-}t\text{-}Bu$ (20 mg, 0.18 mmol) and $t\text{-}BuCH_2OH$ (7 mmol) in hexane (5 mL). The solution was stirred for ca. 12 h at ambient temperature, after which time the solvent was removed in vacuo, and the resulting green solids were washed with hexane. The green compound, obtained in high yield (>50%), was formulated as $[NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8]_x$ and characterized as a THF adduct (see below).

(2) $W_2(O\text{-}t\text{-}Bu)_6$ (250 mg, 0.31 mmol) was reacted with NaO-*t*-Bu (30 mg, 0.31 mmol) and $t\text{-}BuCH_2OH$ (18 mL of 1.1 M $t\text{-}BuCH_2OH$ in toluene) at ambient temperature for ca. 12 h. $[NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8]_x$ was isolated in ca. 30% yield after removal of solvent and washing with hexane. ^{23}Na NMR at 95.5 MHz, 22 °C in THF: δ ($NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$) −5 ($\nu_{1/2}$ = 250 Hz).

$NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8\cdot 2THF$. $[NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8]_x$ (100 mg, 0.09 mmol) was suspended in hexane (5 mL). An excess of THF (2 mL) was added. The volume of the solution was reduced, followed by cooling to 0 °C. Green, crystalline $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8\cdot 2THF$ was isolated in ca. 40% yield. ^1H NMR at 360 MHz, 22 °C in toluene-d_8: δ (OCH_2CMe_3) 1.1 and 1.3 (72 H, s, br); δ (THF) 2.45 and 3.55 (16 H, multiplets); δ (OCH_2CMe_3) 4.35 (16 H, s, br); δ ($W_2\mu\text{-}H$) 9.19 (1 H, s, with satellites, $J_{^{183}W-^1H}$ = 110 Hz). ^1H NMR at 360 MHz, −45 °C in toluene-d_8: δ (OCH_2CMe_3) 0.9–1.5 (72 H, overlapping singlets); δ (THF) 1.4 and 3.6 (16 H, multiplets); δ (OCH_2CMe_3) 4.17 (4 H, ab quartet), 4.45 (4 H, ab quartet), 4.54 (4 H, ab quartet), 4.55 (2 H, s), 4.92 (2 H, s); δ ($W_2\mu\text{-}H$) 9.08 (1 H, s, with satellites). ^{23}Na NMR at 95.5 MHz, 22 °C in toluene-d_8: δ ($NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8\cdot 2THF$) 0 ($\nu_{1/2}$ = 1000 Hz). Anal. Calcd for $NaW_2O_{10}C_{48}H_{105}$: C, 46.75; H, 8.60. Found: C, 44.19; H, 8.04 (sample had lost THF; calcd for $NaW_2O_8C_{40}H_{89}$: C, 44.11; H, 8.25).

Attempted Syntheses of Other $NaW_2(H)(OR)_8$. (1) R = *t*-Bu. $W_2(O\text{-}t\text{-}Bu)_6$ (200 mg, 0.25 mmol) and NaO-*t*-Bu (20 mg, 0.21 mmol) were dissolved in *t*-BuOH/benzene azeotrope (15 mL) and stirred at ambient temperature for 18 h. Removal of the solvent in vacuo and addition of hexane (10 mL) left unreacted NaO-*t*-Bu only. The resulting red hexane solution contained only unreacted $W_2(O\text{-}t\text{-}Bu)_6$ by ^1H NMR spectroscopy.

(2) R = *p*-C_6H_5Me. $W_2(O\text{-}t\text{-}Bu)_6$ (100 mg, 0.12 mmol) and NaO-*t*-Bu (10 mg, 0.10 mmol) were dissolved in THF (10 mL). *p*-Cresol (0.62 M) in toluene (4 mL) was added, and the solution was stirred at ambient temperature for 15 h. Removal of the solvent in vacuo followed by washing with hexane yielded an oily brown solid (slightly soluble in hexane). ^1H NMR spectroscopy showed no evidence of a hydride-containing species, although complete exchange of alkoxides (OPhMe for O-*t*-Bu) had occurred.

(3) R = Et. $W_2(O\text{-}t\text{-}Bu)_6$ (200 mg, 0.25 mmol) was reacted with NaO-*t*-Bu (20 mg, 0.21 mmol) and EtOH (5 mL) in hexane (10 mL). An immediate color change from red to blue was observed. After the mixture was stirred at ambient temperature for ca. 12 h, the solvent was removed in vacuo, and the brown-black solids washed with hexane. No hydride-containing species has been observed in this reaction. (The brown-black insoluble solids result from the decomposition of the unstable blue complex formed by the reaction of $W_2(O\text{-}t\text{-}Bu)_6$ with EtOH. The reaction proceeds similarly without the addition of NaO-*t*-Bu.)

