Conclusions

In concert with the electrochemical and structural results,[2] the present work provides what is perhaps the most complete picture to date of how the collective properties of a molecular metal with structure-enforced stacking respond to fairly drastic changes in off-axis counterions and band filling. It is seen that subtle counterion effects on the band structure are operative and appear at this state to be largely structural in origin. However, these effects are of a considerably lesser magnitude than observed in typical molecular metals such as $(TMTSF)_2X$, $(BEDT-TTF)_2X$, etc., where major structural and, consequently, electrical, optical, and magnetic changes accompany variations in X^-.[3] The response of $[Si(Pc^{\rho+})O]_n$ collective properties to major excursions in ρ is largely understandable in terms of simple tight-binding band theory, however, only if the effects of disorder and defects are taken into account. Such effects are particularly pronounced at low $\rho+$ values.

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Supplementary Material Available: Plots of $\{[Si(Pc)O]X_y\}_n$ conductivity data according to fluctuation-induced tunneling and variable range hopping transport models (5 pages). Ordering information is given on any current masthead page.

Metal Alkoxides. Models for Metal Oxides. 15.[1] Carbon–Carbon and Carbon–Hydrogen Bond Activation in the Reactions between Ethylene and Ditungsten Hexaalkoxides: $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$, $W_2(OR)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, and $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ (Where R = $CH_2\text{-}t\text{-}Bu$, i-Pr, $c\text{-}C_5H_9$, and $c\text{-}C_6H_{11}$). Preparations, Properties, Structures, and Reaction Mechanisms

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Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. *Received September 1, 1988*

Abstract: $W_2(OR)_6(M{\equiv}M)$ compounds and ethylene (1 atm, 22 °C) react in alkane and aromatic hydrocarbon solvents to give $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ compounds and ethane, where R = i-Pr, $c\text{-}C_5H_9$, $c\text{-}C_6H_{11}$, and $CH_2\text{-}t\text{-}Bu$. Under comparable conditions, $W_2(O\text{-}t\text{-}Bu)_6$ and ethylene fail to react. In the formation of $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ compounds, the intermediates $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ and $W_2(OR)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, where R = $c\text{-}C_5H_9$, i-Pr, and $CH_2\text{-}t\text{-}Bu$, have been characterized. For R = i-Pr and $CH_2\text{-}t\text{-}Bu$, the intermediates are shown to be formed *reversibly* from $W_2(OR)_6$ and ethylene. The compound $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ has been fully characterized by an X-ray study and found to contain a metallacyclopentane ring and a $W\text{-}\eta^2\text{-}C_2H_4$ moiety, one at each metal center. The pyridine adduct $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)$ has been fully characterized and shown to contain a novel 1,6-dimetallabicyclo[3.1.0]hex-1(5)-ene organometallic core. All compounds have been characterized by ^{13}C and ^1H NMR studies. Various aspects of the reaction pathway have been probed by the use of isotopically labeled ethylenes, and a proposed general scheme is compared to previous studies of ethylene activation at mononuclear metal centers and carbonyl dinuclear and cluster compounds. Crystal data for $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)\cdot{}^1/_2py$ at −150 °C: a = 10.968 (2) Å, b = 17.507 (4) Å, c = 9.433 (1) Å, α = 93.56 (1)°, β = 96.83 (1)°, γ = 101.29 (1)°, Z = 2, d_{calcd} = 1.693 g cm^{-3}, space group $P\bar{1}$. For $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ at −155 °C: a = 10.069 (2) Å, b = 17.033 (9) Å, c = 17.278 (9) Å, β = 91.38 (3)°, Z = 4, d_{calcd} = 1.808 g cm^{-3}, space group = $P2_1/c$.

