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# Polynuclear Metal Hydrido Alkoxides.[1] Reactions of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ and $W_2(H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ with Carbon−Carbon, Carbon−Oxygen, and Carbon−Nitrogen Multiple Bonds

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**Abstract:** Reactions between the compounds $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$ and $W_2(H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ and olefins, alkynes, allene, 1,3-butadiene, ketones, and nitriles have been studied. Of the olefins, only ethene forms a kinetically persistent compound, and $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ has been fully characterized. Other α-olefins are slowly isomerized to internal olefins, but, in the presence of added hydrogen, hydrogenolysis to give the alkane is kinetically preferred. Reactions employing allene and/or 1,3-butadiene are more complex as a result of ligand scrambling, and only the compound $W_2(O\text{-}c\text{-}C_5H_9)_8(\mu\text{-}CH_2CCH_2)$ has been fully characterized. With aldehydes and ketones, insertion into the metal hydride generally proceeds to give alkoxide ligands, and the complex $W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$ derived from the reaction involving $W_2(H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ and cyclopentanone has been fully characterized. With benzophenone, an adduct is formed, which in the solid state and in solution is believed to have a terminal hydride and is formulated as $W_2(H)(OR)_7(\eta^2\text{-}OCPh_2)$, an analogue of the $W_2(\eta^1\text{-}C_2H_5)(\eta^2\text{-}C_2H_4)$ complex. No single product from the reactions between ethyne and a $W_2(\mu\text{-}H)$-containing compound has been fully characterized, but spectroscopic evidence is strongly in favor of a reaction sequence involving (i) ethyne adduct formation, (ii) insertion to form a $\mu$-vinyl ligand, and (iii) further addition of ethyne and hydride to give a 2-butenylidene complex $W_4(OR)_{16}(C_4H_6)$. With $MeC{\equiv}CMe$ and $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$, the previously characterized compound $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}C_4Me_4)(\eta^2\text{-}C_2Me_2)$ is formed with the elimination of i-PrOH and propene. The reactions employing nitriles give products derived from hydride reduction of the coupled nitriles, and the compound $W_2(O\text{-}i\text{-}Pr)_7(\mu\text{-}\eta^1\text{-}N,\eta^1\text{-}N\text{-}NCPhCPhN(H))$ has been structurally characterized. Crystal data for $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ at −155 °C: $P2_1/a$, $a = 20.237(5)$ Å, $b = 9.938(5)$ Å, $c = 21.660(5)$ Å, $\beta = 113.91(1)°$, $Z = 4$. Crystal data for $W_2(O\text{-}c\text{-}C_5H_9)_8(\mu\text{-}CH_2CCH_2)$ at −171 °C: $P2_1/n$, $a = 18.070(5)$ Å, $b = 24.432(6)$ Å, $c = 9.848(2)$ Å, $\beta = 90.19(1)°$, $Z = 4$. Crystal data for $W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$ at −175 °C: $P2_1/c$, $a = 10.618(1)$ Å, $b = 20.824(2)$ Å, $c = 22.154(5)$ Å, $\beta = 115.22(1)°$, $Z = 4$. Crystal data for $W_2(H)(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}OCPh_2)$ at −172 °C: $P2_1/n$, $a = 11.899(5)$ Å, $b = 19.928(8)$ Å, $c = 15.956(7)$ Å, $\beta = 91.61(2)°$, $Z = 4$. Crystal data for $W_2(O\text{-}i\text{-}Pr)_7(\mu\text{-}\eta^1\text{-}N,\eta^1\text{-}N\text{-}NCPhCPhN(H))$ at = −171 °C: $P\bar{1}$, $a = 18.688(4)$ Å, $b = 22.186(5)$ Å, $c = 10.368(2)$ Å, $\alpha = 94.39(1)°$, $\beta = 92.42(1)°$, $\gamma = 68.5(1)°$, $Z = 4$.

## Introduction

Since the discovery of complexes of the transition elements containing hydride ligands,[2] their chemistry has been intimately involved with the development of organometallic chemistry.[3] Transition metal hydrides are key intermediates in numerous stoichiometric and catalytic reactions including, for olefins, hydrogenation, isomerization, hydroformylation, and hydrocyanation. Most known transition metal hydride ligands are supported by soft $\pi$-acceptor ligands such as tertiary phosphines and phosphites, carbon monoxide, and $\pi$-bonded carbocyclic ligands (e.g. cyclopentadienyl, benzene, etc.). As a part of our program aimed at establishing the organometallic chemistry of the polynuclear metal alkoxides of the early transition elements, we are particularly interested in the chemistry of the polynuclear hydrides $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$,[4] $NaW_2(H)(O\text{-}i\text{-}Pr)_8$-diglyme,[5] $W_2(H)(O\text{-}c\text{-}C_5H_9)_7(L)$ (where L = $HNMe_2$ or other neutral donor ligands),[6] $Mo_4(H)(OCH_2\text{-}t\text{-}Bu)_{12}^-$,[7] $Mo_4(H)_3(O\text{-}t\text{-}Bu)_7(HNMe_2)$,[8] and $W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$[9] whose structures are depicted in Chart I by **I** and **VI**, respectively.

The compound $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ was the first reported polynuclear transition metal hydrido complex supported exclusively by alkoxide ligands. The other compounds noted above have all been reported more recently and we believe are merely the first members in what may be a most significant new class of compounds. To place these compounds into further perspective, it should be noted that Wolczanski[10] has reported the synthesis of a dinuclear tantalum hydrido siloxide $Ta_2H_4(OSi$-

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[1] Part 18 in the series *Metal Alkoxides—Models for Metal Oxides.* For Part 17, see: Chisholm, M. H.; Hammond, C. E.; Johnston, V. J.; Streib, W. E.; Huffman, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 7056.

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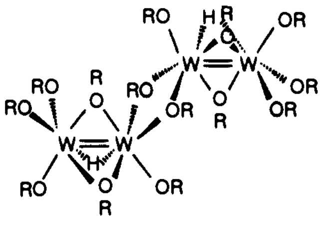
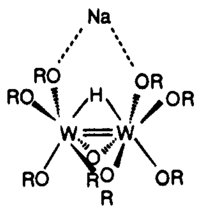
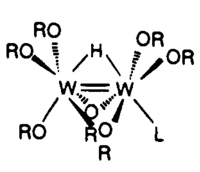
**Chart 1**



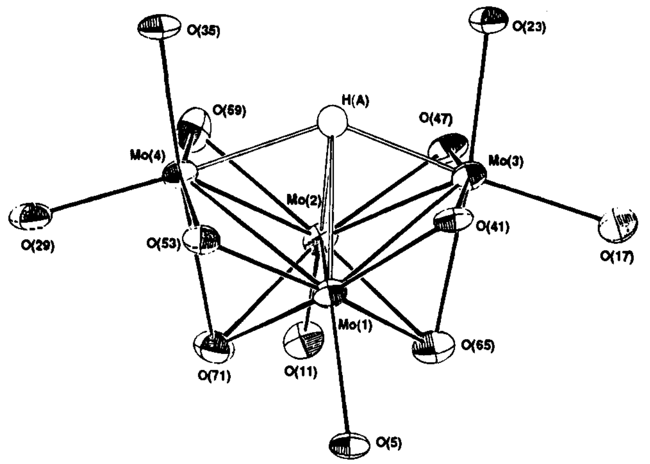
**I** (R = i-Pr)



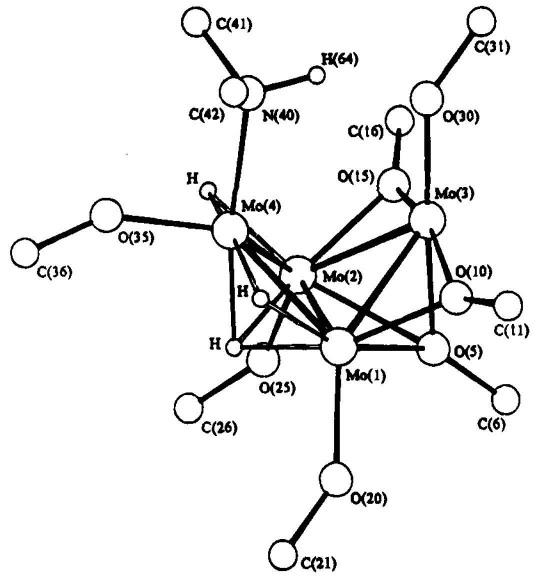
**II** (R = i-Pr)



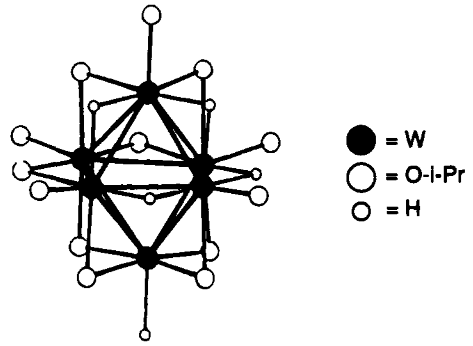
**III** (R = c-$C_5H_9$)



**IV** (O = O–$CH_2$-t-Bu)



**V** (OC = O-t-Bu)

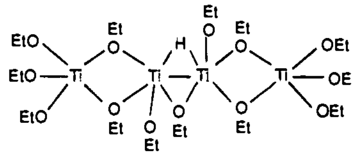


**VI**

t-$Bu_3$)$_4$, along with its remarkable reactivity toward carbon monoxide,[11] and Hoffman[12] has noted the equilibrium, eq 1, involving $Re_3$(O-i-Pr)$_9$.

$$Re_3(\mu\text{-O-i-Pr})_3(\text{O-i-Pr})_6 \rightleftharpoons Re_3(\mu\text{-O-i-Pr})_3(\text{O-i-Pr})_5(\text{H}) + Me_2C{=}O \quad (1)$$

To our knowledge, the only other polynuclear metal hydride supported exclusively by alkoxide ligands is the diamagnetic molecule $Ti_4(OEt)_{13}(H)$ that is proposed to adopt a structure of the type shown in **VII**.[13] However, the compound was not structurally characterized, and the presence of the hydride ligand



**VII**

was inferred on the basis of its reactivity with $CCl_4$, which yielded $CHCl_3$. Elemental analyses and molecular cryoscopy provided for the formulation of the $Ti_4(OEt)_{13}$ fragment. A related phenoxide $Ti_3(H)(OPh)_6$ was reportedly formed in low yield from the reduction of $Ti(OPh)_2Cl_2$ with potassium metal

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(11) Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570.

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or soduim amalgam, and again the hydride ligand was inferred on the basis of the production of $CHCl_3$ upon reaction with $CCl_4$.[14]

The compounds **I**–**VI** have all been structurally characterized by single crystal X-ray crystallography. The presence of the hydride ligands has found support from both the solid-state structural determinations and $^1H$ NMR studies. The latter reveal hydride signals, which, in the case of the tungsten-containing complexes, have satellites due to coupling to $^{183}W$, $I = 1/2$, 14.5% natural abundance.

In this series of papers, we shall examine the reactivity of the hydride ligands in these rather unusual polynuclear complexes containing solely alkoxide ancillary ligands. We start with the simplest of the compounds, namely, those that contain a single hydride such as $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7$ (formed by dissociation of L where L = $HNMe_2$ or $PMe_3$) and $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$, which may be viewed as a dimer $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$. These molecules are coordinatively unsaturated by virtue of their ability to open and close alkoxide bridges. $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ is fluxional on the $^1H$ NMR time scale, showing only one time-averaged alkoxide ligand even at −70 °C, 220 MHz in toluene-$d_8$. It reacts reversibly with donor molecules such as $PMe_3$ or pyridine to yield $W_2(H)(O\text{-}i\text{-}Pr)_7L$ complexes and with NaO-i-Pr to yield $NaW_2(H)(O\text{-}i\text{-}Pr)_8$.[5] Furthermore, while cryoscopy in benzene indicated that $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ is tetranuclear, in the coordinating solvent dioxane, the molecular weight corresponds to that of $W_2(H)(O\text{-}i\text{-}Pr)_7$, which is presumably present as a dioxane solvento complex.[4]

## Results and Discussion

**Studies of Reactivity.** Previously in the full paper describing the synthesis and characterization of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$, it was concluded that the hydride ligands were not acidic on the basis of their lack of reactivity toward bases such as pyridine, amines, and NaO-i-Pr.[4] Furthermore, since there was no reaction of the hydride ligand with excess i-PrOD (no $W_2(\mu\text{-}H)$ to $W_2(\mu\text{-}D)$ transformation occurred), we concluded it was not extremely hydridic in character. In a survey of its reactivity, we noted that with carbon dioxide, insertion into a W−OR bond occurred in preference to the hydride to yield a hydrocarbon insoluble compound, and that with carbon monoxide, $^{13}CO$, $W(CO)_6$ was formed. There was no evidence for formyl, formaldehyde, or methoxide formation. In this regard, the $W_2(\mu\text{-}H)$ moiety is notably less reactive and less basic (hydridic) than the hydrides $Cp_2{}^*ZrH_2$[15] and $Ta_2(H)_4(OSi\text{-}t\text{-}Bu_3)_4$.[11] This is consistent with anticipated M−H bond polarities on the basis of the electronegativity of the transition metal elements that increase in electronegativity from left to right across a row.

Previously it was reported that $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ reacted reversibly with ethene at 22 °C in hydrocarbon solvents.[4] We now show that this is not the case.

**Reactions with Ethene.** The hydrido alkoxides $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ and $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$ react in hydrocarbon solvents at room temperature with ethene (≥2 equiv) to give ethyl−ethene complexes $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ where R = c-$C_5H_9$ and i-Pr. Both compounds are extremely soluble in hydrocarbon solvents and tend to form oily brown crystalline solids upon crystallization from pentane. Crystals suitable for an X-ray study were obtained for R = c-$C_5H_9$. Both compounds appear to be closely related based on NMR spectroscopy.

**Solid-State and Molecular Structure of $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$.** In the space group $P2_1/a$, there are two pairs of enantiomers in the unit cell. Two of the seven cyclopentane rings were disordered and were refined isotropically. The other non-hydrogen atoms were refined anisotropically.

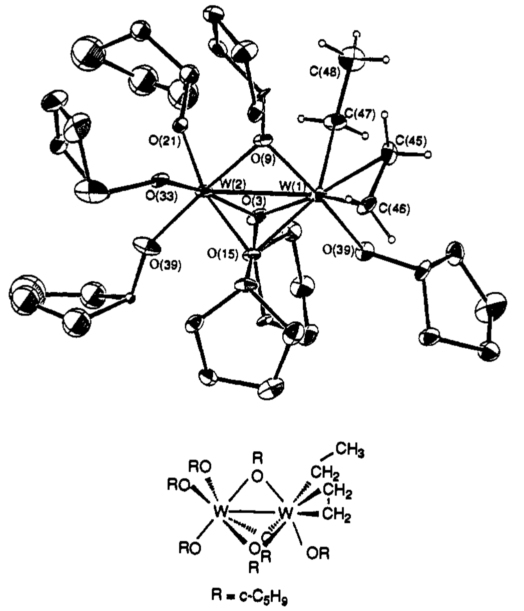

**Figure 1.** ORTEP view of the $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^1\text{-}C_2H_5)(\eta^2\text{-}C_2H_4)$ molecule giving the atom numbering scheme used in the tables. Thermal ellipsoids are of 20% probability. [Selected bond distances: W(1)−W(2) = 2.6684(12) Å, W(1)−C(46) = 2.129(17) Å, W(1)−C(45) = 2.186(16) Å, W(1)−C(47) = 2.186(16) Å, C(45)−C(46) = 1.46(3) Å.]

An ORTEP drawing of one of the enantiomers is shown in Figure 1 along with a stick representation of the molecule. This view of the molecule is perpendicular to the metal−metal axis and emphasizes that the molecule may be viewed as a pseudo-face-shared bioctahedron if the $\eta^2\text{-}C_2H_4$ ligand is taken to occupy one coordination site. There are three bridging and four terminal alkoxide ligands, three being bound to W(2) and one to W(1). The most notable structural feature is the presence of the cis ethene and ethyl ligands. The alkoxide ligand that is trans to the ethyl ligand shows a long W(1)−O distance, 2.22(1) Å, when compared to the other W(1)−O distances, 2.05(1) and 2.06(1) Å, indicative of the high trans-influence of the $\eta^1$-ethyl ligand. The C−C distance in the $\eta^2\text{-}C_2H_4$ ligand is 1.46(3) Å, which, taken together with the relatively short W−C distances 2.13(2) and 2.19(2) Å (these are comparable to the W−C distance of the ethyl ligand, W−C = 2.19(2) Å), implies a strong W-$\eta^2\text{-}C_2H_4$ interaction and an approach to the limiting structural description for a metal−olefin interaction of a metallacycle. In this regard, the $\eta^2\text{-}C_2H_4$ ligand can be viewed as a 2− ligand and the W−W distance of 2.668(1) Å indicative of a $(W{-}W)^{10+}$ core.

Complexes with cis ethyl−ethene ligands are comparatively rare in organometallic chemistry. Indeed, we are aware of only

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[16] (a) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420. (b) Spencer, M. D.; Morse, P. M.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 2057.

[17] A number of cis ethyl−ethylene mononuclear complexes have been reported to be present in solution on the basis of NMR spectroscopic data: (a) Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling S. *J. Am. Chem. Soc.* **1990**, *112*, 2691. (b) Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777. (c) Deutsch, P. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 714. (d) Deutsch, P. P.; Eisenberg, R. *Organometallics* **1990**, *9*, 709. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226. (f) Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, N. C.; Perez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288. (g) Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Carmona, E. *J. Am. Chem. Soc.* **1994**, *116*, 791.

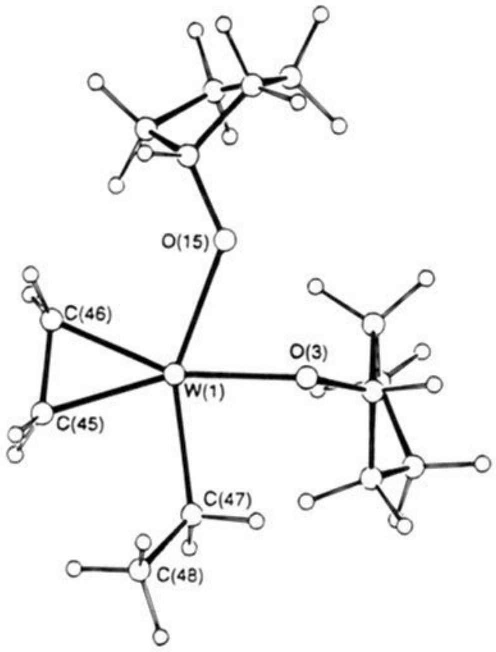

**Figure 2.** View of the $WO_3C_2$ plane containing W(2) in the $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^1\text{-}C_2H_5)(\eta^2\text{-}C_2H_4)$ molecule.