(4) **R = Et.** $NaW_2(H)(O\text{-}i\text{-}Pr)_8$ (100 mg, 0.12 mmol) reacted immediately with neat EtOH (10 mL) to yield quantitatively, on removal of EtOH in vacuo, a green solid, formulated as $[NaW_2(H)(OEt)_8]_x$. This polymeric complex does not form a stable, hydrocarbon-soluble adduct with diglyme or THF. ^1H NMR at 360 MHz, 22 °C in dioxane-d_8: δ (OCH_2CH_3) 1.1–1.4 (24 H, overlapping triplets, broad); δ (OCH_2CH_3) 4.4 (16 H, q, br); δ $(W_2\mu\text{-}H)$ 8.86 (1 H, s, with satellites, $J_{^{183}W-^1H} = 122$ Hz). ^{23}Na NMR at 95.5 MHz, 22 °C in THF: δ $(NaW_2(H)(OEt)_8)$ 0 ($\nu_{1/2} = 350$ Hz).

Attempted Cation Exchange on $NaW_2(H)(O\text{-}i\text{-}Pr)_8$. $NaW_2(H)(O\text{-}i\text{-}Pr)_8$ (50 mg, 0.06 mmol) and 1 equiv of X^+Cl^- ($X^+ = PPN^+$ and NMe_4^+) were dissolved in THF (10 mL). After the mixture was stirred at ambient temperature for 12 h, unreacted $NaW_2(H)(O\text{-}i\text{-}Pr)_8$ was recovered.

Reactions of $NaW_2(H)(OR)_8$ (R = *i*-Pr, CH_2-*t*-Bu) with Protonated Amines. (1) $NaW_2(H)(O\text{-}i\text{-}Pr)_8$ (200 mg, 0.23 mmol) was reacted with $H_2NMe_2^+X^-$ (1 equiv) ($X^- = Cl^-$ and I^-) in *i*-PrOH (5 mL) and hexane (10 mL) for about 2 h at ambient temperature. Solvent was removed in vacuo, hexane (10 mL) was added, and NaX was removed by filtration. Crystalline $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ was obtained by cooling the hexane solution to 0 °C. The filtrate contained mostly $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ by ^1H NMR spectroscopy, thus the yield is nearly quantitative.

(2) $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$ (200 mg, 0.18 mmol) was reacted with $H_2NMe_2^+Cl^-$ (65 mg, 0.38 mmol) in 1.0 M *t*-$BuCH_2OH$ in toluene (10 mL) at ambient temperature for ca. 8 h. Solvent was removed in vacuo, and the green-brown solid was dissolved in hexane and cooled to 0 °C. No pure crystalline compounds were isolated, but an unstable, fluxional complex was observed in low yield, believed to be analogous to $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$. ^1H NMR at 360 MHz, 22 °C in toluene-d_8: δ (OCH_2CMe_3) 1.05 and 1.10 (singlets); δ (OCH_2CMe_3) 4.65 (s); and a small singlet at δ 8.72 (probably a hydride but no ^{183}W satellites were observed).

The major product of this reaction, thought to be $W_2(H)(Cl)(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)$, due to the observation of coordinated $HNMe_2$ (δ 2.25 (d)) and a singlet at δ 9.3 in the ^1H NMR spectrum, was also unstable and was not isolated in pure form.

(3) $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$ (200 mg, 0.18 mmol) was reacted with $H_3NMe^+I^-$ (60 mg, 0.38 mmol) in THF (20 mL) at ambient temperature for ca. 8 h. THF was removed in vacuo, hexane (20 mL) was added, and NaI was removed by filtration. On cooling the green solution to 0 °C, crystalline $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ was obtained in >50% yield. ^1H NMR at 360 MHz, 22 °C in toluene-d_8: δ (OCH_2CMe_3) 1.0 (27 H, s); 1.05 (9 H, s) and 1.5 (18 H, s); δ (H_2NMe) 2.2 (3 H, t); δ (H_2NMe) 2.6 (1 H, br) and 2.8 (1 H, br); δ (OCH_2CMe_3) 3.4 (1 H, d), 4.5 (6 H, ab quartet, br), 4.85 (2 H, d), 5.4 (1 H, d) and 5.5 (2 H, d); δ $(W_2\mu\text{-}H)$ 9.22 (1 H, s, with 2 sets of satellites, $J_{^{183}W-^1H} = 148$ Hz, $J_{^{183}W-^1H} = 95$ Hz). ^1H NMR at 360 MHz, −45 °C in toluene-d_8: δ (OCH_2CMe_3) 0.98 (9 H, s), 1.02 (9 H, s), 1.05 (9 H, s), 1.12 (9 H, s), 1.17 (9 H, s), 1.23 (9 H, s); δ (H_2NMe) buried under protio impurities of toluene-d_8; δ (H_2NMe) 2.5 (1 H, br) and 2.7 (1 H, br); δ (OCH_2CMe_3) 3.35 (1 H, d), 4.2 (2 H, ab quartet), 4.4 (2 H, ab quartet), 4.6 (1 H, d), 4.65 (1 H, d), 4.9 (1 H, d), 5.05 (2 H, ab quartet), 5.45 (1 H, d) and 5.7 (1 H, d); δ $(W_2\mu\text{-}H)$ 9.4 (1 H, s, satellites could not be observed, signal-to-noise not high enough due to solubility problems at this temperature). Anal. Calcd for $W_2O_6N_1I_1C_{31}H_{72}$: C, 35.47; H, 6.93; N, 1.33. Found: C, 35.31; H, 6.78; N, 1.32.