Organotransition-metal chemistry has largely evolved through the use of soft π-acceptor ligands such as carbon monoxide, tertiary phosphines, and $\eta^x\text{-}C_n$ ligands (olefins, dienes, allyl, cyclopentadienyl, arenes, etc.).[2,3] Synthetic and mechanistic aspects of organometallic chemistry have been transported from one area of the periodic table to another in a ligand-dependent approach. The ubiquitous Cp and Cp* ligands (Cp = $\eta^5\text{-}C_5H_5$, Cp* = $\eta^5\text{-}C_5Me_5$) have, within the last decade, been key to important developments in the chemistry of the early transition elements,[4,5] the lanthanides and actinides,[6,7] as well as various later transition[8] and main-group elements.[9] In other instances the existence of metal cluster carbonyl compounds has allowed the reactivity of hydrocarbyl fragments to be investigated as a function of multimetal site attachment.[10] Often striking analogies in bonding modes are seen for hydrocarbyl fragments in metal carbonyl cluster compounds and metal surface chemistry.[11]

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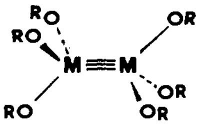
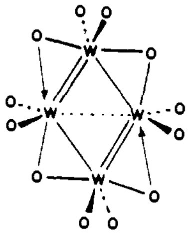
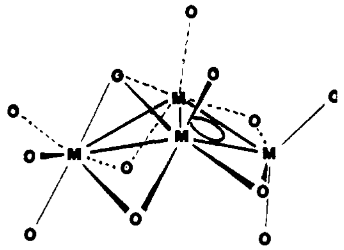
Over the past decade we have been exploring the use of hard, π-donor ligands toward the development of various aspects of organometallic chemistry. In particular, small metal alkoxide clusters can provide models for reduced metal oxides and often the two systems share common cluster units.[12] The choice of a specific alkoxide can allow control of nuclearity as, for example, in the homoleptic alkoxides of tungsten(III) of empirical formula $W(OR)_3$ which have been shown to adopt one of three structural types depicted by I–II and III.



I

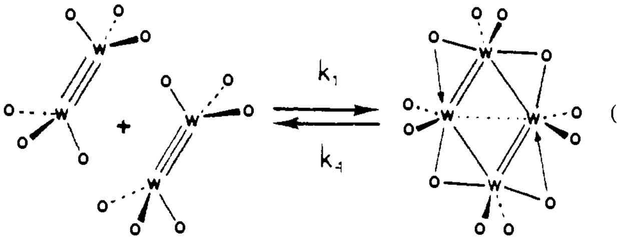


II



III

Compounds of type I are supported by bulky alkoxy ligands: *t*-Bu, CH_2-adamantyl, c-C_6H_{11};[13] II have alkoxide ligands of intermediate steric pressure at the metal,[14] R = *i*-Pr, CH_2-*t*-Bu, c-C_5H_9; while III occur for R = CH_2X where X = cyclohexyl, cyclopentyl, cyclobutyl and *i*-Pr.[15] In solution, equilibria have been established interconverting I and II as shown in eq 1, and III can be quantitatively prepared by alcoholysis of II.

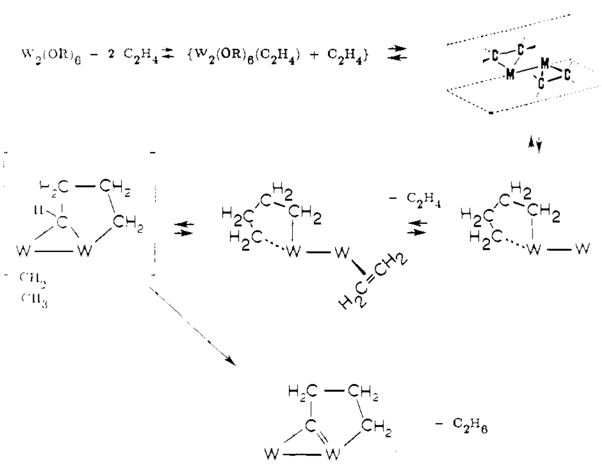


(1)

O = O-*i*-Pr

For each class of metal alkoxides, I–III, the metal–metal bonds provide a reservoir of electrons for substrate activation, and in each class, the metal atoms are coordinatively unsaturated and capable of binding donor ligands. Although the metal centers may *formally* achieve electronic saturation as a result of RO-to-M π bonding, the metal–ligand π electrons remain ligand centered and the LUMO metal centered. The compounds are thus susceptible to nucleophilic attack at the metal atoms providing the alkoxide ligands allow steric penetration. The highest occupied MOs are M–M bonding. Alkoxide clusters and carbonyl clusters have therefore many complementary aspects to their chemistry.[16]