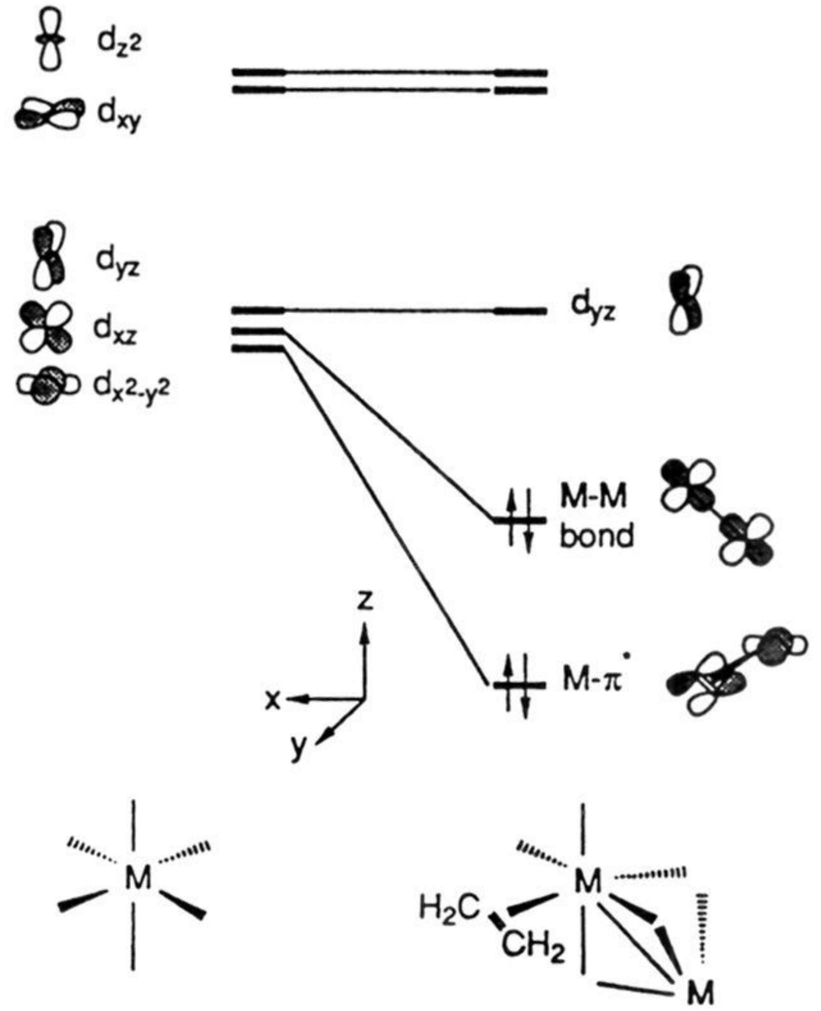

**Figure 3.** Metal $t_{2g}-t_{2g}$ and $t_{2g}$ $(d_\pi)-C_2$ $(\pi^*)$ interactions in the $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^1\text{-}C_2H_5)(\eta^2\text{-}C_2H_4)$ molecule.

two other structurally characterized compounds, both of which are mononuclear.[16,17] Consequently, the coordination environment about W(1) is worthy of further attention.

The coordination of the ethene ligand is slightly asymmetric. The difference in the W(1)−C distances, 2.13(2) and 2.19(2) Å, does not appear to be significant (the two distances are equivalent within $\pm 3\sigma$), but the angles W(2)−W(1)−C(45) and W(2)−W(1)−C(46) are 138.1(4)° and 122.8(4)°, respectively. A view of the coordination geometry about W(1) showing the plane of the octahedron that contains the ethene and ethyl ligands is given in Figure 2. The alkoxide trans to the $\eta^2\text{-}C_2H_4$ ligand is almost in an ideal trans position; the angle from the C−C midpoint to O(3) is 176.4(1)°. However, the other trans angle involving the $\eta^1$-ethyl ligand and the alkoxide in that plane, C(47)−W(1)−O(15), is 146.3(1)°. It is the alkoxide ligand represented by O(15) that deviates most from the octahedral geometry since O(15)−W(1)−O(3) = 70.7(1)° where C(47)−W(1)−O(3) = 81.5(1)°. The sum of the angles in the plane [($\eta^2$-$C_2$-midpoint)−W−O(15) + O(15)−W(1)−O(3) + O(3)−W(1)−C(47) + C(47)−W(1)−($\eta^2$-$C_2$-midpoint)] is 361°, indicating how very nearly planar the four ligands are.

The orientation of the ethene C−C axis is determined by a mutual competition for the metal $t_{2g}$-type orbitals that arises in a pseudooctahedral geometry. In Figure 3, we show the local d−d and $d_\pi-C_2$ $\pi^*$ interactions that allow for the formation of (i) the M−M $\sigma$ bond and (ii) the metallacyclopropane-like nature of the $C_2$−W(1) fragment. The orientation of the C−C axis allows for maximum W $d_\pi-C_2$ $\pi^*$ bonding without a loss of M−M bonding. We would therefore anticipate that there may well be a significant barrier to olefin rotation in this complex, and we shall return to this point later.

The bonding in $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ is in some ways similar to that in $Cp_2Nb(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$.[16a] The frontier orbitals of the bent $Cp_2M$ fragment are three and are confined to lie in the plane perpendicular to the Cp(centroid)M−Cp(centroid) plane.[18] The $Cp_2Nb(\eta^1\text{-}C_2H_5)$ fragment is $d^2$, and thus, formation of the metallacyclopropane-limiting bonding description yields a formal $Nb^{5+}$ center[18] in an analogous manner to our description of $(W-W)^{10+}$ in the present compound. The ethene carbon atoms and the ethyl carbon atom bonded to Nb lie in a plane. The angle C(45)−W(1)−C(47) in the present molecule is 81.4(8)°, while the corresponding angle in $Cp_2Nb(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ is 74.8(3)°, and the C−C nonbonding contacts are 2.85(4) and 2.79(2) Å in the W- and Nb-containing compounds, respectively.

**NMR Studies.** The ethene ligands in $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ compounds show four inequivalent $^1H$ signals, each multiplets, in the $^1H$ NMR spectrum in the range $\delta$ 4.38−1.89. Some of the signals are obscured by alkoxide resonances, but their existence was determined by the use of COSY NMR spectroscopy. Even upon heating to 80 °C in toluene-$d_8$, the ethylenic protons showed no evidence of broadening, thus indicating that the barrier to olefin rotation and dissociation is greater than ca. 15 kcal/mol. The methylene protons of the ethyl ligand are diastereotopic and appear as multiplets centered at $\delta$ 1.94 and 1.64 for R = c-$C_5H_9$ and $\delta$ 1.76 and 1.56 for R = i-Pr. The $^{13}C-^{13}C$ coupling constants for the ethyl and ethene ligands are very similar, being 36 and 34/35 Hz, respectively. The reduction in the value of $^1J_{C-C}$ for the coordinated ethene from that of free ethene, 67 Hz,[19] implies extensive rehybridization as expected for a $d^2\text{-}M\text{-}\eta^2\text{-}C_2H_4$ moiety that is described as a metallacyclopropane. A comparison of C−C distances and values of $^1J_{^{13}C-^{13}C}$ for some early transition metal ethene complexes is given in Table 1.

Low-temperature NMR studies were carried out in an attempt to detect an intermediate in the formation of $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$. These reactions were performed by using $^{13}C_2H_4$ so that they could be readily monitored by $^1H$ and $^{13}C$ NMR spectroscopy. At low temperatures, resonances of the starting $W_2(\mu\text{-}H)$-containing complex and free $^{13}C_2H_4$ were observed, and as the temperature was slowly raised, only resonances assignable to the ethyl−ethene complex grew in. The presumed intermediates $W_2(H)(OR)_7(\eta^2\text{-}C_2H_4)$ and $W_2(OR)_7(C_2H_5)$ are therefore more reactive toward the formation of the ethyl−ethene complex than the starting material is toward the uptake of ethene, which is rate-determining. In a reaction involving $[W_2(\mu\text{-}D)(O\text{-}i\text{-}Pr)_7]_2$ and $^{13}C_2H_4$, the product was exclusively

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(18) Frontier MO's for a bent $Cp_2M$ fragment: Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985; pp 394−400.

(19) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; pp 327 (Table 9.3) and 359.

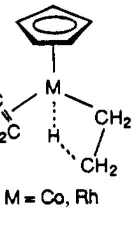
**Table 1.** Structural and NMR Spectroscopic Parameters of Early Transition Metal Ethene Complexes and Related Compounds

| compound | $d_{C-C}$ (Å) | $J_{^{13}C-^{13}C}$ (Hz) |
|---|---|---|
| $C_2H_4$ | 1.339[c] | 67[19] |
| $Cp_2Nb(C_2H_5)(\eta^2\text{-}C_2H_4)$ | 1.406(13)[16a] | |
| $[MoH(OOCCH{=}CH_2)(\eta^2\text{-}C_2H_4)(PMe_3)_2]_2$ | 1.426(9)[d] | |
| $[WH(OOCCH{=}CH_2)(\eta^2\text{-}C_2H_4)(PMe_3)_2]_2$ | 1.443(2)[d] | |
| $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ | 1.43(2)[e] | 25[e] |
| $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ | 1.45(2)[f] | 28[e] |
| $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^1\text{-}C_2H_5)(\eta^2\text{-}C_2H_4)$ | 1.46(3)[a] | 35[a] |
| $Cp^*Ta(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$ | 1.447(4)[g] | |
| $[Li(tmed)]_2[Hf(C_2H_5)_4(\eta^2\text{-}C_2H_4)]$ | 1.51[16b] | |
| $Ti(\eta^2\text{-}C_2H_4)Me_2(\eta^2\text{-dmpe})(\eta^1\text{-dmpe})$ | | 39[16b] |
| $(ArO)_2Ti(\eta^2\text{-}C_2H_4)(PMe_3)$[b] | 1.425(3)[26d] | |
| $C_2H_6$ | 1.538(2)[c] | 34.6[19] |

[a] This work. [b] Ar = 2,6-diphenylphenoxide. [c] Stoicheff, B. P. *Tetrahedron* **1962**, *17*, 135. [d] Alvarez, R.; Carmona, E.; Galindo, A.; Gutiérrez, E.; Marin, J. M.; Monge, A.; Poveda, M. L.; Ruiz, C.; Savariault, J. M. *Organometallics* **1989**, *8*, 2430. [e] Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284. [f] Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Huffman, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1026. [g] Schultz, A. J., Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.

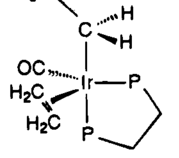
$W_2(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}^{13}C_2H_4)(\eta^1\text{-}^{13}CH_2{}^{13}CH_2D)$. This indicates that the initial insertion of ethene into the hydride is effectively irreversible. When an excess of $^{13}C_2H_4$ was added to a toluene-$d_8$ solution of $W_2(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$, there was no detectable incorporation of $^{13}C$ carbons into the ethyl−ethene starting complex, even after heating the sealed system to 70 °C overnight (ca. 10 h). This demonstrates that the ethene ligand in $W_2(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ is strongly bound and is not labile to dissociative substitution, bimolecular displacement, or insertion into the neighboring tungsten−ethyl bond. Though the ethyl and ethene ligands are mutually cis, migratory insertion does not occur and the starting complex does not act as an ethene polymerization initiator. This we attribute to the extensive W $d_\pi-C_2\ \pi^*$ back-bonding, which is in sharp contrast to $d^0$ olefin−alkyl metal complexes, which are presumably the labile intermediates in olefin polymerization by catalyst precursor complexes such as $[Cp_2ZrMe]^+X^-$.[20] The relative inertness of the $W\text{-}\eta^2\text{-}C_2H_4$ moiety toward substitution (exchange) and the $W\text{-}\eta^1\text{-}C_2H_5$ ligand toward migratory insertion is also underscored by the lack of reactivity of $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ compounds toward $^{13}CO$ and $^{13}C_2H_2$ at room temperature, 1 atm.

The inertness of the $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ compounds contrasts with the other much more reactive cis ethyl−ethene complexes that are known. The ethyl−ethene complexes involving CpCo and CpRh contain an agostic ethyl ligand as shown in **VIII** and rapidly undergo an ethene/ethyl group self-exchange by hydrogen atom transfer.[17a,b] These compounds also act as ethene polymerization catalyst precursors.



**VIII**

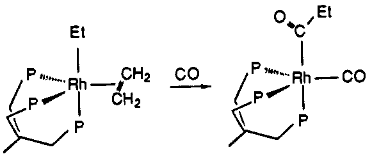
The ethyl−ethene iridium complex, **IX**, contains cis ethyl−ethene ligands and reveals four inequivalent $^1H$ signals for the $\eta^2\text{-}C_2H_4$ moiety by $^1H$ NMR spectroscopy, which implies restricted rotation about the $C_2\text{-}Ir$ axis, and the methylene protons of the ethyl ligand are diastereotopic.[17c,d] However, the complex is labile toward reaction with carbon monoxide to give an $\eta^1$-acyl complex, Ir(COEt)(CO)(dppe), where dppe is bis(dimethylphosphino)ethane.



**IX**

A closely related $(triphos)Rh(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$, **X**, reacts reversibly with ethene as shown in eq 2 and with CO to give the acyl−carbonyl complex shown in **XI**.[17e]

$$(triphos)Rh(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5) \rightleftharpoons (triphos)Rh(H)(\eta^2\text{-}C_2H_4) + C_2H_4 \quad (2)$$



**X** **XI**

**Reactions with Other Alkenes.** The compounds $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7$ and $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$ do not show any apparent reactivity toward propene in hydrocarbon solvents. When sealed in an NMR tube with an excess of propene, the $^1H$ NMR spectrum recorded in benzene-$d_6$ shows only free propene. Similarly, the addition of 1-butene shows no apparent reaction at room temperature, but upon raising the temperature to 60 °C in benzene-$d_6$, isomerization occurs to give a mixture of *cis*- and *trans*-2-butene. A similar isomerization was observed for 1-hexene. When the deuterated complex $[W_2(\mu\text{-}D)(O\text{-}i\text{-}Pr)_7]_2$ was employed, 1-butene was isomerized to a mixture involving *cis*- and *trans*-2-butene and the $W_2(\mu\text{-}H)$ signal was seen to grow in the $^1H$ NMR spectrum. We can conclude that the $W_2(\mu\text{-}H)(OR)_7$ compounds do in fact react with α-olefins to give $W_2(OR)_7$(alkyl) complexes and that, presumably for steric reasons, the $W_2(OR)_7$(alkyl)(alkene) complexes are kinetically labile, being less enthalpically stable than the less sterically demanding $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ compound. If this line of reasoning is correct, then we can write the equilibrium, eq 3, and state that the equilibrium favors the dinuclear hydride and the olefin under ambient conditions.

$$W_2(\mu\text{-}H)(OR)_7 + \text{alkene} \rightleftharpoons W_2(OR)_7(\text{alkyl}) \quad (3)$$

We have made several attempts to trap the $W_2(OR)_7$(alkyl) complexes but without success. For example, when $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7$ is exposed to a 10:1 mixture of propene:ethene in benzene, only the ethyl−ethene complex is observed to be formed. We found no evidence for $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_3H_7)$.

**α-Olefin Hydrogenation.** The complexes $W_2(\mu\text{-}H)(OR)_7$ do not react with molecular hydrogen or $D_2$ in solution at room temperature even at 5 atm. No $W_2(\mu\text{-}H)$ for $W_2(\mu\text{-}D)$ exchange occurred, and no evidence of an $\eta^2\text{-}H_2$ or $\text{-}D_2$ complex was observed.[21] However, we reasoned that if the addition of an

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(20) Jordon, R. F. *J. Chem. Educ.* **1988**, *65*, 285.

(21) References to $\eta^2\text{-}H_2$ complexes: (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

**Table 2.** Results of Catalytic Hydrogenations at 23 °C[a]

| catalyst | pressure of $H_2$ (atm) | substrate | rate[b] | product |
|---|---|---|---|---|
| $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7\text{-}(HNMe_2)$ | 3 | styrene | $2 \pm 1$ | ethylbenzene |
| | 1 | propene | $3.6 \pm 0.5$ | propane |
| | 3 | propene | $7.8 \pm 0.6$ | propane |
| | 1 | 1-butene | $0.6 \pm 0.1$ | butane |
| | 3 | 1-butene | $1.4 \pm 0.2$ | butane |
| $[W_2(\mu\text{-H})(O\text{-i-Pr})_7]_2$ | 3 | styrene | $3.1 \pm 0.8$ | ethylbenzene |
| | 1 | propene | $0.6 \pm 0.2$ | propane |
| | 3 | propene | $8 \pm 2$ | propane |
| | 1 | 1-butene | $0.6 \pm 0.1$ | butane |
| | 3 | 1-butene | $6 \pm 0.2$ | butane |

[a] Values reported after monitoring reaction for ca. 4 days. [b] Moles of substrate/moles of catalyst per hour.

α-olefin to $W_2(\mu\text{-H})(OR)_7$ in a hydrocarbon solvent led to the formation of a kinetically labile $W_2(OR)_7$(alkyl) complex, then this might be intercepted in the presence of molecular hydrogen to give alkane and regenerate the $W_2(\mu\text{-H})(OR)_7$ compound. The nature of this hydrogenolysis could be envisioned to be one of σ-bond metathesis or oxidative addition of $H_2$ to the dinuclear center, followed by reductive elimination. Whether or not our reasoning is correct, α-olefins are hydrogenated by hydrocarbon solutions containing $W_2(\mu\text{-H})(OR)_7$ compounds. The tunrover rates are very modest as is shown in Table 2. Nevertheless, we are confident that the $W_2(\mu\text{-H})(OR)_7$ complexes are actively involved in the catalysis and form the resting state for the $W_2$-containing species involved in the catalytic cycle.

A number of points are worthy of mention. (1) The addition of $D_2$ gas leads to the formation of $W_2(\mu\text{-D})(OR)_7$, and the *n*-alkane is deuterated in the 1 and 2 positions, $RCHDCH_2D$. (2) At short reaction times, formation of $RCH_2CH_2D$ can be detected, which is consistent with the fact that the initial reaction was insertion of the α-olefin into a hydride–tungsten bond. (3) Under these conditions (α-olefin in the presence of $H_2$ at 25 °C), α-olefin isomerization is not observed. (4) The compounds $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$, where R = $c\text{-}C_5H_9$ and i-Pr, do not react with $H_2$ (5 atm) in hydrocarbon solvents even at 80 °C. (5) When $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7$ is allowed to react with a 1:1 mixture of $^{13}C_2H_4$:$H_2$ (present in excess) in benzene-$d_6$ at ca. 22 °C, the formation of $W_2(O\text{-c-}C_5H_9)_7(\eta^2\text{-}^{13}C_2H_4)(\eta^1\text{-}^{13}C_2H_5)$ and ethane is observed. From an analysis of the residual mixture of ethene to ethane, we can estimate that a reactive intermediate $W_2(OR)_7(C_2H_5)$ reacts at a "similar" rate with $H_2$ and $C_2H_4$. Uptake of $C_2H_4$ to give the ethyl–ethene complex quenches the otherwise catalytic formation of ethane by hydrogenolysis.