Reaction of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ with 2NaO-*i*-Pr. $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ (50 mg, 0.03 mmol) was reacted with 2 equiv of NaO-*i*-Pr (5 mg, 0.06 mmol) in *i*-PrOH (10 mL) and hexane (10 mL) at ambient temperature for ca. 8 h. Solvent was removed in vacuo. The yellow-orange solids were suspended in hexane (10 mL), and diglyme (0.25 mL) was added. After several hours at ambient temperature, the volume was reduced and the solution cooled to 0 °C. $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme was isolated in greater than 50% yield and identified by ^1H NMR spectroscopy.

Crystallographic Studies. General operating procedures and listings of programs have been given previously.[31]

$NaW_2H(O\text{-}i\text{-}Pr)_8\cdot$diglyme. A well-formed parallelogram shaped crystal was cleaved from a large crystal and transferred to the goniostate with inert atmosphere handling techniques. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and extinctions corresponding to space group $P2_1/a$ (alternate setting of $P2_1/c$).

Data were collected at −155 °C and the structure solved by Patterson techniques. All non-hydrogen atoms were readily located, and most hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen contributors. ψ scans indicated an absorption correction was necessary, and the data were thus corrected before proceeding. Close examination of a difference Fourier phased on the corrected data allowed location of nearly all hydrogen atoms. Attempts to locate the hydride between the two metals, however, were unsuccessful. For this reason all hydrogens were included in the final cycles in fixed, idealized positions. The hydrogen atoms shown in the bridging position in the figures was obtained by locating the centroid of the four O atoms located "above" the W–W bond.

A final difference Fourier was essentially featureless, with numerous peaks of density 0.4–0.7 e/Å^3 located throughout the cell.

$W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$. A small, nearly equidimensional fragment of maximum dimension 0.12 mm was cleaved from a larger crystal and transferred to the goniostat with inert gas techniques. The sample was then cooled to −158 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, leading to the assignment of a triclinic space group. Subsequent solution and refinement confirmed the centrosymmetric space group $P\bar{1}$.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. Because of the uneven faces of the cleaved crystal, no absorption correction was made. All hydrogen atoms except the hydride were located and refined. While there were several peaks in positions which were chemically reasonable for the hydride, numerous other peaks of similar magnitude in the vicinity indicated that refinement of any one peak would be unjustified. A final difference Fourier was essentially featureless, with one peak of 0.92 e/Å^3 located near W(1) and all other peaks less than 0.42 e/Å^3.

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Registry No. $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$, 84028-39-7; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; $[W(O\text{-}i\text{-}Pr)_3]_n$, 70160-64-4; $W_2(NMe_2)_6$, 54935-70-5; $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$, 76187-98-9; $W_2(O\text{-}i\text{-}Pr)_6(py)_2$, 70178-75-5; W, 7440-33-7; $NaW_2(H)(O\text{-}i\text{-}Pr)_8$, 99416-61-2; $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme, 99439-44-8; $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8$, 99398-71-7; $W_2(OCH_2\text{-}t\text{-}Bu)_6(NHMe_2)_2$, 83437-02-9; $NaW_2(H)(OCH_2\text{-}t\text{-}Bu)_8\cdot 2THF$, 99398-73-9; NaO-*t*-Bu, 865-48-5; EtOH, 64-17-5; $H_2NMe_2^+Cl^-$, 506-59-2; $H_2NMe_2^+I^-$, 51066-74-1; $W_2(H)(Cl)(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)$, 99416-62-3; $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$, 99398-74-0; $NaW_2(H)(OEt)_8$, 99398-75-1; NaO-*i*-Pr, 683-60-3; $H_3NMe^+I^-$, 14965-49-2.

Supplementary Material Available: Anisotropic thermal parameters, complete listings of bond distances and angles, VERSORT drawings and stereoviews, and listings of F_o and F_c for $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme and $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$ (71 pages). For ordering information see any current masthead page. The complete structure reports are available in microfische form only from the Indiana University Library at a cost of $2.50 per copy. Request Report No. 84028 for $NaW_2(H)(O\text{-}i\text{-}Pr)_8\cdot$diglyme and No. 84077 for $W_2(H)(I)(OCH_2\text{-}t\text{-}Bu)_6(H_2NMe)$.

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