Scheme I



In this paper we describe the reactions between ethylene and $W_2(OR)_6$ compounds. These reactions proceed under extremely mild conditions (≤22 °C, 1 atm) in hydrocarbon solvents and show a marked dependence upon the steric properties of R. Preliminary findings have been communicated.[17,18]

Results and Discussion

General Synthetic Considerations. A general reaction pathway describing the reaction between $W_2(OR)_6$ compounds and ethylene is proposed in Scheme I, and the overall reaction proceeds according to the stoichiometry shown in eq 2.

$$W_2(OR)_6 + 3C_2H_4 \xrightarrow[\text{hexane}]{22\ ^\circ C} W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2) + C_2H_6 \quad (2)$$

The relative rates of the formation of the $W_2(\mu$-$CCH_2CH_2CH_2)$-containing compounds show a dependence on the nature of R such that R = *i*-Pr > c-C_5H_9 > c-C_6H_{11} > CH_2-*t*-Bu. $W_2(O$-*t*-$Bu)_6$ fails to show any reactivity at room temperature and 1 atm of ethylene, which is somewhat surprising based on its reactivity toward acetylene[19] and allene.[20]

The reasons for this rather unusual ordering of the ligands can be understood in terms of the equilibria discussed later. Though several aspects of the proposed reaction pathway remain uncertain in detail, the overall sequence shown in Scheme I can be substianted for this grouping of alkoxide ligands. Perhaps most significantly we can now rule out a reaction pathway involving the initial formation of a σ,π-vinyl ligand, conversion to a μ-vinylidene, and addition of ethylene, eq 3.[17]

(3)

We start by presenting the characterization data for the isolated compounds and then move to a discussion of the reaction pathways.

$W_2(OCH_2$-*t*-$Bu)_6(C_2H_4)_2$. $W_2(OCH_2$-*t*-$Bu)_6$ and ethylene (>2 equiv) react rapidly in hydrocarbon solvents at 0 °C to give yellow-orange solutions of $W_2(OCH_2$-*t*-$Bu)_6(\eta^2$-$C_2H_4)_2$ that can be obtained as an analytically pure crystalline solid by cooling these solutions to −20 °C. Regrettably no crystals suitable for a single-crystal X-ray diffraction study have been isolated. All crystals examined by X-ray crystallography appeared twinned and consequently the detailed structure remains unknown, though

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NMR characterization data as described below limits the possibilities.

When a pure sample of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ is dissolved in benzene-d_6 or toluene-d_8 it is apparent from ^1H and ^{13}C NMR spectra that it exists in equilibrium with free ethylene and $W_2(OCH_2\text{-}t\text{-}Bu)_6$, eq 4.

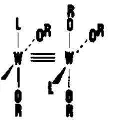
$$W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2 \rightleftarrows W_2(OCH_2\text{-}t\text{-}Bu)_6 + 2C_2H_4 \qquad (4)$$

The equilibrium is temperature dependent and at higher temperatures is driven to the right, as defined in eq 4, presumably by entropy. The equilibrium 4 is, however, *slow* on the NMR time scale. This contrasts with analogous equilibria involving $W_2(OR)_6$ compounds and neutral ligands such as pyridine and tertiary phosphines, eq 5.[21] The latter exhibit line broadening

$$W_2(OR)_6 + 2L \rightleftarrows W_2(OR)_6L_2 \qquad (5)$$

of ^1H and ^{31}P signals due to rapid NMR time-scale exchange. This observation implies that there is a higher kinetic barrier to the coordination of ethylene than to a simple σ-donor ligand. A similar situation is seen in the relative rates of exchange: $L_2Pt(X) \rightleftarrows L_2Pt + X$, where X = ethylene or a monodentate phosphine and L_2 = a bidentate phosphine.[22] It is also worthy of note that the species $[W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)]$ is not detected by NMR spectroscopy in the equilibrium 4. This implies that the monoethylene adduct is more reactive and a higher energy species relative to $W_2(OCH_2\text{-}t\text{-}Bu)_6$ and $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$.[23]