**Reactions with Allene and 1,3-Butadiene.** The reaction between a coordinatively unsaturated $W_2(H)(OR)_7$ fragment and allene or 1,3-butadiene might well have been expected to lead to coordinately saturated $W_2(OR)_7L$ complexes, where L = $\eta^3$-allyl or -1-methylallyl. However, although in hydrocarbon solutions there are rapid reactions involving both allene and 1,3-butadiene and the $W_2(H)(OR)_7$ compounds, the above products do not appear to be formed, or, if they are formed, subsequent reaction chemistry occurs that we have yet to sort out. There appear to be intermolecular reactions involving ligand exchange, and the mixture of products has not been satisfactorily characterized. The compounds are extremely hydrocarbon soluble and difficult to crystallize. One compound has, however, been obtained pure in a crystallographically characterizable form, namely $W_2(O\text{-c-}C_5H_9)_8(\mu\text{-}CH_2CCH_2)$. The presence of eight OR groups at the $W_2$ center and the lack of the hydride ligand and/or its derivative are a clear indication that intermolecular chemistry has occurred, leading to ligand scrambling.

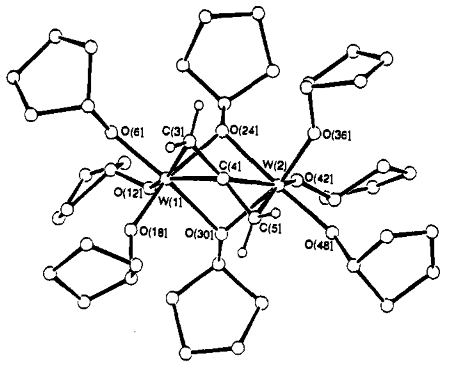

**Figure 4.** Ball-and-stick drawing of the $W_2(O\text{-c-}C_5H_9)_8(\mu\text{-}CH_2CCH_2)$ molecule giving the atom numbering scheme used in the tables. [Selected bond distances: W(1)–W(2) = 3.053(2) Å, W(1)–C(3) = 2.166(24) Å, W(2)–C(5) = 2.202(22) Å, C(4)–C(5) = 1.39(3) Å, W(1)–C(4) = 2.117(27) Å, W(2)–C(4) = 2.149(27) Å, C(3)–C(4) = 1.43(3) Å.]

**Solid-State and Molecular Structure of $W_2(O\text{-c-}C_5H_9)_8(\mu\text{-}CH_2CCH_2)$.** The allene-bridged compound crystallizes in the space group $P2_1/n$ with four molecules in the unit cell. The molecule is chiral, and the unit cell contains two pairs of enantiomers. There were problems encountered during the refinement of some of the cyclopentane rings, and attempts to apply an absorption correction failed to improve matters. Although the disorder problems give rise to significant uncertainties within the metrical parameters, the connectivity of the atoms and the general formulation of the compound as proposed are unambiguous. Because of the large thermal parameters associated with some of the cyclopentane rings, the thermal ellipsoids are not shown and a ball-and-stick drawing of the molecule is shown in Figure 4. This view of the molecule is perpendicular to the W–W bond and reveals the twist of the $C_3$ allene moiety with respect to the W–W axis. Each tungsten atom is coordinated to three terminal OR ligands, two bridging OR ligands, and one C–C double bond of the allene. If the allene is viewed to occupy one coordination site per metal, then the coordination geometry corresponds to that of a distorted octahedron.

The W–W distance of 3.053(2) Å may be viewed as a nonbonding distance, and each $C_2$–W interaction may be described in terms of the limiting metallacyclopropane model. In this way, the compound may be viewed as the sum of the hypothetical reaction between $W_2(O\text{-c-}C_5H_9)_8$ and allene wherein allene undergoes a four-electron reduction by the $(W{\equiv}W)^{8+}$ center. The nature of the μ-allene ligand is quite different from that seen in $W_2(O\text{-t-Bu})_6(\mu\text{-}CH_2CCH_2)$ where the allene is rehybridized such that there is a planar central $W_2C_3$ moiety.[22] In the present compound, the μ-allene ligand is of the "normal" type in the sense that the π-systems remain orthogonal. The C–C–C angle of 147(3)° is in the usual range for coordinated allene complexes, and the bonding of the μ-allene ligand may be compared favorably with that in $Rh_2(CO)_2(acac)_2(\mu\text{-}CH_2CCH_2)$, which has no Rh–Rh bond,[23] and that in $Cp_2Mo_2(CO)_4(\mu\text{-}CH_2CCH_2)$,[24] where there is a Mo–Mo bond required to satisfy the 18-electron rule.

**Reactions with Aldehydes and Ketones.** The $W_2(H)(OR)_7$ compounds react with aldehydes and ketones to generate alkoxide ligands by insertion of the hydride into the C=O bond,

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(22) Chacon, S. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. *Organometallics* **1991**, *10*, 3722.

(23) Racanelli, P.; Pantini, G.; Immirzi, A.; Allegra, G.; Porri, L. *J. Chem. Soc., Chem. Commun.* **1969**, 361.

(24) Chisholm, M. H.; Rankel, L. A.; Bailey, W. I., Jr.; Cotton, F. A.; Murillo, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 1261; **1978**, *100*, 802.

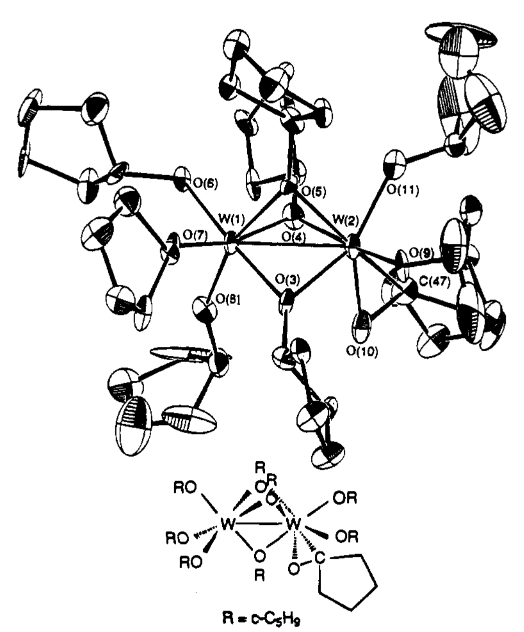

**Figure 5.** ORTEP drawing of the $W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$ molecule giving the atom numbering scheme used in the tables. Thermal ellipsoids are of 50% probability. [Selected bond distances: W(1)−W(2) = 2.6738(10) Å, W(2)−O(10) = 1.931(12) Å, W(2)−C(47) = 2.155(16) Å, O(10)−C(47) = 1.370(20) Å.]

$M_2(H) + RR'C{=}O \rightarrow M_2(OCHRR')$. There are problems in isolating these compounds because of (i) ligand scrambling (alkoxide ligand exchange) and (ii) further uptake of aldehyde or ketone to give thermally unstable aldehyde or ketone adducts. One such adduct has been fully characterized, namely $W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$, the product obtained from the reaction between $W_2(H)(O\text{-}c\text{-}C_5H_9)_7$ and 2 equiv of cyclopentanone. In the case of the more sterically demanding benzophenone, a 1:1 adduct has been isolated, $W_2(H)(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}OCPh_2)$.

**Solid-State and Molecular Structure of $W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$.** The molecule crystallizes in the space group $P2_1/c$ with four molecules in the unit cell. Each molecule is chiral, and the unit cell contains two pairs of enantiomers. Only some of the hydrogen atoms could be located, so all were placed in calculated positions. All non-hydrogen atoms were refined by using anisotropic thermal parameters. Only one cyclopentane ring showed a slight disorder.

An ORTEP drawing of one of the enantiomers, showing the chemically most reasonable atom position for the disordered cyclopentane ring, is given in Figure 5.

If the $\eta^2$-cyclopentanone ligand is considered to occupy one coordination site, then the geometry of the dinuclear complex may be described in terms of a confacial bioctahedron. The W−W distance of 2.674(1) Å is consistent with a $(W{-}W)^{10+}$ moiety, and the $\eta^2\text{-}O\text{-}c\text{-}C_5H_8$ ligand may be counted as a $2^-$ ligand. There is then an obvious analogy between $W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$ and the ethyl−ethene complex $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$. The O(10)−C(47) distance of 1.37(2) Å is elongated from that of the free ketone, consistent with extensive W $d_\pi$−C−O $\pi^*$ back-bonding. The W(2)−O(CO) distance of 1.93(1) Å is within the range of a terminal alkoxide O−W distance, and the W(2)−C(47) distance of 2.16(2) Å is comparable to that seen for the $\eta^2\text{-}C_2H_4$ ligand in $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$.

Molecules containing $\eta^2$-ketone ligands are still relatively rare,[25] and only a few have been structurally characterized. Pertinent structural data for the known (structurally characterized) $\eta^2$-ketone complexes are given in Table 3 for the purposes of obtaining a useful comparison.

**Table 3.** Pertinent Structural Parameters for Molecules Containing $\eta^2$-Ketone Ligands

| molecule | W−C | W−O | C−O | Σ (deg)[a] | ref |
|---|---|---|---|---|---|
| $W_2(H)(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}OCPh_2)$ | 2.14(1) | 1.94(1) | 1.39(1) | 340 | *b* |
| $W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$ | 2.16(2) | 1.93(1) | 1.37(3) | 335 | *b* |
| $WCl_2(\eta^2\text{-}OCMe_2)_2(PMePh_2)_2$ | 2.175(7) | 1.948(4) | 1.379(8) | 338 | 26b |
|  | 2.203(7) | 1.933(4) | 1.390(8) | 338 | 26b |
| $W(OCH_2\text{-}t\text{-}Bu)_4(py)_2(\eta^2\text{-}OCPh_2)$ | 2.23(1) | 1.970(6) | 1.40(1) | 345 | 26c |
| $[Os(NH_3)_5(\eta^2\text{-}OCMe_2)](CF_3SO_3)_2$ |  |  | 1.32(1) |  | 26a |
| $Ni(\eta^2\text{-}OCPh_2)(PEt_3)_2$ |  |  | 1.335(4) | 353 | 27 |
| $(ArO)_2Ti(\eta^2\text{-}OCPh_2)(PMe_3)$[c] |  |  | 1.397(8) |  | 26d |

[a] Σ represents the sum of the angles about the ketone carbon atom bonded to the metal atom. This is a measure of the pyramidal nature of the $\eta^2$-ketone ligand. [b] This work. [c] ArO = 2,6-diphenylphenoxide.

The four tungsten-containing compounds that are now structurally characterized all show rather similar structural features (see Table 3). In particular, the short W−O distances arise from the oxophilic nature of tungsten and the reduction of the ketone to a formal $2^-$ ligand. The C−O distances span a small range, 1.37(2)−1.40(1) Å, and the W−C distances are 2.23(1)−2.16(2) Å. The sum of the angles at carbon are all less than 360° (335−345°), consistent with a rehybridization from trigonal planar toward pyramidal. There appears to be greater metal $d_\pi$−CO $\pi^*$ back-bonding in the tungsten-containing complexes than in either $[Os(NH_3)_5(\eta^2\text{-}OCMe_2)]^+[O_3SCF_3]^-$ [26a] or $(Et_3P)_2Ni(\eta^2\text{-}OCPh_2)$.[27]

**Molecular Structure of $W_2(H)(O\text{-}i\text{-}Pr)_7$ ($\eta^2$-$OCPh_2$) in Solution and in the Solid State.** As noted earlier, benzophenone forms a 1:1 adduct in contrast to $W_2(OR)_8(\eta^2\text{-}OCR_2')$ complexes. Perhaps this is because of steric factors, although electronic factors cannot be overruled since diaryl ketones are more readily reduced than dialkyl ketones and aldehydes. In solution, we are confident in our formulation of the compound as one containing a terminal hydride and an adjacent $\eta^2\text{-}OCPh_2$ ligand supported by seven alkoxides. The presence of the terminal hydride is implicated by a $^1H$ signal at $\delta$ ca. 13 ppm flanked by satellites due to coupling to $^{183}W$, $I = {}^1/_2$, 14.5% natural abundance $^1J_{W-H} = 126$ Hz. When the $^{13}C$-labeled benzophenone is used, the hydride signal appears as a doublet flanked by satellites of doublets. The doublets arise from the coupling $^2J_{^1H-^{13}C} = 8$ Hz. Similar two-bond coupling transmissions via a metal atom ($J_{CMH}$) have been found. For example, in the case of $HMn(CO)_5$, $^2J_{H-C_{trans}} = 7.0$ Hz and $^2J_{H-C_{cis}} = 14.0$ Hz.[28] The spectrum of the hydride ligand is shown in Figure 6. The infrared spectrum also provides evidence for a terminal hydride ligand. The W−H band appears at 1875 cm$^{-1}$, which moves to 1278 cm$^{-1}$ in the deuterated compound, $W_2(D)(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}OCPh_2)$.

In the solid-state structure, location of the hydride is problematic. A ball-and-stick drawing of the molecule is given

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(25) Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298.

(26) (a) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223. (b) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298. (c) Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 607. (d) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771. (e) An $\eta^2$-benzaldehyde complex has recently been reported: Orth, S. D.; Barrera, J.; Sabat, M.; Harman, D. W. *Inorg. Chem.* **1994**, *33*, 3026.

(27) Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311.

(28) (a) Whitesides, G. M.; Maglio, G. *J. Am. Chem. Soc.* **1969**, *91*, 4980. (b) A referee pointed out that the $^2J_{^{13}C-^1H}$ value is intermediate to those observed in the more closely related $Cp^*Cl_2(H)Ta(\mu\text{-}\eta^2\text{-}CHO)TaCl_2Cp^*$ (20 Hz) [Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 2858] and exo-$Cp_2^*M(CH_2{=}CHR)(H)$ (M = Nb, Ta) (≈2 Hz) [Doherty, N. N.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670].

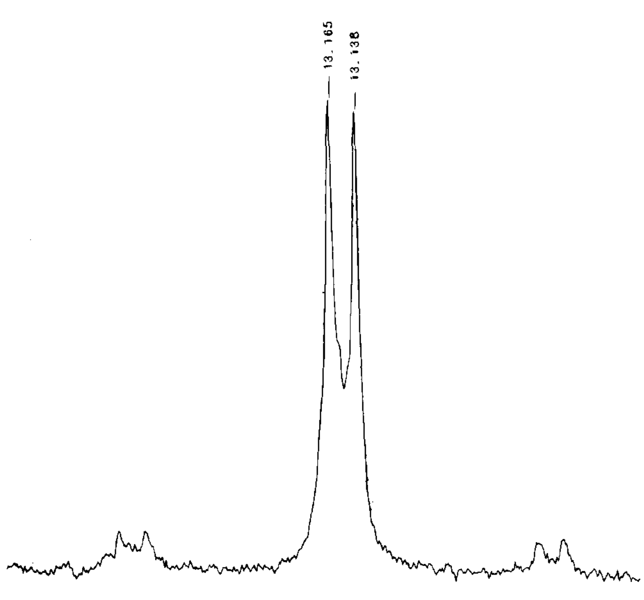

**Figure 6.** Hydride signal of $W_2(H)(O\text{-i-Pr})_7(\eta^2\text{-}O^{13}CPh_2)$ recorded in toluene-$d_8$ at 22 °C, 300 MHz, showing the couplings due to $^{13}C-^1H$ and $^{183}W-^1H$.

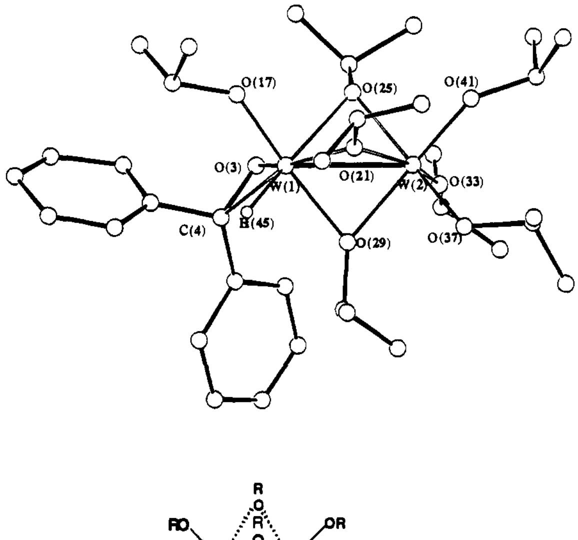

**Figure 7.** Ball-and-stick drawing of the $W_2(H)(O\text{-i-Pr})_7(\eta^2\text{-}OCPh_2)$ molecule giving the atom numbering scheme used in the tables. The hydride ligand was not located but is shown in an anticipated location with respect to W(1) and the ketonic carbon C(4). [Selected bond distances: W(1)−W(2) = 2.650(3) Å, W(1)−C(4) = 2.141(16) Å, W(1)−O(3) = 1.940(12) Å, O(3)−C(4) = 1.394(19) Å.]

in Figure 7. It is quite evident that W(2) has a pseudooctahedral $WO_6$ geometry and that there are three bridging ligands. The hydride ligand was not crystallographically located. It was placed in an idealized position as a terminal hydride on W(1) to complete the metal's octahedral coordination sphere as shown in Figure 7. The location of the hydride ligand was acceptable to the HYDEX program,[29] and this location provided a significantly lower potential energy minimum relative to the alternative solution of placing the hydride bridging between W(1) and W(2). The coordination about W(1) is reminiscent of that in $W_2(O\text{-c-}C_5H_9)_8(\eta^2\text{-}O\text{-c-}C_5H_8)$ wherein one terminal OR ligand is replaced by a hydride ligand. A similarity is thus also maintained with the $W_2(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ complex. The orientation of the single faced π-acceptor ligand ($\eta^2\text{-}C_2H_4$ or $\eta^2\text{-}OCR_2$) is determined by the metal $d_\pi$−CO $\pi^*$ or $-C_2\pi^*$ back-bonding in mutual competition with the formation of the M−M single bond for what is effectively a $(W-W)^{10+}$ moiety. Note the similarity in the W−W distances in all three compounds. Finally, it is worth emphasizing how similar the parameters are for the W-$\eta^2$-OC moiety in both the cyclopentanone and benzophenone adduct. The sum of the angles at the ketonic carbon is 339°, comparable to other $d^2$-W-$\eta^2$-$OCR_2$-containing complexes (Table 3).

**Reactions with Alkynes.** Internal alkynes, larger than 2-butyne, and terminal alkynes, RC≡CH, yield complex reaction mixtures upon reaction with $W_2(\mu\text{-}H)(OR)_7$ compounds. No pure single product was obtained from these reactions. Reactions with larger alkynes appear to form $W(O)(OR)_4$[30] as well as other products of unknown identity.

Reaction with 2-butyne, MeC≡CMe, resulted in a complex reaction mixture, from which the products were identified spectroscopically. A white solid could be sublimed in low yields (10−15%) from large scale reactions and was identified to be $W(O)(OR)_4$.[30] In the case of $W_2(H)(O\text{-i-Pr})_7$, the formation of $W(O)(O\text{-i-Pr})_4$ is due to ligand decomposition, (β-hydride elimination resulting in loss of propene and 2-propanol). The volatile components were isolated in a separate experiment, and their identities were confirmed by both $^1H$ NMR and GC/MS. The second organometallic product in the reaction of $W_2(\mu\text{-}H)(O\text{-i-Pr})_7$ and MeC≡CMe was determined to be $W_2(O\text{-i-Pr})_6(C_4Me_4)(C_2Me_2)$; again, it was confirmed by spectroscopic methods and identified from its independent synthesis.[31] The reaction can be expressed as shown in eq 4.

$$[W_2(\mu\text{-}H)(OR)_7]_2 + Me_2C_2 \rightarrow W_2(OR)_6(C_4Me_4)(C_2Me_2) + HOR + C_3H_6 + W(O)(OR)_4 \quad (4)$$

The fate of the hydride ligand is undetermined at this point; the formation of products appears to be independent of the number of equivalents of alkyne added to the reaction mixture as well as the temperature at which the reaction is run (25 to −10 °C). At lower temperatures, no reaction is observed ($Me_2C_2$ freezes at −32 °C).

Reaction with ethyne resulted in different chemical behavior. Detailed NMR studies of reactions employing various isotopically labeled ethynes were undertaken.

The initial reaction between $[W_2(\mu\text{-}H)(O\text{-i-Pr})_7]_2$ and ethyne in toluene-$d_8$ at low temperatures appears to yield the ethyne adduct $W_2(\mu\text{-}H)(O\text{-i-Pr})_7(\eta^2\text{-}C_2H_2)$. The $^1H$ NMR spectrum shows four inequivalent i-Pr ligands in the ratio 2:2:2:1. This compound is formulated as having the ethyne ligand trans to the hydride and is the kinetically formed product at −70 °C. After 30 min at −70 °C, this compound completely rearranges to a new ethyne adduct that shows seven inequivalent alkoxide resonances of equal integral intensity. The kinetically formed ethyne adduct shows a bridging hydride signal with coupling constants $^1J_{^{183}W-^1H}$ = 56 and 82 Hz, while the thermodynamic ethyne adduct has a μ-hydride ligand with coupling constants $^1J_{^{183}W-^1H}$ = 79 and 102 Hz. The proton−tungsten coupling constants presumably reflect, in part, the strength of the W−H bonds. The smallest coupling constant arises when the $\eta^2\text{-}C_2H_2$ ligand is in the trans position. This is formed first because of

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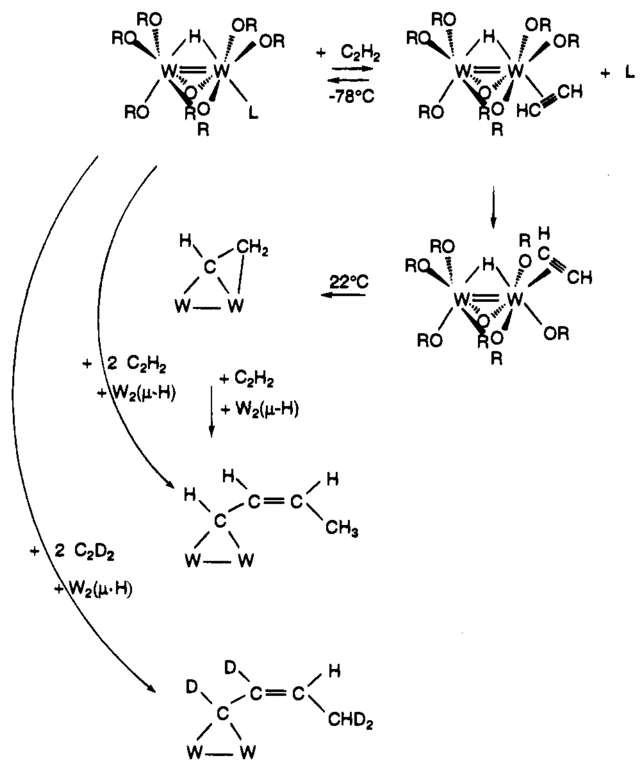
[29] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

[30] Clegg, W.; Errington, J. R.; Kraxner, P.; Redshaw, C. *J. Chem. Soc., Dalton Trans.* **1992**, 1431.

[31] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806.

Scheme 1



the high trans effect of the W$-\mu$-H bond.[32] This is, of course, all mere speculation, but the $^1$H NMR spectra are consistent with the geometries shown in Scheme 1, and it is known that in the molecular structure of $[W_2(\mu\text{-H})(\text{O-i-Pr})_7]_2$, the W$-$O bonds trans to the $\mu$-H moiety are longer than those that are trans to W$-$O bonds.[4] We are extrapolating from the observed high trans influence of the hydride[32] to its presumed high trans effect, which would account for the kinetically formed ethyne adduct.

Evidence for a terminal ethyne ligand is seen in the $^{13}$C NMR spectrum of these low-temperature studies. The kinetic and thermodynamic isomers both show $^{13}$C signals in a chemical shift range much lower than those seen for $W_2(\mu\text{-}C_2H_2)$-containing compounds, e.g. *ca.* 190$-$180 ppm relative to 120$-$130 ppm for $W_2(\mu\text{-}C_2H_2)(OR)_6$-containing compounds.[33,34] Moreover, the magnitude of the coupling constants $^1J_{^{183}W-^{13}C}$ ca. 40 Hz, their satellite integral intensities (ca. 14$-$16%), and the magnitude of $J_{^{13}C-^{13}C} \sim 25$ Hz are comparable to the $\eta^2$-$C_2H_2$ ligand in $W_2(\text{O-i-Pr})_6(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)$.[33]

The hydrido-bridged $\eta^2$-ethyne complexes can be isolated in the absence of free ethyne at or below $-72$ °C by application of a dynamic vacuum with careful shaking of the NMR tube and by use of a J. Young valve.

Upon warming the $\eta^2$-ethyne adduct to room temperature in the absence of free ethyne, a migratory insertion reaction occurs to give a $\sigma,\pi$-vinyl ligand. The CH moiety shows a $^{13}$C signal at $\delta$ 145.0 with $^1J_{^{13}C-^{13}C} = 20$ Hz and $^1J_{^{13}C-^1H} = 165$ Hz and a signal at 9.63 ppm in the $^1$H NMR spectrum. One of the $^1$H NMR signals for the $CH_2$ moiety is at $\delta$ 3.18, while the other is obscured by alkoxide resonances $\delta(^{13}C) = 61.4$.[34] These parameters are very similar to those reported for $W_2(OSiMe_2\text{-t-Bu})_7(\mu\text{-CHCH}_2)$ in which we observed for C*H*, $\delta(^1H) = 10.99$ and $\delta(^{13}C) = 189.2$, and for C*H*$_2$, $\delta(^1H) = 6.23$ and 1.24 and $\delta(^{13}C) = 66.5$.[35]

The room-temperature reactions involving $[W_2(H)(\text{O-i-Pr})_7]_2$ or $W_2(H)(\text{O-c-}C_5H_9)_7L$, where L = $HNMe_2$ or $PMe_3$, and ethyne reveal the facile coupling of two $C_2$ units to form a 2-butenylidene ligand as shown in Scheme 1. These compounds are extremely difficult to isolate in a pure form, and only the cyclopentoxide yielded a clean solid material for which elemental analyses are consistent with the formula $W_4(\text{O-c-}C_5H_9)_{16}(C_4H_6)$. If this formulation is correct then an intermolecular ligand exchange process must have occurred, which was analogous to the reactions described earlier involving allene. NMR tube reactions involving $[W_2(H)(\text{O-i-Pr})_7]_2$ and ethyne also indicate formation of the 2-butenylidene ligand, and reactions employing $C_2D_2$ demonstrate that the protons from the $W_2(\mu\text{-H})$ moiety end up *exclusively* in the $\gamma$ and $\delta$ positions of the butenylidene ligand. See Scheme 1.

By $^1$H and $^{13}$C NMR spectroscopy, we also find that the $\sigma,\pi$-vinyl complex reacts with further ethyne to produce the 2-butenylidene ligand. The overall mechanism or reaction pathway leading to the formation of the butenylidene ligand is unknown, and on the basis of the labeling result, employing $C_2D_2$ would appear quite fascinating. One possibility is that the $\sigma,\pi$-vinyl rearranges to a $\mu$-ethylidyne and that this undergoes C$-$C bond formation with added ethyne to give a $W_2(\mu\text{-CDCDCCHD}_2)$-containing complex. [We have noted previously the coupling of $\mu$-alkylidyne with alkyne ligands in the chemistry of $X_2W(\mu\text{-CSiMe}_3)_2WX_2$ compounds, where X = $CH_2SiMe_3$ and O-i-Pr.[36] The latter reactions generated $X_2W(\mu\text{-CSiMe}_3)(\mu\text{-CRCRCSiMe}_3)WX_2$ complexes.] Then, by an intermolecular reaction involving a $W_2(\mu\text{-H})$ group, a $W_4(\mu\text{-CDCDCHDCHD}_2)$-containing complex could be formed. It is hoped that by employing alkoxide ligands other than R = i-Pr and c-$C_5H_9$ we shall be able to obtain a crystalline sample of the 2-butenylidene-containing complex in the future.

Since we were able to obtain a $W_2(\mu\text{-H})(\eta^2\text{-}C_2H_2)$-containing complex at low temperatures, we studied the competition between $C_2H_4$ and $C_2H_2$ for $W_2(\mu\text{-H})(OR)_7$ species. At low temperatures, $-70$ °C and below, only the $\eta^2$-$C_2H_2$ complex is formed. In the absence of further free ethyne, ethene does not react at a significant rate until temperatures of $\geq -20$ °C, at which point the only observable species to be detected is $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$. When mixtures (1:1) of ethyne and ethene are allowed to compete for $W_2(H)(OR)_7$ compounds, it is possible to follow the formation of $W_2(OR)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ in the presence of $W_2(\mu\text{-H})(OR)_7(\eta^2\text{-}C_2H_2)$. Thus, although ethyne coordination is favored, the migratory insertion of ethene to yield the ethyl ligand is kinetically more facile than the insertion of ethyne to yield the vinyl ligand. This finding is complementary to $\beta$-hydrogen elimination reactions involving alkyl and vinyl ligands bonded to Ir and Rh[37] and probably reflects the greater degree of order (larger $-\Delta S^{\ddagger}$ value) and rehybridization that is required for the formation or decomposition of the vinyl ligand. In these competition reactions, there was also some evidence for the formation of a product or products derived from the coupling of ethyne and ethene. A coupling of a coordinated ethyne with ethene was seen in the reaction between $W_2(OSiMe_2\text{-t-Bu})_6(\mu\text{-}C_2H_2)(py)$ and ethene at $-20$ °C in hydrocarbon solvents to give the fully

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

[33] Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

[34] For a discussion of the $\delta(^{13}C)$ values of $\eta^2$-$C_2H_2$ complexes bonded to $W(OR)_x$ moieties, see ref 31.

[35] Chisholm, M. H.; Cook, C. M.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Dalton Trans.* **1991**, 929.

[36] (a) Chisholm, M. H.; Huffman, J. C.; Heppert, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5116. (b) Chisholm, M. H.; Heppert, J. A. *Adv. Organomet. Chem.* **1986**, *26*, 97. (c) Chisholm, M. H.; Ontiveros, C. D. *Polyhedron Symposium-in-Print* **1988**, *7*, 1015.

[37] Schwartz, J.; Hart, D. W.; McGiffert, B. *J. Am. Chem. Soc.* **1974**, *96*, 5613.

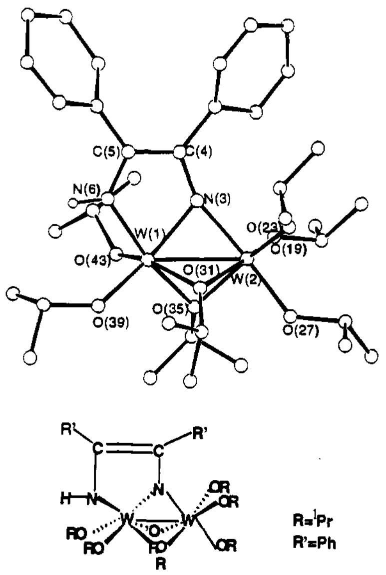

**Figure 8.** Ball-and-stick drawing of the $W_2(O\text{-}i\text{-}Pr)_7(\mu\text{-}\eta^1\text{-}N,\eta^1\text{-}N\text{-}NCPhCPhN(H))$ molecule giving the atom numbering scheme used in the tables. [Selected bond distances: W(1)−W(2) = 2.5909(21) Å, W(1)−N(6) = 2.022(23) Å, W(1)−N(3) = 2.010(26) Å, W(2)−N(3) = 2.002(27) Å, N(6)−C(5) = 1.34(4) Å, C(4)−C(5) = 1.38(5) Å, N(3)−C(4) = 1.36(4) Å.]

characterized compound $W_2(H)(OSiMe_2\text{-}t\text{-}Bu)_6(\mu\text{-}CCHCHCH_3)$.[38] In the present study, the nature of the product or products formed from ethyne−ethene coupling is not known.

**Reactions with Nitriles.** The $W_2(H)(OR)_7$ compounds react with nitriles (PhC≡N, MeC≡N, and t-BuC≡N) in hydrocarbon solvents to give compounds of formula $W_2(OR)_7(\mu\text{-}\eta^1\text{-}N,\eta^1\text{-}N\text{-}NCRCRN(H))$. The compounds are spectroscopically very similar and have a characteristic N−H stretch in the infrared spectrum at ca. 3360 $cm^{-1}$ and a single downfield $^1H$ NMR resonance at ca. $\delta = 9$ ppm that does not contain tungsten satellites. The evidence that two nitrile moieties have been coupled comes from the NMR spectra that reveal two types of Ph, t-Bu, or Me groups. At room temperature, the isopropoxide shows the seven methyne groups as three resonances in the ratio 1:4:2 but the methyl signals appear as two signals and integrate as 42 protons. Upon being cooled to −80 °C in toluene-$d_8$, the methyl groups become split into seven sets and there is some change in the methylene resonances. However, the molecule that is apparently dynamic in solution is not completely frozen out or at least not completely "resolved" with respect to the attainment of the structure found in the solid state described below.

**Solid-State and Molecular Structure of $W_2(O\text{-}i\text{-}Pr)_7(\mu\text{-}\eta^1\text{-}(N),\eta^1(N)\text{-}NCPhCPhN(H))$.** In the space group $P\bar{1}$, there are two independent molecules in the asymmetric unit. A least-squares fit employing S. C. Nyburg's program (see Experimental Section) indicates that the molecules differ slightly in their conformation, but chemically equivalent bonds show no significant difference. All non-hydrogen atoms were located, while the hydrogen atoms were placed in fixed idealized positions for the final cycles of refinement. An imperfect absorption correction or a possible slight splitting of the crystal resulted in only the tungsten atoms being refined anisotropically. Non-hydrogen atoms were refined isotropically, and hydrogen atoms were assigned as fixed atom contributors.

An ORTEP drawing of the molecule is given in Figure 8 along with a stick drawing. Each tungsten atom is in a pseudooctahedral geometry, and the two metal atoms share a face formed by two O-i-Pr-bridging ligands and an imido bridge of the metallacycle. The W−W distance of 2.58 Å corresponds to a M−M single bond, i.e. a $(W-W)^{10+}$ central moiety. The structure is very similar to that of $W_2(O\text{-}i\text{-}Pr)_7(\mu\text{-}\eta^1\text{-}N,\eta^1\text{-}C\text{-}NC(Ph)CHCH_2)$ where the imido-bridged metallacycle was formed from the coupling of a $\mu$-ethyne ligand and a molecule of added PhC≡N, followed by the addition of a hydrogen atom from i-PrOH.[39] The five atoms of the metallacycle are contained in a plane, but W(2) is not contained in this plane. The sum of the angles at the $\mu$-N (imido) atom is 356°. The terminal W−OR distances of ca. 1.90 Å and bridging W−OR distances of ca. 2.10 Å are not exceptional. The W−O distances trans to the amido and imido nitrogen atoms are larger than the others, consistent with the higher trans influence[32] of the stronger $\pi$-donating amido/imido ligands. The W−$\mu$-N distances of 2.01(2) and 2.00(2) Å indicate the symmetrical bridging nature of the imido ligand, while the terminal amido W−N distance of 2.02(2) Å is notably longer than those in $W_2(NMe_2)_6$ compounds, W−N = 1.96 Å.[40] In the present compound, there are only two vacant $t_{2g}$ orbitals for receiving $\pi$-electrons from alkoxide/amido and imido ligands (the other $t_{2g}$ orbital is used in forming the M−M $\sigma$ bond), and so metal−ligand $\pi$-bonding is delocalized principally over the terminal-alkoxide, -amide, and bridging imido bonds.

**Reactions Involving Carbon Monoxide.** As noted earlier, neither CO nor $CO_2$ reacts with $W_2(\mu\text{-}H)(OR)_7$ compounds to give products of insertion into the hydride ligand. This is clearly indicated by NMR studies employing $^{13}CO$. The evidence is in favor of $CO_2$ inserting into W−OR ligands since several $^{13}C$ signals are seen in the region $\delta = 180$, typical of $O_2{}^{13}COR$ resonances.[41] In the case of reactions involving CO, products suggestive of ligand migration and valence disproportionation are observed; e.g. in the reaction between $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$ and CO, the previously characterized compound $W_2(O\text{-}i\text{-}Pr)_6(CO)_4$[42] was isolated, and in the reaction between $W_2(H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ and CO, $W(CO)_5(HNMe_2)$ was isolated.[43] The fate of the hydride is not known.

## Concluding Remarks

The reactions of the $W_2(\mu\text{-}H)$-containing compounds supported by alkoxide ligands indicate that the hydride is labile to a number of insertion reactions with C−C and C−O double bonds and with nitriles as shown in Scheme 2. In the presence of molecular hydrogen, hydrogenation of α-olefins is catalytic and presumably involves the hydrogenolysis of a reactive $W_2(OR)_7(R')$ intermediate. The lack of reactivity of the hydride with carbon monoxide contrasts with the activity of zirconium[15] and tantalum hydrides.[10,11] This may merely reflect the gradation of the hydridic character of the M−H bond in changing from group 4 and 5 to group 6. It may, however, have much to do with the ligand set since, in a $W_2(H)(OR)_7$ compound, the metal may be much less oxophilic, having already nearly a full complement of metal−oxygen bonds. In any event, these early studies of the reactivity of polynuclear hydrido alkoxides of tungsten suggest that the reactivities of the other more

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[38] Chisholm, M. H.; Cook, C. M.; Huffman, J. C.; Streib, W. E. *Organometallics* **1993**, *12*, 2677.