The ^1H NMR spectrum of pure, isolated $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$, in the presence of excess ethylene to maintain the integrity of the bis(ethylene) adduct, is shown in Figure 1. There are three types of neopentoxide ligands in the integral ratio 1:1:1, each having diastereotopic methylene protons, and one type of coordinated ethylene ligand. The integral ratio of neopentoxide to ethylene protons as well as the elemental analysis data (see Experimental Section) set the empirical formula as $[W(OCH_2\text{-}t\text{-}Bu)_3(C_2H_4)]_n$. It is likely, based on further reaction chemistry, that metal–metal bonding is retained and $n = 2$ although higher degrees of oligomerization cannot be ruled out. These data are consistent with an adduct of the type shown in IV, though usually for L = py or PR_3 rotation about the central M≡M bond is not frozen out until ca. −70 °C at 360 MHz.



IV, R = $CH_2\text{-}t\text{-}Bu$

The ^1H signals associated with the bound ethylene ligand appear as four multiplets in the region 1.5–3.0 ppm. This requires that all the hydrogen atoms are chemically inequivalent H_a, H_b, H_c, and H_d, which can only be the case for a molecule having a virtual (time-averaged) C_2 axis of molecular symmetry and restricted rotation about the $M\text{–}\eta^2\text{-}C_2H_4$ vector.

In order to probe the ABCD spin system generated by the coordinated ethylene ligand, we have employed the use of the following deuterated ethylene molecules *gem*-, *cis*-, and *trans*-$C_2H_2D_2$. Since the gyromagnetic ratio of D is approximately one-sixth of that of H and for D, $I = 1$, the effect of D for H substitution greatly simplifies the spectra. Essentially one observes, by ^1H NMR spectroscopy, only H–H couplings with the $^1H\text{–}^2H$ coupling giving rise to some broadening of the signals. Selected spectra are shown in Figure 2 for the η^2-ethylene signals. From these experiments it is possible to measure directly and assign the six *gem*-, *cis*-, and *trans*-H–H coupling constants. The geminal relationship of the proton resonances was also confirmed by a heteronuclear 2D chemical shift correlated experiment. The measured coupling constants and chemical shifts were used to generate a simulated spectrum that is a reasonable fit for the experimental spectrum. It should be noted that the ^1H spectra obtained for the *gem-*, *cis-*, *and trans-*$C_2H_2D_2$ *indicate that no isomerization is involved in the reversible coordination of the ethylene, eq 4.* This would seem to rule out the presence of mischievous metal–hydride formation and olefin metathesis reactions. We shall, however, return to more detailed mechanistic comments later.

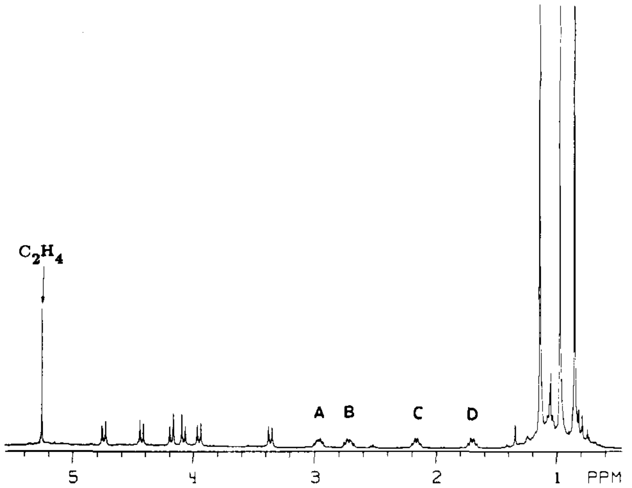


Figure 1. ^1H NMR spectrum (360 MHz, +10 °C, benzene-d_6) of $W_2(O\text{-}CH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ in the presence of added ethylene to maintain the position of equilibrium 4 to the left.