[39] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

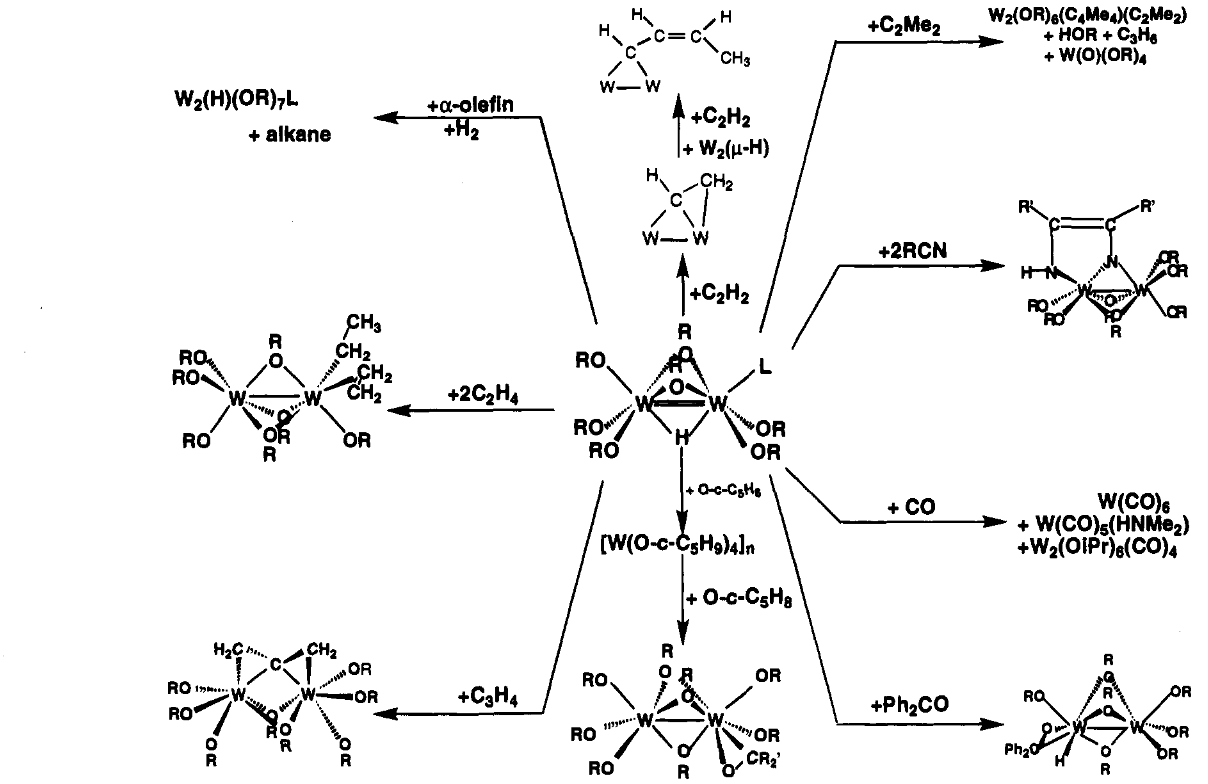
[40] (a) M = Mo: Chisholm, M. H.; Cotton, F. A.; Frenz, B. A.; Reichert, W. W.; Shive, L. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4469. (b) M = W: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477.

[41] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 1727.

[42] Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1983**, *105*, 5639.

[43] Förke, U.; Haupt, H.-J. *Z. Kristallogr.* **1990**, *191*, 298; Chacon, S. T.; Chisholm, M. H.; Folting, K. To be published.

Scheme 2



complex molecules mentioned in the introduction should surely be worthy of investigations. A final point worthy of comment or speculation concerns the potential mode of reactivity of a bridging hydride. Does a bridging hydride have to become a terminal hydride prior to reaction with a bound substrate? We believe that this is most plausible and that reactions reported here with ethene and ketones proceed through reactive intermediates wherein the hydride and unsaturated substrate are cis as is seen in $W_2(O\text{-}i\text{-}Pr)_7(H)(\eta^2\text{-}OCPh_2)$.

## Experimental Section

Dry and deoxygenated solvents and atmospheres were employed at all times. The preparations of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$[4] and $W_2(H)(O\text{-}c\text{-}C_5H_9)_7$[6] have been described previously, though an improved synthesis of the former is given below.

Ethyne, ethene, propene, 1-butene, 1-hexene, benzonitrile, acetonitrile, *tert*-butyl nitrile, and molecular hydrogen were obtained from commercial sources. The labeled gases $^{13}C_2H_2$, $^{13}C_2H_4$, and $C_2D_2$ were from Cambridge Isotopes. These were used without purification. $^1H$ and $^{13}C$ NMR spectra were recorded on Varian XL-300 (300 and 75 MHz, respectively) and Bruker AM-500 (500 and 126 MHz, respectively) NMR spectrometers and referenced to the residual solvent proton or carbon nuclei relative to TMS. Infrared spectra were recorded on a Perkin-Elmer 283 IR spectrophotometer or a Nicolet S10P FTIR spectrophotometer as KBr disks. Elemental analyses were obtained from Oneida Research Services Inc., Whitesboro, NY, with the exception of $W_2(H)(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}OCPh_2)$, which was obtained from Atlantic Microlabs, Inc., Norcross, GA. GC/MS were recorded with a HP5890 GC coupled to a HP5971 mass selective detector interfaced to a Hewlett-Packard Chem Station. The GC column used was a Supelco SPBS (60 m, 0.25 mm i.d.). The analyses of the products of the catalytic reactions were carried out with a Hewlett-Packard 5890 Series II gas chromatograph using a 2 m, 1 mm i.d. HayeSep S Micropack column. The chromatograph was connected to a Hewlett-Packard calculation integrator.

**Improved Synthesis of $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$.** The yield of this reaction has been improved substantially from those previously reported of 30% and 46% as follows. $W_2(NMe_2)_6$ (2.50 g, 3.95 mmol) was placed in a 100 mL Schlenk flask equipped with a Teflon-coated stir bar. Hexanes (35 mL) were added with stirring, and then 2-propanol (15 mL) was added. The solution was stirred for 4 days, after which time the solvent was removed in vacuo and the solid was recrystallized from pentane at −20 °C. Three batches of dark red crystals were isolated to give a total yield of 78% (2.41 g).

**Reactions: Preparation of $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$.** $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$ (1.383 g, 1.370 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and hexanes (5 mL) were added via cannula. The solution was frozen, the flask was evacuated, and 3 equiv of ethene was added with a calibrated vacuum manifold. The solution was allowed to warm to room temperature, the flask back-filled with nitrogen, and the solution allowed to stir overnight. After the solution was cooled overnight at −20 °C, small brown crystals of $W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)$ (0.971 mg, 0.951 mmol) was isolated in 69% yield. X-ray quality crystals were obtained by recrystallization from pentane at −20 °C. The crystals were always coated with an oil; therefore, elemental analysis was not performed. $^1H$ NMR (300 MHz, 22 °C, toluene-$d_8$, $\delta$): O-c-$C_5H_9$, C*H* 5.76 (br, 4H), 4.83 (br, 3H); $C_2H_4$ 4.30 (m, 1H), 3.61 (m, 1H), 3.61 (m, 1H), 2.22* (m, 1H), 1.89* (m, 1H), 2.36 (m, 3H, $CH_2CH_3$); $CH_2$-$CH_3$ 1.94* (m, 1H), 1.65* (m, 1H); O-c-$C_5H_9$, $CH_2$ 2.05−1.26 (br, overlapping m). Obscured peaks marked with an asterisk were located by using COSY experiments (500 MHz, 22 °C, toluene-$d_8$, $\delta$).

Signals of the $\eta^2\text{-}C_2H_4$ and $\eta^1\text{-}C_2H_5$ ligands were confirmed by reaction with $C_2D_4$. $^1H$ NMR (300 MHz, −20 °C, toluene-$d_8$, $\delta$): O-c-$C_5H_9$, C*H* 5.77 (m, 3H), 4.92 (m, 1H), 4.81 (m, 1H), 4.73 (m, 1H), 4.45 (m, 1H); $C_2H_4$ 4.16 (m, 1H), 3.57 (m, 1H), 2.33 (m, 3H, $CH_2CH_3$); O-c-$C_5H_9$, $CH_2$ 2.46−1.37 (overlapping multiplets). $^{13}C\{^1H\}$ NMR (126 MHz, 22 °C, toluene-$d_8$, $\delta$): O-c-$C_5H_9$, *C*H 89−84 (br s), 85.3 (s); $C_2H_4$ 54.3 (br s), 48.4 (s, $^1J_{C-W}$ = 27 Hz, 19%), 42.3 (s, $^1J_{C-W}$ = 96 Hz, 16%, $CH_2CH_3$); O-c-$C_5H_9$, $CH_2$ 37−32 (br), 37.0 (s), 35.6 (s), 35.5 (s), 35.2 (s), 34.2 (s), 24.5−23.7 (br), 24.3 (s), 24.1 (s), 23.9 (s); 18.2 (s, $CH_2CH_3$).

**$W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}^{13}C_2H_4)(\eta^1\text{-}^{13}C_2H_5)$.** $^{13}C$ NMR (75.7 MHz, 20 °C, toluene-$d_8$, $\delta$): $C_2H_4$ 54.3 ($^1J_{C-C}$ = 35 Hz, $^1J_{C-H}$ = 149 Hz), 48.5 ($^1J_{C-C}$ = 35 Hz, $^1J_{C-H}$ = 148 Hz); 42.5 (dt, $^1J_{C-C}$ = 36 Hz, $^1J_{C-H}$ = 113 Hz, $CH_2CH_3$); 18.0 (dq, $^1J_{C-C}$ = 36 Hz, $^1J_{C-H}$ = 124 Hz, $CH_2CH_3$).

**Reaction of $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(PMe_3)$ with $C_2H_4$.** $W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(PMe_3)$ (288 mg, 0.277 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and hexanes (5 mL) were added by cannula transfer. The solution was frozen in liquid nitrogen and evacuated, and 3 equiv of (0.83 mmol) ethene was added using a calibrated vacuum manifold. The solution was allowed to stir overnight at room temperature, reduced in vacuo, and placed at −20 °C to crystallize. About 20 mg were obtained, and the $^1$H NMR spectrum was identical to that obtained for $\mathrm{W_2(O\text{-}c\text{-}C_5H_9)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)}$.

**Preparation of $\mathrm{W_2(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)}$.** $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ (0.730 g, 0.466 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and hexanes (15 mL) were added by cannula transfer. The flask was frozen in liquid nitrogen and evacuated, and 4 equiv of ethene (1.845 mmol) was added via a calibrated vacuum manifold. The solution was allowed to warm to room temperature with stirring, back-filled with nitrogen, and stirred overnight. The solvent was removed *in vacuo*, and the remaining solid was recrystallized from pentane at −20 °C. $\mathrm{W_2(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}C_2H_4)(\eta^1\text{-}C_2H_5)}$ (331 mg, 0.395 mmol) was isolated as a brown solid in 42% yield. $^1$H NMR (500 MHz, 20 °C, toluene-$d_8$, $\delta$): $\mathrm{OC}H\mathrm{(CH_3)_2}$ 5.6−4.6 (br, overlapping m), 4.47 (septet, $J_{\mathrm{H(a)-H(i)}}$ = 6 Hz, $J_{\mathrm{H(a)-H(j)}}$ = 6 Hz, H(a), 1H); $\mathrm{C_2}H_4$ 4.38 (ddd, $J_{\mathrm{H(b)-H(b)-H(c)}}$ = 3 Hz, $J_{\mathrm{H(b)-H(c)}}$ = 10 Hz, $J_{\mathrm{H(b)-H(f)}}$ = 10Hz, H(b), 1H), 3.46 (ddd, $J_{\mathrm{H(c)-H(e)}}$ = 10 Hz, $J_{\mathrm{H(c)-H(f)}}$ = 10 Hz, H(c), 1H), 2.06 (ddd, $J_{\mathrm{H(e)-H(f)}}$ = 6 Hz, H(e), 1H), 1.93 (ddd, H(f), 1H); 2.31 (dd, $J_{\mathrm{H(d)-H(g)}}$ = 8 Hz, $J_{\mathrm{H(d)-H(i)}}$ = 7 Hz, H(d), 3H, $\mathrm{CH_2C}H_3$); $\mathrm{C}H_2\mathrm{CH_3}$ 1.76 (dt, $J_{\mathrm{H(g)-H(h)}}$ = 13.2 Hz, H(g), 1H), 1.56 (dt, H(h), 1H); $\mathrm{OCH(C}H_3)_2$ 1.37 (d, $J_{\mathrm{H-H}}$ = 6 Hz), 1.29 (d, $J_{\mathrm{H-H}}$ = 6 Hz), 1.5−1.1 (br, overlapping d), 0.97 (d, $J_{\mathrm{H-H}}$ = 6 Hz, H(i), 3H), 0.91 (d, $J_{\mathrm{H-H}}$ = 6 Hz, H(j), 3H). Coupling constants were established by using proton-decoupling experiments. H(a)−H(i) were used as arbitrary labels to identify the coupling constants. $^{13}$C{$^1$H} NMR (126 MHz, 22 °C, toluene-$d_8$, $\delta$): $\mathrm{O}C\mathrm{H(CH_3)_2}$ 79−74 (br, overlapping s), 76.7 (s), 75.8 (s); $C\mathrm{H_2CH_2}$ 53.3 (br s), 48.0 (s, $J_{\mathrm{C-W}}$ = 30 Hz, 16%), 42.6 (s, $J_{\mathrm{C-W}}$ = 100 Hz, 16%, $C\mathrm{H_2CH_3}$); $\mathrm{OCH(}C\mathrm{H_3)_2}$ 28.5−23.5 (br, overlapping s), 27.6 (s), 26.3 (s), 25.0 (s), 24.0 (s), 23.8 (s), 17.9 (s, $\mathrm{CH_2}C\mathrm{H_3}$).

**$\mathrm{W_2(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}{}^{13}C_2H_4)(\eta^1\text{-}{}^{13}C_2H_5)}$.** $^{13}$C NMR (76 MHz, 22 °C, toluene-$d_8$, $\delta$): $C_2\mathrm{H_4}$ 53.3 (dt, $^1J_{\mathrm{C-C}}$ = 34 Hz, $^1J_{\mathrm{C-H}}$ = 151 Hz), 47.9 (dt, $^1J_{\mathrm{C-C}}$ = 34 Hz, $^1J_{\mathrm{C-H}}$ = 149 Hz), 42.4 (dt, $^1J_{\mathrm{C-C}}$ = 36 Hz, $^1J_{\mathrm{C-H}}$ = 118 Hz, $C\mathrm{H_2CH_3}$), 17.9 (dq, $^1J_{\mathrm{C-C}}$ = 36 Hz, $^1J_{\mathrm{C-H}}$ = 123 Hz, $\mathrm{CH_2}C\mathrm{H_3}$).

**$\mathrm{W_2(\mu\text{-}H)(OR)_7L}$ + α-Olefins.** $\mathrm{W_2(\mu\text{-}H)(OR)_7L}$ (0.02 g, 0.01 mmol) was placed in an NMR tube, and toluene-$d_8$ (0.3 mL) was added under a nitrogen atmosphere. The solution was frozen and evacuated, and 10 equiv of olefin was added using a calibrated vacuum manifold. The tube was sealed with a torch, and the solution was warmed to room temperature. $^1$H NMR spectra were taken over a period of 2 weeks without any observable change. Variable temperature spectra of the sample were run from 60 °C to −60 °C, and no change in organometallic species was observed. For 1-butene and 1-hexene, $^1$H NMR resonances were consistent with a mixture of the isomerized olefin (i.e. *cis*- and *trans*-2-butene from 1-butene).

**α-Olefin Hydrogenation.** $\mathrm{W_2(\mu\text{-}H)(OR)_7L}$ (0.02 g, 0.01 mmol) was placed in an NMR tube equipped with a J. Young valve, and toluene-$d_8$ (0.3 mL) was added under a nitrogen atmosphere. Olefin (10 equiv) was added via syringe under a nitrogen atmosphere (styrene), and the solution was frozen and evacuated; or the solution was frozen and evacuated and the olefin was condensed in by using a calibrated vacuum manifold. An excess (3 atm) of $\mathrm{H_2}$ was then added using a calibrated vacuum manifold. The tube was closed, and the solution was warmed to room temperature. The $^1$H NMR spectra were monitored over the next 4 days at certain time intervals. The signals for olefin and alkane were integrated during each run to permit determination of the concentration of species present. A plot of ln[olefin] vs time yields a slope from which the turnover rate was determined.

**Catalytic Runs for Propene and 1-Butene at 1 atm.** In the hydrogenation reaction, the catalyst [0.03 mmol of $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ or 0.05 mmol of $\mathrm{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)}$], toluene (1.0 mL), and a Teflon-coated stir bar were placed in a 30 mL Schlenk flask fitted with a rubber septum under nitrogen. The flask was then frozen and evacuated. The olefin substrate (0.60 mmol for reaction with $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$; 0.51 mmol for reaction with $\mathrm{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)}$) was condensed into the flask. $\mathrm{H_2}$ (1 atm) was then transferred into the flask using a calibrated vacuum manifold. The flask was then removed from the liquid nitrogen and allowed to warm to room temperature. The solution was stirred for 10 min to allow for equilibrium. The solution was sampled at regular intervals by using a 20 μL GC syringe via the rubber septum, and the samples (10 μL aliquots) were analyzed with a gas chromatograph equipped with a hydrocarbon column.

**Reaction of $\mathrm{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)}$ with $\mathrm{C_3H_4}$.** $\mathrm{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)}$ (0.937 g, 0.928 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and pentane (10 mL) was added via cannula transfer. The flask was frozen in liquid nitrogen and evacuated, and 3 equiv (2.8 mmol) of allene was added by using a calibrated vacuum manifold. Upon warming to room temperature, some color changes were observed. Immediately, upon the melting of the solvent, a yellow-brown precipitate was formed. As the solution was warmed further, the precipitate dissolved and a green solution was obtained after about 10 min. After 1 h, the solution appeared brown-red, and the color did not change after stirring overnight at room temperature. The solution was then reduced in vacuo and cooled to −20 °C. Two types of crystals formed, brown cubes and brown needles, which were not separated, to give a total yield of 330 mg of solid. The crystal structure of the brown cubes was obtained, and the product was $\mathrm{W_2(O\text{-}c\text{-}C_5H_9)_8(\mu\text{-}CH_2CCH_2)}$. The spectroscopic data are from the mixture of products. $^1$H NMR (300 MHz, 22 °c, toluene-$d_8$, $\delta$): O-c-$\mathrm{C_5H_9}$, C$H$ 5.77 (m, 2H), 5.57 (m, 4H), 5.28 (m, 1H), other resonances are broad and unresolved; $\mathrm{C_3}H_4$ 4.87 (m, 2H), 4.60 (m, 2H), 3.70 (s, 4H); O-c-$\mathrm{C_5H_9}$, C$H_2$ 1.92−1.58 (overlapping multiplets). $^1$H NMR (300 MHz, −40 °C, toluene-$d_8$, $\delta$): O-c-$\mathrm{C_5H_9}$, C$H$ 6.30 (m, 1H), 6.00 (m, 1H), 5.84 (m, 1H), 5.58 (m, 1H), 5.02 (m, 1H), 4.90 (m, 1H), 4.86 (m, 1H), 4.50 (m, 1H), $\mathrm{C_3}H_4$ 5.02 (m, 1H), 4.54 (m, 1H), 4.38 (d, 1H), 4.16 (d, 1H), 5.98 (m, 1H), 3.72 (s, 2H); O-c-$\mathrm{C_5H_9}$, C$H_2$ 2.3−1.2 (overlapping multiplets).

**Reaction of $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ with $\mathrm{C_3H_4}$.** $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ (664 mg, 0.424 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and pentane (5 mL) was added via cannula transfer. The solution was frozen in liquid nitrogen and evacuated, and 6 equiv of allene (2.55 mmol) was added using a calibrated vacuum manifold. No color change was observed as the red brown solution was warmed to 0 °C, and upon the solution being warmed to room temperature, it became green. The solution was stirred overnight, reduced in vacuo, and cooled to −20 °c. A brown solid was isolated (478 mg). This solid also appeared to contain a mixture of products, and the spectroscopic data are from this mixture. No elemental analysis was performed on this mixture, but single crystals of one component were examined by X-ray diffraction. $^1$H NMR (300 MHz, 20 °C, toluene-$d_8$, $\delta$): $\mathrm{C_3}H_4$ 6.83 (m, 1H), 6.10 (m, 1H), 4.76 (m, 2H), 4.49 (m, 2H), 3.73 (m, 4H); $\mathrm{OC}H\mathrm{(CH_3)_2}$ 5.8−4.3 (overlapping septets); $\mathrm{OCH(C}H_3)_2$ 1.1−1.6 (overlapping d). $^1$H NMR (300 MHz, −40 °C, toluene-$d_8$, $\delta$): $\mathrm{C_3}H_4$ 6.93 (m, H(a), 1H), 6.16 (m, H(b), 1H), 4.87 (m, H(c), 1H), 4.82 (m, H(d), 1H), 4.57 (m, H(e), 1H), 4.40 (m, H(f), 1H), 3.72 (s, 4H); $\mathrm{OC}H\mathrm{(CH_3)_2}$ 5.92, 5.32, 4.64, 4.12, 4.08 (overlapping septets); $\mathrm{OCH(C}H_3)_2$ 1.82−0.89 (overlapping d).

Decoupling experiments determined that the following protons couple to each other: [H(a) and H(b)], [H(c) and H(e)], and [H(d) and H(f)].

**$\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ + 1,3-Butadiene.** $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ 0.200 g, 0.128 mmol) was placed in a 100 mL Schlenk flask equipped with a Teflon-coated stir bar, and approximately 20 mL of hexanes was added via cannula transfer. The solution was frozen and evacuated, and 2 equiv of 1,3-butadiene (0.256 mmol) was added using a calibrated vacuum manifold. The solution was slowly warmed to room temperature. The mixture was stirred overnight and turned a pine green color. The solvent was removed in vacuo, leaving a green oil. The oil was redissolved in approximately $^1/_2$ mL of pentane and stored at −20 °C for 2 weeks but did not yield any crystalline and/or solid material. Under slow evaporation of the solvent in a static vacuum, a white fluffy volatile material came out of the oil. This material was identified to be $\mathrm{W(O)(O\text{-}i\text{-}Pr)_4}$ from $^1$H NMR spectroscopy. The oil was then dried in vacuo.

**Green Oil.** $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 8.61 (dd, 1H, $J_{\mathrm{H-H}}$ = 2 Hz, $J_{\mathrm{H-H}}$ = 15 Hz), 8.42 (dd, 1H, $J_{\mathrm{H-H}}$ = 3 Hz, $J_{\mathrm{H-H}}$ = 12 Hz); $\mathrm{OC}H\mathrm{(CH_3)_2}$ 5.31 (sep, 5H), 4.96 (br, s, 7H), 2.22 (dd, 4H, $J_{\mathrm{H-H}}$ = 2 Hz, $J_{\mathrm{H-H}}$ = 7 Hz); $\mathrm{OCH(C}H_3)_2$ 1.41 (d, 32H), 1.32 (d, 42H).

**$\mathrm{W(O)(O\text{-}i\text{-}Pr)_4}$.** $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 5.09 (sep, 1H, $\mathrm{OC}H\mathrm{(CH_3)_2}$), 1.34 (d, 6H, $\mathrm{OCH(C}H_3)_2$.

In a separate experiment, the volatile components were isolated and a $^1$H NMR spectrum was run. The major products were determined to be propene and 2-propanol from $^1$H NMR spectroscopy and GC/MS.

**$W(O)(O\text{-i-Pr})_4$.** $W(O)(O\text{-t-Bu})_4$ (0.200 g, 0.479 mmol) was placed in a 50 mL Schlenk flask equipped with a Teflon-coated stir bar, and approximately 5 mL of hexanes was added via cannula transfer. 2-Propanol (520.6 $\mu$L, 6.70 mmol) was added via syringe. The mixture was stirred, and within 1 min, a white material precipitated out of solution. The solvent was removed in vacuo, leaving a white solid. $^1$H NMR spectroscopic data of the crude material revealed that complete alcoholysis had occurred. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 5.09 (sep, 1H, $OC\mathit{H}(CH_3)_2$), 1.34 (d, 6H, $OCH(C\mathit{H}_3)_2$.

**$W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$ + 1,3-Butadiene.** $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$ (0.200 g, 0.198 mmol) was placed in a 100 mL Schlenk flask equipped with a Teflon-coated stir bar, and approximately 5 mL of hexanes was added via cannula transfer. The solution was frozen and evacuated, and 2 equiv of 1,3-butadiene (0.390 mmol) was added using a calibrated vacuum manifold. The solution was slowly warmed to room temperature. The mixture was stirred overnight and turned a pine green color. The solvent was removed in vacuo, leaving a green oil. The oil was dissolved in approximately $^1/_2$ mL of pentane and stored at −20 °C for 2 weeks without formation of crystalline material. The oil was dried in vacuo. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 8.5 (dd); $O\text{-c-}C_5H_9$, $C\mathit{H}$ 6.2−4.6 (br, overlapping m), 5.6 (br s), 5.2 (br s), 3.1 (s), 2.6 (m), 2.2 (dd); $O\text{-c-}C_5H_9$, $C\mathit{H}_2$ 2.2−1.0 (br, overlapping s), 0.88 (m). (Due to significant line broadening and a possible mixture of products, integrals were not obtained.) $^{13}C\{^1H\}$ NMR (300 MHz, 22 °C, toluene-$d_8$, $\delta$): 151.7, 151.0, 148.8, 93.1, 92.2, 87.8, (d), 87.0, 86.8, 86.3, 85.8, 85.4, 85.1, 82.0, 41.3, 38.3 (d), 37.4, 36.9, 36.7, 35.6, 35.7, 33.7, 28.3, 28.2, 24.2, 24.0, 18.8, 1.4. IR (cm$^{-1}$): 2900 (w), 2850 (w), 2363 (s), 2300 (s), 1250 (w), 1150 (w), 950 (m), 800 (w).

**$W(O)(O\text{-c-}C_5H_9)_4$.** $W(O)(O\text{-t-Bu})_4$ (0.200 g, 0.479 mmol) was placed in a 50 mL Schlenk flask equipped with a Teflon-coated stir bar, and approximately 5 mL of hexanes was added via cannula transfer. Cyclopentanol (434.3 $\mu$L, 4.78 mmol) was added via syringe. The mixture was stirred overnight. The solvent was removed in vacuo, leaving a white solid. $^1$H NMR spectroscopic data of the crude material revealed complete exchange of O-t-Bu for $O\text{-c-}C_5H_9$. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 5.21 (br s, $O\text{-c-}C_5H_9$, $C\mathit{H}$, 1H); $O\text{-c-}C_5H_9$, $C\mathit{H}_2$ 1.96 (br s, 2H), 1.77 (br s, 4H), 1.68 (br s, 2H).

**Preparation of $W_4(O\text{-c-}C_5H_9)_{16}$.** $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$ (586 mg, 0.580 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and hexanes (10 mL) were added by cannula transfer. One equivalent of cyclopentanone (51 $\mu$L) was added by syringe, and the solution was stirred overnight, during which time it darkened in color from red-brown to brown. The solvent was removed in vacuo, and the solid was recrystallized from pentane at −20 °C. Three batches of brown solid (326 mg, 0.155 mmol) were isolated in 53% yield. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): $C\mathit{H}$ 5.96, 5.66, 5.5, 4.82, 4.01 (br, overlapping m); $C\mathit{H}_2$ 2.92, 1.85, 1.58 (br, overlapping m).

Anal. Calcd for $C_{20}H_{36}O_4W$: C, 45.81; H, 6.92. Found: C, 45.67; H, 6.82.

**Preparation of $W_2(O\text{-c-}C_5H_9)_8(\eta^2\text{-O-c-}C_5H_8)$.** $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$ (384 mg, 0.380 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and hexanes (5 mL) were added via cannula transfer. Two equivalents of cyclopentanone ($O\text{-c-}C_5H_8$, 67 $\mu$L) was added by syringe, and the solution was stirred overnight at room temperature. The solvent was reduced in vacuo and cooled to −20 °C overnight.

$W_2(O\text{-c-}C_5H_9)_8(\eta^2\text{-O-c-}C_5H_8)$ (167 mg, 0.147 mmol) was isolated in 38% yield. This solid decomposed after 2 days at room temperature in a nitrogen atmosphere. $^1$H NMR (500 MHz, 22 °C, benzene-$d_6$, $\delta$): $O\text{-c-}C_5H_9$, $C\mathit{H}$ 5.97 (br), 5.63 (br m), 4.08 (br), 2.89 (br m); $O\text{-c-}C_5H_9$, $C\mathit{H}_2$ 2.10−1.37 (overlapping m). $^{13}C\{^1H\}$ NMR (126 MHz, 22 °C, benzene-$d_6$, $\delta$): 103.6, 84.4, 40.6, 36.7, 36.2, 35.0, 34.9, 34.8, 34.7, 27.6, 23.8, 23.7, 23.6, 23.4, 23.3, 23.2, 23.0, 22.9.

**Preparation of $W_2(H)(O\text{-i-Pr})_7(\eta^2\text{-}OCPh_2)$.** $[W_2(\mu\text{-H})(O\text{-i-Pr})_7]_2$ (0.100 g, 0.0639 mmol) and benzophenone (0.045 g, 0.247 mmol) were placed in a 50 mL Schlenk flask equipped with a Teflon-coated stir bar, and pentane (10 mL) was added via cannula transfer. The solution was stirred overnight at room temperature. The solvent was reduced in vacuo and cooled to −20 °C overnight. Medium-sized dark green crystals were isolated (0.120 g) in 97% yield. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): Ph 8.05 (d, 1H), 7.68 (br d, 1H), 7.25 (t, 1H), 7.18 (t, 1H), 6.99 (br m, 2H); $OC\mathit{H}(CH_3)_2$ 5.40 (sep, 4H), 4.3−5.0 (br m, 2H), 3.53 (sep, 1H); $OCH(C\mathit{H}_3)_2$ 2.00 (d, 3H), 1.93 (d, 3H), 1.39 (d, 6H), 1.31 (d, 18H), 1.21 (d, 6H), 1.07 (d, 3H), 0.67 (d, 3H); terminal H 13.17 ($J_{W-H} = 126$ Hz, 16%). $^1$H NMR (300 MHz, −20 °C, toluene-$d_8$, $\delta$): all signals same as above, broadened a bit except for $OC\mathit{H}(CH_3)_2$ 5.42 (sep, 4H), 4.88 (sep, 1H), 4.46 (br sep, 1H), 3.53 (sep, 1H). IR (cm$^{-1}$): 2971 (br m, s), 1875 (w, W−H), 1597 (w), 1491 (w), 1445 (w), 1375 (m), 1327 (m), 1163 (m), 1111 (s), 980 (s), 841 (m), 745 (w), 704 (m), 679 (w), 600 (m). Anal. Calcd for $W_2(H)(O\text{-i-Pr})_7(\eta^2\text{-}OCPh_2)$, $W_2O_8C_{34}H_{60}$: C, 42.33; H, 6.28. Found: C, 42.40; H, 6.21.

**$W_2(D)(O\text{-i-Pr})_7(\eta^2\text{-}OCPh_2)$.** IR (cm$^{-1}$): 2971 (br m, s), 1597 (w), 1491 (w), 1375 (m), 1327 (m), 1278 (w, W−D), 1163 (m), 1111 (s), 980 (s), 841 (m), 745 (w), 704 (m), 679 (w), 600 (m).

**Preparation of $W_2(H)(O\text{-i-Pr})_7(\eta^2\text{-}O^{13}CPh_2)$.** $[W_2(\mu\text{-H})(O\text{-i-Pr})_7]_2$ (0.010 g, 0.006 mmol) and $O^{13}CPh_2$ (0.005 g, 0.025 mmol) were placed in an NMR tube. Benzene-$d_6$ (0.5 mL) was added, the tube was shaken, and the reaction mixture was allowed to sit overnight. $^1$H and $^{13}$C NMR spectra were taken the following day. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): all signals are the same as $W_2(H)(O\text{-i-Pr})_7(\eta^2\text{-}OCPh_2)$ except that for the hydride, 13.17 (d, $^2J_{^{13}C-H} = 8$ Hz, $J_{W-H} = 126$ Hz). $^{13}C\{^1H\}$. (300 MHz, 22 °C, benzene-$d_6$, $\delta$): $\eta^2\text{-}O\mathit{C}Ph_2$ 93.58 ($J_{W-C} = 23$ Hz). $^{13}$C (300 MHz, 22 °C, benzene-$d_6$, $\delta$): Ph 133.12 (t), 130.99 (t), 129.47 (m), 127.29 (m), 109.19 (s); $\eta^2 O\mathit{C}Ph_2$ 93.53 (d, $^2J_{^{13}C-H} = 8$ Hz); $O\mathit{C}H(CH_3)_2$ 79.37 (m), 75.22 (s), 73.34 (s), 57.44 (s), 55.83 (s); $OCH(\mathit{C}H_3)_2$ 25.76 (m).

**Preparation of $W_2(H)(O\text{-c-}C_5H_9)_7(\eta^2\text{-}OCPh_2)$.** $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$ (0.200 g, 0.198 mmol) and benzophenone (0.053 g, 0.274 mmol) were placed in a 50 mL Schlenk flask equipped with a Teflon-coated stir bar, and pentane (10 mL) was added via cannula transfer. The mixture was stirred overnight, during which it turned dark brown. The solvent was reduced in vacuo and cooled to −20 °C overnight. Brown crystals (0.191 g) were isolated in 84% yield. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): hydride 13.61 (s, 1H, $J_{W-H} = 126$ Hz); Ph 8.07 (d, 1H), 7.71 (d, 1H), 7.27 (dt, 2H), 7.01 (m, 2H); $O\text{-c-}C_5H_9$, $C\mathit{H}$ 4.3−6.0 (br, overlapping m, 4H), 3.07 (br m, 1H), 2.83 (br m, 1H); $O\text{-c-}C_5H_9$, $C\mathit{H}_2$ 1.2−2.4 (br overlapping, m). IR (cm$^{-1}$): 2957 (br m), 1860 (w), 1661 (w), 1597 (w), 1491 (w), 1447 (m), 1337 (m), 1277 (m), 1167 (m), 1003 (s), 939 (w), 860 (m), 808 (m), 747 (m), 704 (s), 621 (w), 546 (w). Anal. Calcd for $W_2(H)(O\text{-c-}C_5H_9)_7(\eta^2\text{-}OCPh_2)$, $W_2O_8C_{48}H_{74}$: C, 50.27; H, 6.52. Found: C, 50.45; H, 6.00.

**Low-Temperature Solution NMR Studies of the Reaction of $[W_2(\mu\text{-H})(O\text{-i-Pr})_7]_2$ with $C_2H_2$.** $[W_2(\mu\text{-H})(O\text{-i-Pr})_7]_2$ (20 mg, 0.01 mmol) was placed in an NMR tube, and toluene-$d_8$ (0.3 mL) was added under a nitrogen atmosphere. The solution was frozen and evacuated, and 4 equiv (0.04 mmol) of $C_2H_2$ was added using a calibrated vacuum manifold. The tube was sealed with a torch, warmed to −72 °C, and then placed in the NMR spectrometer at −40 °C. $^1$H NMR (300 MHz, −40 °C, toluene-$d_8$, $\delta$): 12.55 (br, $J_{H-W} = 56$ Hz (15%), $J_{H-W} = 82$ Hz (15%), 1.5H, $\mu\text{-}\mathit{H}$, trans to $C_2H_2$), 10.87 (s, $J_{H-W} = 102$ Hz (11%), $J_{H-W} = 79$ Hz (13%), 1H, $\mu\text{-}\mathit{H}$, cis to $C_2H_2$); $C_2H_2$ 11.91, 11.90 (overlapping s, 4H); $OC\mathit{H}(CH_3)_2$ 5.86−4.36 (overlapping septets, 17H); $OCH(C\mathit{H}_3)_2$ 1.78−0.86 (overlapping d, 105H).

After a few minutes, the hydride resonance at $\delta$ 12.55 disappeared.

**Low-Temperature Solution NMR Studies of the Reaction of $[W_2(\mu\text{-H})(O\text{-i-Pr})_7]_2$ with $^{13}C_2H_2$.** $[W_2(\mu\text{-H})(O\text{-i-Pr})_7]_2$ (20 mg, 0.01 mmol) was placed in an NMR tube, and toluene-$d_8$ (0.3 mL) was added under a nitrogen atmosphere. The solution was frozen and evacuated, and 4 equiv (0.04 mmol) of $^{13}C_2H_2$ was added using a calibrated vacuum manifold. The tube was sealed with a torch, warmed to −72 °C, and then placed in the NMR spectrometer at −40 °C. $^1$H NMR (300 MHz, −40 °C, toluene-$d_8$, $\delta$): 11.89 (dt, $^1J_{H-C} = 200$ Hz, $^2J_{H-C} = 25$ Hz, $J_{H-H} = 25$ Hz), and other resonances similar to above experiment. $^{13}$C NMR (76 MHz, 22 °C, toluene-$d_8$, $\delta$): 195.2 (dd, $^1J_{C-H} = 176$ Hz, $^2J_{C-H} = 26$ Hz), 187.0 (dt, $^1J_{C-H} = 202$ Hz, $^2J_{C-H} = 25$ Hz, $J_{C-C} = 25$ Hz, $J_{C-W} = 43$ Hz, 16%). The resonance at $\delta$ 195.2 disappeared with time.

**Low-Temperature Solution NMR Studies of the Reaction of $W_2(\mu\text{-H})(O\text{-C-}C_5H_9)_7(HNMe_2)$ with $^{13}C_2H_2$.** $W_2(\mu\text{-H})(O\text{-c-}C_5H_9)_7(HNMe_2)$ (10 mg, 0.01 mmol) was placed in an NMR tube equipped with a J. Young valve, and toluene-$d_8$ (0.3 mL) was added under nitrogen. The solution was frozen, and 1 equiv (0.01 mmol) of $^{13}\mathrm{C_2H_2}$ was added with a calibrated vacuum manifold. The solution was warmed to −72 °C in a dry ice/acetone bath, and a vacuum was applied with shaking until the solution was well-degassed and the excess ethyne removed. $^1$H NMR (300 MHz, −40 °C, toluene-$d_8$, $\delta$): 12.56 (s, $J_{\mathrm{H-W}} = 54$ Hz (14%), $J_{\mathrm{H-W}} = 83$ Hz (14%), $\mu$-$H$), 11.94 (dt, $^1J_{\mathrm{H-C}} = 200$ Hz, $^2J_{\mathrm{H-C}} = 25$ Hz, $J_{\mathrm{H-C}} = 25$ Hz, $J_{\mathrm{H-H}} = 25$ Hz, $\mathrm{C_2}H_2$); O-c-$\mathrm{C_5H_9}$, C$H$ 6.11 (br m, 1H), 5.96 (br m, 1H), 5.78 (br m, 1H), 5.22 (br m, 1H), 5.10 (br m, 1H), 4.99 (br m, 1H), 4.66 (br m, 1H), 2.6−1.2 (br overlapping m, O-c-$\mathrm{C_5H_9}$, C$H_2$). $^{13}$C NMR (76 MHz, −40 °C, toluene-$d_8$, $\delta$): 186.1 (dt, $^1J_{\mathrm{C-H}} = 200$, $^2J_{\mathrm{C-H}} = 25$ Hz, $J_{\mathrm{C-C}} = 25$ Hz, $J_{\mathrm{C-W}} = 40$ Hz, 15%, $C_2\mathrm{H_2}$).