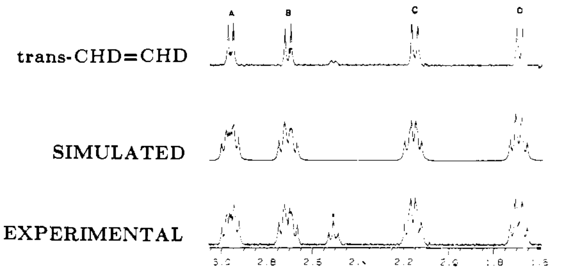


Figure 2. Bottom: A portion of the ^1H NMR spectrum (360 MHz, +10 °C, benzene-d_6) of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ expanded in the region of the ethylenic protons. Top: ^1H NMR spectrum of the ethylenic region of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}trans\text{-}CHD{=}CHD)_2$ showing that no scrambling of the deuterium label had occurred. The coupling constants derived from decoupling experiments on this and other isotopomers were used to generate the simulated spectrum shown in the middle. The resonance marked with an asterisk (*) is due to the α-methylenic protons of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}CCH_2CH_2CH_2)$.

Reactions employing $^*C_2H_4$, where *C represents 99 mol % ^{13}C, yield the labeled bis(ethylene) adduct $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}^*C_2H_4)_2$. This allows for the direct determination of the magnitude of $^1J_{^{13}C\text{–}^{13}C}$ from the ^{13}C NMR spectrum of the labeled compound. The value of 28 Hz, so determined, is significantly smaller than that expected for two coordinated sp^2 hybridized carbon atoms.[24] The ^1H-decoupled ^{13}C NMR spectrum showing the ethylenic carbons is shown in Figure 3. The appearance of two distinct carbon resonances at ca. δ 61 and 64 ppm is again an indication of restricted rotation (frozen out on the NMR time scale) about the $W\text{–}C_2H_4$ vector. Each carbon atom is also coupled to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance, $J_{W\text{–}C}$ = 36 Hz. This value is similar to the values obtained for η^2-acetylene ligands.[25] From the satellite intensity it is apparent that each

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[21] Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

[22] Clark, H. C.; Hampden-Smith, M. J.; Furgerson, G.; Kaitner, B.; Rugger, H. *Polyhedron* **1988**, *7*, 1349.

[23] A similar situation was found in studies of equilibrium 5 for L = neutral donor ligands such as pyridine and PMe_3. See: Reference 21.

[24] Compare $^1J_{^{13}C\text{-}^{13}C}$ = 67 Hz in unligated ethylene. For a listing of typical $^1J_{^{13}C\text{–}^{13}C}$ values, see: Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; p 327, Table 9.3.

[25] Compare $^1J_{^{13}C\text{–}^{13}C}$ = 54.5 Hz and $^1J_{^{183}W\text{–}^{13}C}$ = 40.4 Hz for the $\eta^2\text{-}C_2H_2$ ligand in the ^{13}C-labeled compound $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}C_4H_4)(\eta^2\text{-}^*C_2H_2)$, where *C represents 99 mol % ^{13}C: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806.

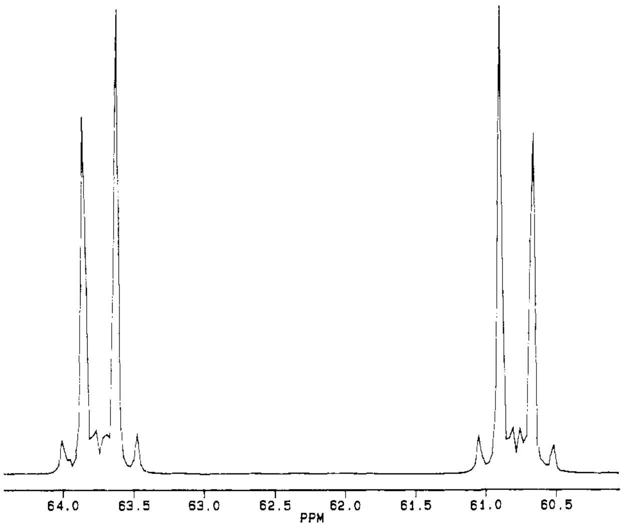


Figure 3. $^{13}C\{^1H\}$ NMR spectrum (125.8 MHz, 21 °C, benzene-d_6) of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}^*C_2H_4)_2$ where *C represents 99% ^{13}C enrichment. The carbon–carbon coupling constant can be measured directly from the spectrum, and the coupling to a single tungsten nucleus (^{183}W, $I = {}^1/_2$, 14% natural abundance) can be observed.