The solution was then allowed to warm to room temperature for 3 h, and the spectra were recorded again. $^1$H NMR (300 MHz, 22 °C, toluene-$d_8$, $\delta$): 9.63 (dt, $J_{\mathrm{H-C}} = 165$ Hz, $J_{\mathrm{H-H}} = 5$ Hz, $\mathrm{W_2C}H\mathrm{{=}CH_2}$); O-c-$\mathrm{C_5H_9}$, C$H$ 5.57 (br m, 3H), 5.32 (br m, 4H), 3.18 (dd, $J_{\mathrm{H-C}} = 155$ Hz, $J_{\mathrm{H-H}} = 5$ Hz, $\mathrm{W_2CH{=}C}H_2$), 2.0−1.5 (br, overlapping m, O-c-$\mathrm{C_5H_9}$, C$H$). $^{13}$C NMR (76 MHz, 22 °C, toluene-$d_8$, $\delta$): 145.0 (dd, $J_{\mathrm{C-C}} = 20$ Hz, $J_{\mathrm{C-H}} = 165$ Hz, $J_{\mathrm{C-W}} = 60$ Hz, 16%), 61.4 (br dt, $J_{\mathrm{C-H}} = 154$ Hz, $J_{\mathrm{C-C}}$ obscured by width of peak).

When ethyne was added to this NMR tube, the obtained final product containing $\mathrm{W_2CHCH{=}CHCH_3}$ was the same as that for the room-temperature reaction.

**Reaction of $\mathbf{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)}$ with $\mathbf{C_2H_2}$.** $\mathrm{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)}$ (744 mg, 0.737 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and toluene (5 mL) was added via cannula transfer. The solution was frozen in liquid nitrogen and evacuated, and 2 equiv of $\mathrm{C_2H_2}$ (1.5 mmol) was added by using a calibrated vacuum manifold. As the brown-orange solution was warmed to room temperature, there was no color change after 10 min. After the solution was stirred for 1 h at room temperature, it appeared dark wine red. The solution was allowed to stir overnight at room temperature. Then the solution was filtered to remove polyacetylene, and the solvent was removed from the filtrate in vacuo. A brown-red solid was crystallized from pentane at −20 °C. Red-brown microcrystals were isolated by recrystallization from pentane at −20 °C (364 mg). $^1$H NMR (300 MHz, 22 °C, toluene-$d_8$, $\delta$): 7.99 (d, $^3J_{\mathrm{H-H}} = 13$ Hz, 1H, $\mathrm{W_2C}H\mathrm{CH{=}CHCH_3}$), 6.34 (ddq, $^3J_{\mathrm{H-H}} = 13$ Hz, $^3J_{\mathrm{H-H}} = 15$ Hz, $^4J_{\mathrm{H-H}} = 1$ Hz, 1H, $\mathrm{W_2CHC}H\mathrm{{=}CHCH_3}$), 4.56 (dq, $^3J_{\mathrm{H-H}} = 15$ Hz, $^3J_{\mathrm{H-H}} = 6$ Hz, 1H, $\mathrm{W_2CHCH{=}C}H\mathrm{CH_3}$), 2.53 (dd, $^3J_{\mathrm{H-H}} = 6$ Hz, $^4J_{\mathrm{H-H}} = 1$Hz, 3H, $\mathrm{W_2CHCH{=}CHC}H_3$) 5.52 (br m, 8H, O-c-$\mathrm{C_5H_9}$, C$H$), 2.02−1.3 (br overlapping m, 128H, O-c-$\mathrm{C_5H_9}$, C$H_2$). $^1$H NMR (300 MHz, −80 °C, toluene-$d_8$, $\delta$): 7.96 (d, 1H, $\mathrm{W_2C}H\mathrm{CH{=}CHCH_3}$), 6.35 (t, 1H, $\mathrm{W_2CHC}H\mathrm{{=}CHCH_3}$), 4.56 (dq, 1H, $\mathrm{W_2CHCH{=}C}H\mathrm{CH_3}$), 2.53 (dd, 3H, $\mathrm{W_2CHCH{=}CHC}H_3$); O-c-$\mathrm{C_5H_9}$, C$H$ 6.67 (m, 2H), 6.12 (m, 2H), 5.64 (m, 2H), 5.46 (m, 1H), 4.96 (m, 2H), 3.95 (m, 1H), 2.87 (m, 3H) 2.3−1.3 (br, overlapping m, O-c-$\mathrm{C_5H_9}$, C$H_2$).

**Solution NMR Studies of the Reaction of $\mathbf{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)}$ with $\mathbf{^{13}C_2H_2}$.** $\mathrm{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_3)}$ (10 mg, 0.01 mmol) was placed in an NMR tube, and benzene-$d_6$ (0.3 mL) was added under a nitrogen atmosphere. The solution was frozen in liquid nitrogen and evacuated, and 2 equiv of $^{13}\mathrm{C_2H_2}$ (0.02 mmol) was added using a calibrated vacuum manifold. The tube was sealed with a torch, and the solution was allowed to warm to room temperature. $^{13}$C NMR (76 MHz, 22 °C, benzene-$d_6$, $\delta$): 165.6 (dd, $J_{\mathrm{C-C}} = 38$ Hz, $J_{\mathrm{C-H}} = 138$ Hz, $J_{\mathrm{C-W}} = 70$ Hz, 22%, $\mathrm{W_2}C\mathrm{HCH{=}CHCH_3}$), 144.5 (ddd, $J_{\mathrm{C-C}} = 38$ Hz, $J_{\mathrm{C-C}} = 70$ Hz, $J_{\mathrm{C-H}} = 145$ Hz, $\mathrm{W_2CH}C\mathrm{H{=}CHCH_3}$), 120.6 (dd, $J_{\mathrm{C-C}} = 45$ Hz, $J_{\mathrm{C-C}} = 70$ Hz, $J_{\mathrm{C-H}} = 149$ Hz, $\mathrm{W_2CHCH{=}}C\mathrm{HCH_3}$), 16.8 (dq, $J_{\mathrm{C-C}} = 45$ Hz, $J_{\mathrm{C-H}} = 125$ Hz, $\mathrm{W_2CHCH{=}CH}C\mathrm{H_3}$). IR (cm$^{-1}$, KBr): 2040 (s), 2900 (sh m), 2860 (m), 2324 (w), 1460 (w), 1483 (w), 1335 (m), 1160 (m), 1030 (m), 995 (s), 970 (sh), 932 (w), 860 (w). Anal. Calcd for $\mathrm{W_4(O\text{-}c\text{-}C_5H_9)_{16}(C_4H_6)}$, $\mathrm{W_4O_{16}C_{84}H_{150}}$: C, 46.89; H, 7.03. Found: C, 46.82; H, 6.88.

**Reaction of $\mathbf{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(PMe_3)}$ with $\mathbf{C_2H_2}$.** $\mathrm{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(PMe_3)}$ (10 mg, 0.01 mmol) was placed in an NMR tube, and toluene-$d_8$ (0.3 mL) was added under a nitrogen atmosphere. The solution was frozen in liquid nitrogen and evacuated, and 1 equiv of $\mathrm{C_2H_2}$ (0.01 mmol) was added using a calibrated vacuum manifold. The tube was sealed with a torch, the solution was warmed to −40 °C, and NMR spectra were run immediately. The presence of the $\mathrm{PMe_3}$ ligand appeared to slow down the ethyne coupling. Warming to room temperature for 10 min allowed for the observation of the ethyne complex and the coupled $\mathrm{W_2(CHCH{=}CHCH_3)}$-containing product with an NMR spectrum identical to that observed for the product obtained from the reaction with $\mathrm{W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)}$, but no $\mathrm{W_2\text{-}CHCH_2}$-containing product was present.

**Reaction of $\mathbf{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ with $\mathbf{C_2H_2}$.** $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ (526 mg, 0.336 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and toluene (5 mL) was added via cannula transfer. The solution was frozen in liquid nitrogen and evacuated and 4 equiv of $\mathrm{C_2H_2}$ (1.34 mmol) was added using a calibrated vacuum manifold. The solution was warmed to room temperature and stirred overnight. The solution was filtered to remove the polyacetylene precipitate. The solvent was removed in vacuo, and the resulting brown-red solid was recrystallized from pentane at −20 °C. A brown solid was obtained (92 mg). The spectroscopic properties of this solid indicate no incorporation of ethylene, and the spectra are different from those of in situ solution studies that follow. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 5.25 (septet, $J_{\mathrm{H-H}} = 5$ Hz, 1H), 1.32 (d, 6H). $^{13}$C NMR (126 MHz, 22 °C, toluene-$d_8$, $\delta$): 76.8 (dm, $^1J_{\mathrm{C-H}} = 125$ Hz), 25.0 (qm, $J_{\mathrm{C-H}} = 145$ Hz). IR (cm$^{-1}$): 2960 (s), 2916 (m), 2883 (m), 2860 (m), 2345 (w), 1370 (m), 1360 (m), 1320 (w), 1160 (m), 1110 (s), 960 (s), 840 (m), 600 (m), 238 (m). Anal. Calcd for $\mathrm{W_2(O\text{-}i\text{-}Pr)_7}$, $\mathrm{C_{21}H_{49}O_7W_2}$: C, 32.28; H, 6.32. Found: C, 32.25; H, 5.85. Note that we are not implying here that this is a discrete compound of formula $\mathrm{W_2(O\text{-}i\text{-}Pr)_7}$.

**Room-Temperature NMR Studies of the Reaction of $\mathbf{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ with $\mathbf{^{13}C_2H_2}$.** $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ (20 mg, 0.01 mmol) was placed in an NMR tube, and toluene-$d_8$ (0.3 mL) was added under a nitrogen atmosphere. The solution was frozen and evacuated, and 4 equiv (0.04 mmol) of $^{13}\mathrm{C_2H_2}$ was added using a calibrated vacuum manifold. The tube was sealed with a torch, and the solution was warmed to room temperature. $^1$H NMR (300 MHz, 22 °C, toluene-$d_8$, $\delta$): 8.13 (dm, $J_{\mathrm{H-C}} = 135$ Hz, 1H, $\mathrm{W_2C}H\mathrm{CH{=}CHCH_3}$), 6.47 (dm, $J_{\mathrm{H-C}} = 153$ Hz, 1H, $\mathrm{W_2CHC}H\mathrm{{=}CHCH_3}$), 4.47 (dm, 1H, $J_{\mathrm{H-C}} = 150$ Hz, $\mathrm{W_2CHCH{=}C}H\mathrm{CH_3}$), 2.53 (dq, $J_{\mathrm{H-C}} = 129$ Hz, 3H, $\mathrm{W_2CHCH{=}CHC}H_3$), and other resonances as above. $^{13}$C NMR (76 MHz, 22 °C, toluene-$d_8$, $\delta$): 164.1 (dd, $J_{\mathrm{C-C}} = 38$ Hz, $J_{\mathrm{C-H}} = 134$ Hz, $\mathrm{W_2}C\mathrm{HCH{=}CHCH_3}$), 145.4 (ddd, $J_{\mathrm{C-C}} = 38$ Hz, $J_{\mathrm{C-C}} = 70$ Hz, $J_{\mathrm{C-H}} = 146$ Hz, $\mathrm{W_2CH}C\mathrm{H{=}CHCH_3}$), 120.9 (ddd, $J_{\mathrm{C-C}} = 44$ Hz, $J_{\mathrm{C-C}} = 70$ Hz, $J_{\mathrm{C-H}} = 150$ Hz, $\mathrm{W_2CHCH{=}}C\mathrm{HCH_3}$), 16.9 (qd, $J_{\mathrm{C-C}} = 44$ Hz, $J_{\mathrm{C-H}} = 125$ Hz, $\mathrm{W_2CHCH{=}CH}C\mathrm{H_3}$).

**Reactions with Nitriles.** The following procedure was carried out for each nitrile used in this study (benzonitrile, trimethylacetonitrile, and acetonitrile). Benzonitrile is used in the general synthetic precedure.

**$\mathbf{W_2(O\text{-}i\text{-}Pr)_7(\mu\text{-}\eta^1\text{-}N,\eta^1\text{-}N\text{-}NCPhCPhN(H))}$.** (a) $\mathrm{[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2}$ (0.173 g, 0.111 mmol) was placed in a 50 mL Schlenk flask equipped with a Teflon-coated stir bar, and approximately 3 mL of hexanes was added via cannula transfer. Benzonitrile (45.15 $\mu$L, 0.442 mmol) was added via syringe. The mixture was stirred overnight and turned a pine green color. The solvent was removed in vacuo, leaving a green solid. The solid was redissolved in approximately $^1/_2$ mL of DME and stored at −20 °C overnight. Large thin plates formed, which were isolated (68.6% yield) and dried *in vacuo*. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 9.1 (s, 1H, N$H$); Ph 7.60 (d, 2H), 7.35 (d, 2H), 7.08 (t, 4H), 6.98 (m, 2H); $\mathrm{OC}H\mathrm{(CH_3)_2}$ 5.48 (sep, 1H), 5.05 (br m, 4H), 4.89 (br m, 2H); $\mathrm{OCH(C}H_3)_2$ 1.42 (br d, 6H), 1.32 (d, 36H). $^1$H NMR (300 MHz, −20 °C, toluene-$d_8$, $\delta$): 9.1 (s, 1H, N$H$); Ph 7.60 (d, 2H), 7.35 (d, 2H), 7.08 (t, 4H), 6.98 (m, 2H); $\mathrm{OC}H\mathrm{(CH_3)_2}$ 5.48 (sep, 1H), 5.05 (br m, 4H), 4.89 (br m, 2H); $\mathrm{OCH(C}H_3)_2$ 1.7 (br, 6H), 1.42 (br d, 12H), 1.32 (d, 12H), 1.24 (d, 6H), 1.0 (br, 6H). $^1$H NMR (300 MHz, −60 °C, toluene-$d_8$, $\delta$): 9.1 (s, 1H, N$H$); Ph 7.7 (d, 2H), 7.3 (d, 2H), 7.10 (m, 4H), 6.9 (m, 2H); $\mathrm{OC}H\mathrm{(CH_3)_2}$ 5.48 (sep, 1H), 5.05 (mm, 4H), 4.7 (br m, 2H); $\mathrm{OCH(C}H_3)_2$ 1.8 (br d, 6H), 1.5 (br d, 12H), 1.35 (d, 6H), 1.27 (d, 6H), 1.24 (d, 6H), 0.95 (d, 6H). $^{13}$C{$^1$H} NMR (126 MHz, 22 °C, toluene-$d_8$, $\delta$): Ph 155.8, 139.1, 138.6, 126.6; $\mathrm{O}C\mathrm{H(CH_3)_2}$ 77.5, 75.4, 72.2; $\mathrm{OCH(}C\mathrm{H_3)_2}$ 27.6, 26.7, 25.63, 24.68. IR (cm$^{-1}$): 3360 (w), 2967 (s), 2950 (s), 1600 (w), 1430 (w), 1368 (s), 1300 (s), 1111 (s), 980 (s), 845 (s), 800 (w), 698 (m), 598 (s). Anal. Calcd for $\mathrm{W_2(O\text{-}i\text{-}Pr)_7(NHCPhCPhN)}$, $\mathrm{W_2N_2O_7C_{35}H_{60}}$: C, 42.52; H, 6.12; N, 2.83. Found: C, 39.51; H, 5.80; N, 2.24. Although the elemental analysis is in poor agreement with the formulated compound, the spectroscopic data that agree with the solid-state structure do not reveal any other compounds.

(b) This is an alternate method of synthesizing W$_2$(O-i-Pr)$_7$($\mu$-$\eta^1$-N,$\eta^1$-N-NCPhCPhN(H)) from W$_2$(O-i-Pr)$_6$ + 2PhCN + HO-i-Pr. W$_2$(O-i-Pr)$_6$py$_2$ (0.320 g, 0.379 mmol) was placed in a 50 mL Schlenk flask equipped with a Teflon-coated stir bar, and approximately 5 mL of hexanes was added via cannula transfer. Benzonitrile (75.0 $\mu$L, 0.735 mmol) and 2-propanol (15.0 $\mu$L, 0.379 mmol) were added via syringe. The mixture was stirred overnight and turned a pine green color. The solvent was removed in vacuo, leaving a green solid. The solid was redissolved in approximately $^1/_2$ mL of DME and stored overnight at $-20$ °C. A small batch of large thin plates formed, which were isolated (15% yield). The remaining material was a viscous oil that did not crystallize.

**W$_2$(O-i-Pr)$_7$($\mu$-$\eta^1$-N,$\eta^1$-N-NCPhCPhN(D)).** [W$_2$($\mu$-D)(O-i-Pr)$_7$]$_2$ (0.02 g, 0.01 mmol) was placed in an NMR tube, and benzene-$d_6$ (0.3 mL) was added under a nitrogen atmosphere. Benzonitrile (40.0 $\mu$L, 0.39 mmol) was added via syringe under a nitrogen atmosphere. The tube was allowed to sit in the drybox overnight, and the $^1$H NMR spectrum was taken the following day on the brown-green solution. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): Ph 7.60 (d, 2H), 7.33 (d, 2H), 7.08 (t, 4H), 6.98 (m, 2H); OC*H*(CH$_3$)$_2$ 5.47 (sep, 1H), 5.05 (sep, 4H), 4.86 (sep, 2H); OCH(C*H*$_3$)$_2$ 1.42 (d, 6H), 1.32 (d, 36H).

**W$_2$(O-c-C$_5$H$_9$)$_7$($\mu$-$\eta^1$-N,$\eta^1$-N-NCPhCPhN(H)).** W$_2$($\mu$-H)(O-c-C$_5$H$_9$)$_7$(HNMe$_2$) (0.02 g, 0.02 mmol) was placed in an NMR tube, and benzene-$d_6$ (0.3 mL) was added under a nitrogen atmosphere. Benzonitrile (10.0 $\mu$L, 0.10 mmol) was added via syringe under a nitrogen atmosphere. The tube was sealed and allowed to sit overnight. The solution turned pine green in color. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 9.2 (s, 1H, NH); Ph 7.60 (d, 2H), 7.30 (d, 2H), 7.07 (m, 4H), 6.80 (m, 2H); 5.85–5.16 (br overlapping multiplets, 7H, O-c-C$_5$H$_9$, C*H*), 2.19–1.53 (br overlapping multiplets, 28H, O-c-C$_5$H$_9$, C*H*$_2$).