Table I. Carbon–Carbon Coupling Constants and Distances in $\eta^2\text{-}C_2H_4$ Complexes and Related Compounds

compound	$J_{^{13}C-^{13}C}$/Hz	d(C–C)/Å	ref
C_2H_4	67	1.34	24, 33
HPC_2H_4	*a*	1.502	6
$W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$	28	*a*	this work
$W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$	35	1.43 (2)	this work
$(Cy_3P)_2Pt(\eta^2\text{-}C_2H_4)$	31	1.440 (7)	22
$[(MePh_2P)_3Ir(\eta^2\text{-}C_2H_4)_2]^+$	44	1.40, 1.43	*b*
$[(MePh_2P)_3Ir(\eta^2\text{-}C_2H_4)Me_2]^+$	*a*	1.41 (5)	*c*

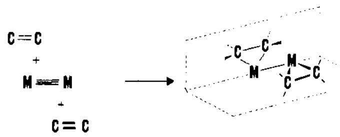
[a] Data not available. [b] Caulton, K. G.; Huffman, J. C.; Lundquist, E. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165. [c] Caulton, K. G.; Huffman, J. C.; Lundquist, E. G., unpublished results.

ethylene ligand is bonded to one tungsten atom.

The C–C coupling constants and chemical shifts for the coordinated ethylene ligand in $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ are given in Table I and compared to those in free ethylene and those in certain other "activated" ethylene complexes. By stating "activated" we imply extensively rehybridized toward the metallacyclopropane limiting valence bond description for a coordinated ethylene. The similarity between the H–H coupling constants within the coordinated ethylene ligands of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ with those reported for phosphiranes[26] are also consistent with highly activated ethylene ligands. Unfortunately, the values of $^1J_{CH}$ cover a range of 146–163 Hz and do not unequivocally distinguish between the two extremes of ethylene coordination.

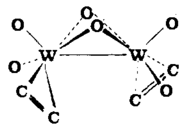
Given the apparent activated nature of the ethylene ligand, it is perhaps at first surprising that it should be reversibly coordinated according to eq 4. Though we have not quantitatively studied the equilibrium as a function of temperature, we observe that solutions of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$, in a closed system, dissociate ethylene until an equilibrium mixture of the three species is reached. The dissociation of ethylene is presumably entropically favored. Furthermore, though in the ethylene complex there is apparently strong tungsten–ethylene bonding, this must be made at the expense of metal–metal bonding and C–C π bonding. We can represent the formal addition of two C–C double bonds to a M–M triple bond in the reaction between $W_2(OR)_6$ and ethylene by the schematic 2 + 2 + 2 reaction shown in eq 6.

The filled C–C π orbital can donate to a vacant metal orbital at each metal center without any restriction of the C–C and W–W vectors. However, for back-bonding, Wd_π to C_2 π^*, the C–C axis must be aligned along the W–W axis. In this way we would predict a rather rigid molecule having C_2 symmetry since the M–M π orbitals are orthogonal.



(6)

It is, of course, possible to envisage alternative structures that have C_2 molecular symmetry and that satisfy all the NMR data. Structure V, for example, has a C_2 axis of molecular symmetry,



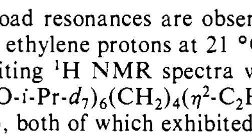
V

satisfies the spectroscopic data, and is related to the structure found for $W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4(\eta^2\text{-}C_2Me_2)_2$.[27] However, the latter compound, in contrast to $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$, shows facile rotation about the W–C_2 axes and does not dissociate alkyne. We believe other structures in which both ethylene ligands are coordinated to the same metal atom are unlikely. Suffice it to say that at this time we cannot satisfactorily distinguish between IV and V.

$W_2(OR)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. a. $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. Hydrocarbon solutions of $W_2(O\text{-}i\text{-}Pr)_6$ (M≡M) react with ethylene at 0 °C to give $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, which can be isolated as a dark red-brown crystalline solid by cooling to −78 °C. It is, however, reactive both in the solid state and in solution at room temperature to yield the alkylidyne bridged compound and ethane according to the stoichiometric reaction shown in eq 7.

$$W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4) \rightarrow W_2(O\text{-}i\text{-}Pr)_6(\eta\text{-}CCH_2CH_2CH_2) + C_2H_6 \quad (7)$$

$W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ is fluxional on the NMR time scale though low temperature limiting spectra (^1H and ^{13}C) are consistent with the structure depicted by VI. See Figures 4 and 5.