**W$_2$(O-i-Pr)$_7$($\mu$-$\eta^1$-N,$\eta^1$-N-NC-t-BuC-t-BuN(H)).** $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 7.49 (s, 1H, N*H*); OC*H*(CH$_3$)$_2$ 5.94 (sep, 1H), 5.27 (sep, 2H), 5.04 (sep, 4H); OCH(C*H*$_3$)$_2$ 1.62 (br d, 3H), 1.55 (d, 3H), 1.44 (s, 9H, C(C*H*$_3$)$_3$), 1.40 (d, 12H); OCH(C*H*$_3$)$_2$ 1.27 (s, 9H, C(C*H*$_3$)$_3$), 1.19 (d, 3H, OCH(C*H*$_3$)$_2$). IR (cm$^{-1}$): 3418 (s), 2967 (s), 1630 (w), 1474 (w), 1375 (w), 1262 (w), 1107 (m), 1020 (w), 949 (w), 802 (m). Anal. Calcd for W$_2$(O-i-Pr)$_7$($\mu$-$\eta^1$-N,$\eta^1$-N-NC-t-BuC-t-BuN(H)), W$_2$N$_2$O$_7$C$_{31}$H$_{68}$: C, 39.25; H, 7.24; N, 2.95. Found: C, 37.58; H, 6.76; N, 2.62. As for the previously reported nitrile-coupled product, the poor elemental analysis is not readily accounted for.

**W$_2$(O-c-C$_5$H$_9$)$_7$($\mu$-$\eta^1$-N,$\eta^1$-N-NC-t-BuC-t-BuN(H)).** $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 9.32 (s, 1H, N*H*) 5.85–5.30 (br overlapping multiplet, 7H, O-c-C$_5$H$_9$, C*H*), 2.14–1.5 (br overlapping multiplet, 28H, O-c-C$_5$H$_9$, C*H*$_2$). The t-Bu groups were not detected, presumably due to them being obscured by the CH$_2$ groups.

**W$_2$(O-i-Pr)$_7$($\mu$-$\eta^1$-N,$\eta^1$-N-NCMeCMeN(H)).** $^1$H NMR (300 MHz, 22 °c, benzene-$d_6$, $\delta$): 8.9 (s, 1H, N*H*), 5.7 (sep, 1H, OC*H*(CH$_3$)$_2$), 5.66–5.06 (br overlapping multiplet, 6H, OC*H*(CH$_3$)$_2$), 2.60 (s, 3H, CC*H*$_3$), 2.01 (s, 3H, CC*H*$_3$), 1.55 (br d, 6H, OCH(C*H*$_3$)$_2$), 1.49 (br overlapping d, 36H, OCH(C*H*$_3$)$_2$).

**Reaction of [W$_2$($\mu$-H)(O-i-Pr)$_7$]$_2$ with $^{13}$CO$_2$.** [W$_2$($\mu$-H)(O-i-Pr)$_7$]$_2$ (20 mg, 0.01 mmol) was placed in an NMR tube, and benzene-$d_6$ (0.3 mL) was added under a nitrogen atmosphere. The solution was frozen in liquid nitrogen and evacuated, and 4 equiv of $^{13}$CO$_2$ was added using a calibrated vacuum manifold. The tube was sealed with a torch and allowed to warm to room temperature. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): OC*H*(CH$_3$)$_2$ 8.24 (br), 8.15 (br), 8.10 (br), 7.95 (br), 7.73 (br), 7.41 (br), 6.0–3.7 (overlapping septets), 2.7–0.9 (overlapping d, OCH(C*H*$_3$)$_2$). $^{13}$C NMR (75 MHz, 22 °C, benzene-$d_6$, $\delta$): 182.4, 181.6, 176.5, 172.6, 171.1, 124.7 (free $^{13}$CO$_2$). After 2 days at room temperature, the peaks at $\delta$ 182.4 and 171.1 had disappeared.

**Reaction of [W$_2$($\mu$-H)(O-i-Pr)$_7$]$_2$ with CO.** [W$_2$($\mu$-H)(O-i-Pr)$_7$]$_2$ (600 mg, 0.383 mmol) was placed in a 30 mL Schlenk flask equipped with a Teflon-coated stir bar, and pentane (10 mL) was added by cannula transfer. The solution was frozen in liquid nitrogen and evacuated, and 6 equiv of CO (2.3 mmol) was added by back-filling with an atmosphere of CO using a calibrated vacuum manifold. As the solution was allowed to warm to room temperature, a brown solid immediately formed. The solution was allowed to stir overnight. The solid was isolated by filtration and recrystallized from toluene to give brown needles of W$_2$(O-i-Pr)$_6$(CO)$_4$ that formed a purple solution upon dissolution. A second brown microcrystalline solid product was recrystallized from the supernatant liquid that gave the following spectroscopic data. $^1$H NMR (300 MHz, 22 °C, benzene-$d_6$, $\delta$): 5.24 (septet, $J_{\text{H-H}} = 6$ Hz, 1H, OC*H*(CH$_3$)$_2$), 1.31 (d, $J_{\text{H-H}} = 6$ Hz, 6H, OCH(C*H*$_3$)$_2$).

**Reaction of W$_2$($\mu$-H)(O-c-C$_5$H$_9$)$_7$(HNMe$_2$) with $^{13}$CO.** W$_2$($\mu$-H)(O-c-C$_5$H$_9$)$_7$(HNMe$_2$) (10 mg, 0.01 mmol) was placed in an NMR tube, and benzene-$d_6$ (0.3 mL) was added under a nitrogen atmosphere. The solution was frozen in liquid nitrogen and evacuated, and 4 equiv of $^{13}$CO was added by back-filling from a calibrated vacuum manifold. The tube was sealed with a torch and allowed to warm to room temperature. $^{13}$C NMR (76 MHz, 22 °C, benzene-$d_6$, $\delta$): 212.8 (s), 212.1 (t, $J_{\text{C-C}} = 3$ Hz), 206.4 (s), 205.8 (t, $J_{\text{C-C}} = 3$ Hz).

**Characterization of W$_2$(O-i-Pr)$_6$(CO)$_4$.** $^1$H NMR (500 MHz, 22 °C, toluene-$d_8$, $\delta$): OC*H*(CH$_3$)$_2$ 5.24 (br, 2H), 5.08 (br, 2H), 4.76 (br, 2H); OCH(C*H*$_3$)$_2$ 1.39 (br, 12H), 1.19 (br, 12H), 0.99 (br, 12H). $^{13}$C NMR (126 MHz, 22 °C, toluene-$d_8$, $\delta$): 213.2, 207.0. IR (cm$^{-1}$): 2962 (m), 2920 (w), 1995 (m, CO), 1860 (br s, CO), 1840 (s, CO), 1800 (s, CO), 1452 (w), 1375 (w), 1362 (w), 1315 (w), 1160 (w), 1123 (w), 1099 (m), 960 (m), 880 (w), 850 (w), 812 (m), 618 (m), 599 (m).

**Characterization of W(CO)$_5$(HNMe$_2$).** $^1$H NMR (500 MHz, 22 °C, benzene-$d_6$, $\delta$): 1.66 (d, $J_{\text{H-H}} = 6$ Hz, 6H, HN(C*H*$_3$)$_2$), 0.89 (br m, 1H, *H*N(CH$_3$)$_2$). $^{13}$C NMR (126 MHz, 22 °C benzene-$d_6$, $\delta$): 50.6 (qq, $^1J_{\text{C-H}} = 138$ Hz, $^3J_{\text{C-H}} = 5$ Hz, HN(*C*H$_3$)$_3$). IR (cm$^{-1}$): 3280 (w, HNMe$_2$), 2060 (m, CO), 1980 (s, CO), 1925 (br vs, CO), 1835 (br vs, CO), 1468 (m), 1580 (m), 1466 (s), 1400 (m), 1026 (m), 1006 (m), 899 (m), 590 (s), 548 (m), 362 (s).

**Single Crystal X-ray Crystallography.** General operating procedures and programs have been described.[44] A summary of crystal data is given in Table 4.

**W$_2$(O-c-C$_5$H$_9$)$_7$($\eta^2$-C$_2$H$_4$)($\eta^1$-C$_2$H$_5$).** A sample of a suitable size was mounted in a nitrogen atmosphere glovebag by using silicone grease, and it was then transferred to a goniostat where it was cooled to $-155$ °C for characterization and data collection. A search of a limited hemisphere of reciprocal space revealed intensities with Laue symmetry and systematic absenses consistent with space group $P2_1/a$, which was later confirmed by the successful solution of the structure. Following complete data collection, data processing gave a residual of 0.077 for the averaging of 4667 unique intensities that had been observed more than once. Four standards measured every 300 data showed no significant trends. No correction was made for absorption.

The structure was solved by using a combination of direct methods (MULTAN78) and Fourier techniques. The tungsten positions were determined from an E map. The remaining non-hydrogen atoms were obtained from subsequent iterations of least-square refinement and difference Fourier calculation. Two of the seven five-membered rings were badly disordered. An attempt was made to model the disorder by including additional carbon atoms and refining the occupancies of all carbon atoms in the disordered groups (C(22–6) + C(52–3) and C(28–32) + C(49–51)). Hydrogens were included in fixed calculated positions on all carbons except those noted above in the disordered ligands.

In the final cycles of least-squares refinement, the carbons in the disordered ligands were refined with isotropic thermal parameters and all other non-hydrogens were refined with anisotropic thermal parameters to a final $R(F) = 0.059$. The largest peak in the final difference map was a tungsten residual of 1.6 e/Å$^3$.

**W$_2$(O-c-C$_5$H$_9$)$_8$($\mu$-CH$_2$CCH$_2$).** The sample consisted of clumps of black crystals with an oily covering. Two distinct crystalline forms appeared to be present, a nearly equidimensional multifaceted form and thin needles growing with a common seed. Attempts to utilize the larger multifaceted crystals failed, with only broad diffraction observed at low angles. The crystals appeared to be quite plastic in character. Several of the needles were then examined, with most being split or twinned. The sample that was finally chosen was an irregular fragment cleaved from one of the larger masses. There was a considerable amount of the oily residue on the crystal, which made it

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[44] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

**Table 4.** Summary of Crystal Data

| | | | | | |
|---|---|---|---|---|---|
| empirical formula | $W_2C_{39}H_{72}O_7$ | $W_2C_{43}H_{76}O_8$ | $W_2C_{45}H_{80}O_9$ | $W_2C_{34}H_{60}O_8$ | $W_2C_{35}H_{60}N_2O_7$ |
| color of crystal | black | black | dark brown | black | orange-brown |
| crystal dimensions (mm) | 0.25 × 0.30 × 0.40 | 0.10 × 0.10 × 0.25 | 0.30 × 0.20 × 0.40 | 0.13 × 0.15 × 0.14 | 0.08 × 0.70 × 0.70 |
| space group | $P2_1/a$ | $P2_1/n$ | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ |
| cell dimensions | | | | | |
| temperature (°C) | −155 | −171 | −175 | −172 | −171 |
| $a$ (Å) | 20.237(5) | 18.070(5) | 10.618(1) | 11.899(5) | 18.688(4) |
| $b$ (Å) | 9.938(2) | 24.432(6) | 20.824(2) | 19.928(8) | 22.186(5) |
| $c$ (Å) | 21.660(5) | 9.848(2) | 22.154(5) | 15.956(7) | 10.368(2) |
| α (deg) | | | | | 94.39(1) |
| $\beta$ (deg) | 113.91(1) | 90.19(1) | 115.22(1) | 91.61(2) | 92.42(1) |
| $\gamma$ (deg) | | | | | 68.51(1) |
| $Z$ (molecule/cell) | 4 | 4 | 4 | 4 | 4 |
| volume (Å$^3$) | 3982.16 | 4348.09 | 4431.49 | 3782.15 | 3987.51 |
| calculated density (gm/cm$^3$) | 1.703 | 1.663 | 1.698 | 1.694 | 1.647 |
| wavelength (Å) | 0.71069 | 0.71069 | 0.71069 | 0.71069 | 0.71069 |
| molecular weight | 1020.69 | 1088.77 | 1132.82 | 964.54 | 988.57 |
| linear absorption coefficient (cm$^{-1}$) | 59.409 | 54.479 | 53.503 | 62.519 | 59.316 |
| detector-to-sample distance (cm) | 22.5 | 22.5 | 22.5 | 22.5 | 22.5 |
| sample-to-source distance (cm) | 23.5 | 23.5 | 23.5 | 23.5 | 23.5 |
| average $\omega$ scan width at half height | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| scan speed (deg/min) | 8.0 | 8.0 | 8.0 | 8.0 | 8.0 |
| scan width (deg + dispersion) | 1.8 | 2.0 | 1.9 | 1.8 | 2.0 |
| individual background (s) | 4 | 4 | 4 | 3 | 3 |
| aperture size (mm) | 3.0 × 4.0 | 3.0 × 4.0 | 3.0 × 4.0 | 3.0 × 4.0 | 3.0 × 4.0 |
| $2\theta$ range (deg) | 6−45 | 6−45 | 6−45 | 6−45 | 6−45 |
| total number of reflections collected | 10751 | 6042 | 6998 | 8747 | 12490 |
| number of unique intensities | 5238 | 5680 | 5806 | 4938 | 10393 |
| number with $F > 0.0$ | 4935 | 4961 | 5391 | 4643 | 9827 |
| number with $F > 2.33\sigma(F)$ | | 3490 | 4364 | 3570 | 7893 |
| number with $F > 3*(F)$ | 4443 | | | | |
| $R(F)$ | 0.0588 | 0.0734 | 0.0592 | 0.0468 | 0.0949 |
| $R_w(F)$ | 0.0577 | 0.0709 | 0.0616 | 0.0470 | 0.0964 |
| goodness of fit for the last cycle | 1.343 | 1.316 | 1.501 | 1.116 | 3.367 |
| maximum $\delta/\sigma$ for last cycle | 0.95 | 0.43 | 0.11 | 0.06 | 0.12 |

difficult to accurately measure the crystal dimensions. All manipulations were performed in a dry nitrogen atmosphere. The chosen sample was affixed to a glass fiber by using silicon grease and transferred to the goniostat where it was cooled to −171 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima with symmetry and systematic absences correspnding to the unique monoclinic space group $P2_1/n$. Subsequent solution and refinement confirmed this choice.

Data were collected by using a moving crystal, moving detector technique with fixed backgrounds at each extreme of the scan. Data were corrected for Lorentz and polarization terms and equivalent data averaged to yield a set of unique intensities.

The structure was solved by direct methods (MULTAN) and Fourier techniques and refined by full matrix least squares. A few of the hydrogen atoms were visible, but attempts to refine all hydrogens were unsuccessful, so idealized fixed hydrogen atom positions were utilized in the final cycles. Attempts to refine all non-hydrogen atoms anisotropically led to several of the carbon atoms converging to nonpositive definite thermal parameters and little improvement in the residuals. Attempts to apply an absorption correction led to higher residuals and was discarded.

A final difference Fourier revealed eight peaks of intensity from 1.0 to 2.3 e/Å$^3$, all in the vicinity of the two tungsten atoms. These residuals are undoubtedly due to a lack of absorption correction.

**$W_2(O\text{-}c\text{-}C_5H_9)_8(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$.** All species in the flask were splits or twins. All attempts to divide such a crystal into monocrystal parts failed. So we were forced to collect data by using a sample of irregular form, which had a fragment on it. This crystal was mounted by using silicone grease, transferred to a goniostat, and cooled to −175 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed symmetry and systematic absences corresponding to the unique monoclinic group $P2_1/c$. No absorption correction was made.

The structure was solved by a usual combination of direct methods (MULTAN78) and Fourier techniques. The tungsten atom positions were obtained from an initial E-map, and the remainder of the non-hydrogen atoms were found in subsequent interations of least-squares refinement and difference Fourier calculations. After partial refinement and the non-hydrogen atoms, a difference Fourier revealed some but not all hydrogen atoms. All hydrogen atoms were introduced in fixed calculated positions. In the final cycles of least-squares refinement, all non-hydrogen atoms were varied with anisotropic thermal parameters. A total of 4364 reflections with $F > 2.33\sigma(F)$ were used for refining 506 parameters.

A final difference Fourier was featureless. There were tungsten residuals of 2.2−4.9 e/Å$^3$. One cyclopentane ligand (C(52)−C(56)) is slightly disordered.

**$W_2(H)(O\text{-}i\text{-}Pr)_7(\eta^2\text{-}OCPh_2)$.** A small well-formed crystal was cleaved from a larger sample and affixed to the end of a glass fiber by using silicone grease, and the mounted sample was then transferred to the goniostat where it was cooled to −172 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of reflections with monoclinic symmetry and systematic absences corresponding to space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected by using a standard moving crystal, moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms and equivalent data averaged. An absorption correction was also used, on the basis of approximate indicies for the faces of the fragment used. The structure was solved by direct methods (MULTAN78) and Fourier techniques. It was obvious that severe disorder was present in four of the seven $OCHMe_2$ groups. Careful examination of difference Fourier maps allowed the disorder to be resolved. In the figures, only one possible configuration for each of the four disordered groups is shown. There was no disorder present in the $Ph_2CO$ group. Hydrogen atoms were not located, and those shown are placed in idealized calculated positions only to show the predicted geometry. No contribution from the hydrogen atoms was included in the least-squares analysis.

A final difference Fourier was essentially featureless, the largest peak being 0.72 e/Å$^3$.

**$W_2(O\text{-}i\text{-}Pr)_7(\mu\text{-}\eta^1\text{-}N,\eta^1\text{-}N\text{-}NCPhCPhN(H))$.** The sample consisted of very thin plates of varying sizes that ranged from orange to brown depending upon the thickness. Any attempt to utilize a plate thicker than approximately 0.1 mm revealed a split crystal parallel to the thin plate. After numerous attempts, a nearly transparent orange plate that was not split was located, and it was used for data collection. The selected crystal was affixed to the end of a glass fiber by using silicone grease and transferred to the goniostat where it was cooled to −171 °C for characterization and data collection. All handling was performed in an inert nitrogen atmosphere.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no apparent symmetry of systematic absences, indicating a triclinic space group. Subsequent solution and refinement of the structure indicated the centrosymmetric $P\bar{1}$ space group was the correct choice.

Data were collected by using a continuous $\theta$, $2\theta$ scan technique with fixed background counts at each extreme of the scan. After correction for Lorentz, polarization, and absorption effects, equivalent data were averaged to yield a unique set of 10 393 reflections. The structure was readily solved by a combination of direct methods (MULTAN78) and Fourier techniques. The non-hydrogen atoms were readily located, and all hydrogen atoms were placed in fixed idealized positions for the final cycles of refinement. Attempts to refine any atoms other than the tungsten atoms anisotropically led to nonpositive definite thermal parameters. This is most probably due to an imperfect absorption correction or possibly due to a slight splitting of the crystal, which was not otherwise apparent. As a result, only the four tungsten atoms were assigned anisotropic thermal parameters. Other atoms were refined isotropically, except for the hydrogen atoms that were considered as fixed atom contributors.

There are two independent molecules present in the asymmetric unit. A least-squares fit using S. C. Nyburg's[45] program indicates that the molecules differ somewhat in their conformation, but chemically equivalent bonds show no significant differences. A final difference Fourier was essentially featureless with the exception of numerous peaks of up to 2 e/Å$^3$ at the tungsten sites.

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**Supplementary Material Available:** Listings of atomic coordinates, bond distances and angles, VERSORT diagrams, and stereodrawings (86 pages); listing of observed and calculated structure factors (65 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[45] Nyberg, S. C. *J. Appl. Crystallogr.* **1979**, *12*, 258.