VI

Only three broad resonances are observed in the ^1H NMR spectrum for the ethylene protons at 21 °C; see Figure 4. Low temperature limiting ^1H NMR spectra were obtained for the compounds $W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ and $W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$, both of which exhibited simplified spectra as a result of deuterium labeling. Integration of the low-temperature ^1H NMR spectrum of $W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ indicated that the molecule possessed 12 (or a multiple thereof) ethylene-derived protons, while the low-temperature spectrum of $W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$ indicated that all 6 alkoxide ligands are inequivalent. Integration of the low temperature limiting ^1H NMR spectrum of the fully protio derivative together with the elemental analysis data set the empirical formula as $[W_2(O\text{-}i\text{-}Pr)_6(C_2H_4)_3]_n$. The single-crystal X-ray diffraction study confirmed that $n = 1$. The variable-temperature ^{13}C NMR spectra of $W_2(O\text{-}i\text{-}Pr)_6(^*CH_2)_4(\eta^2\text{-}^*C_2H_4)$, where *C represents 99% ^{13}C, are shown in Figure 5a. At room temperature only three resonances are observed, a broad resonance at approximately 67 ppm, a sharp resonance at 53 ppm with ^{183}W satellites showing a small coupling

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[26] Goldwhite, H.; Rowsell, D.; Vertal, L.; Bowers, M. T.; Copper, M. A.; Maratt, S. L. *Org. Magn. Reson.* **1983**, *21*, 494. Goldwhite, H.; Bowers, M. T.; Beandet, R. A.; Tang, R. *J. Am. Chem. Soc.* **1969**, *91*, 17.

[27] Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 861.

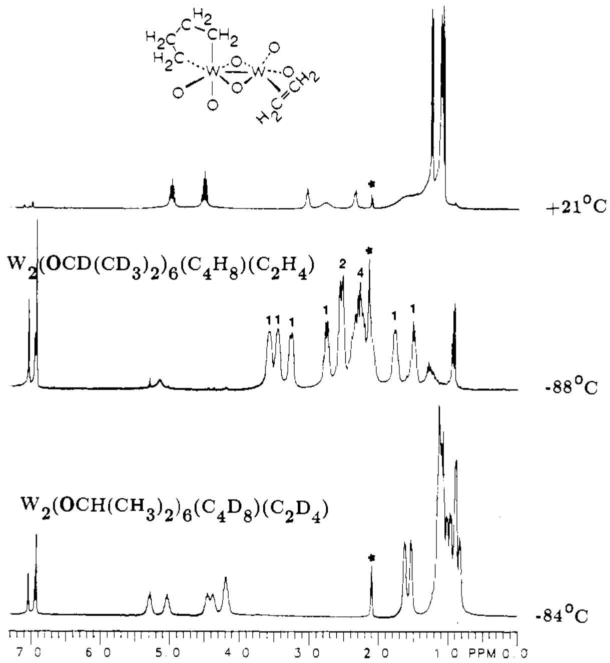
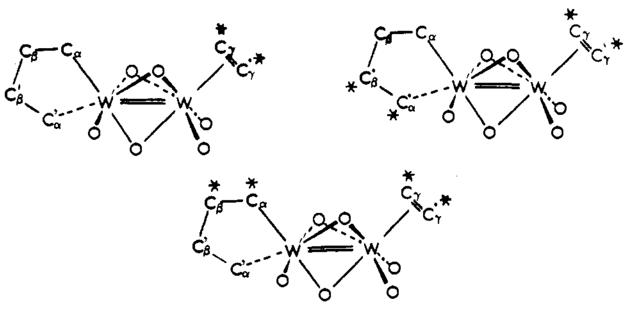


Figure 4. Top: ^1H NMR spectrum (300 MHz, 21 °C, toluene-d_8) of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ showing the time-averaged resonances of both the isopropoxide- and ethylene-derived protons. Middle: Low temperature limiting ^1H NMR spectrum (300 MHz, −88 °C, 70:30 Freon-12/toluene-d_8) of $W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ emphasizing the integrated ratios of the ethylene-derived protons. Bottom: Low temperature limiting ^1H NMR spectrum (300 MHz, −85 °C, 70:30 Freon-12/toluene-d_8) of $W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$ emphasizing the chemical inequivalence of all six isopropoxide ligands. The resonance marked with an asterisk (*) is due to the methyl protio impurities in toluene-d_8.

(~29 Hz) to one tungsten atom, and a multiplet at 37 ppm. As the temperature of this sample was lowered, the broad resonance at 67 ppm sharpened to form two multiplets at 64 and 69 ppm and the sharp resonance at 53 ppm collapsed and reappeared as an AB pattern at 52 and 54 ppm. The resonance at 37 ppm showed little temperature variation. The multiplets at 69, 64, and 37 ppm appeared to exhibit ^{183}W coupling, but were complicated by the extent of carbon–carbon coupling. In order to simplify the spin system, a reaction was carried out in which the ^{13}C-enriched ethylene was diluted 1:3 with C_2H_4 containing only the natural-abundance ^{13}C isotope. The variable-temperature ^{13}C NMR spectra were remeasured (Figure 5b), and under the conditions that the spectra were recorded (see Experimental Section), only the major species shown were observed.



The two original multiplets at 69 and 64 ppm were then observed as doublets with large couplings to ^{183}W of 88 and 77 Hz, respectively, in the range normally attributed to W–C σ bonds.[28] These resonances can therefore be assigned to C_α and $C_{\alpha'}$. The original multiplet at 37 ppm is observed as two doublets with no coupling to ^{183}W and can be assigned to C_β and $C_{\beta'}$. The AB spin system derived from the sharp singlet at 54 ppm at room temperature is unaffected by the isotope dilution experiment and the resonances may therefore be assigned to the coordinated ethylene ligand, C_γ and $C_{\gamma'}$, consistent with the relatively small value observed for the $J_{^{13}C-^{183}W}$ coupling constant. The pairwise retention of the ^{13}C label confirms that no carbon atom metathesis has taken place, and the absence of $J_{C_\beta-C_{\beta'}}$ coupling demonstrates that the metallacyclopentane ring is derived from two intact ethylene molecules.

Table II. Summary of Crystal Data

compound	I[a]	II[b]
empirical formula	$W_2O_6C_{24}H_{54}$	$C_{27}H_{53}NO_6W_1\cdot{}^1/_2C_5H_5N$
color of cryst	black	black
cryst dimens, mm	0.25 × 0.25 × 0.25	0.28 × 0.30 × 0.32
space group	$P2_1/c$	$P\bar{1}$
cell dimens		
temp, °C	−155	−150
a, Å	10.069 (5)	10.968 (2)
b, Å	17.033 (9)	17.507 (4)
c, Å	17.278 (9)	9.433 (1)
α, deg		93.56 (1)
β, deg	91.38 (3)	96.83 (1)
γ, deg		101.29 (1)
A, molecules/cell	4	2
V, $Å^3$	2962.41	1756.88
d_{calcd}, gm/cm^3	1.808	1.693
wavelength, Å	0.71069	0.71069
mol wt	806.39	895.46
linear abs coeff, cm^{-1}	79.587	67.203
detector to sample dist, cm	22.5	22.5
sample to source dist, cm	23.5	23.5
av ω scan width at halfheight	0.25	0.25
scan speed, deg/min	4.0	8.0
scan width, deg + dispersn	2.0	1.6
individl bkgd, s	6	6
aperture size, mm	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6–45	6–45
total no. of reflctns collected	4244	4750
no. of unique intensities	3869	4613
no. of $F > 0.0$	3637	4417
no. of $F > 2.33\sigma(F)$	3264	
no. of $F > 3.0\sigma(F)$		4087
$R(F)$	0.0393	0.0310
$R_w(F)$	0.0398	0.0342
goodness of fit for last cycle	0.900	0.928
max δ/σ for last cycle	0.05	0.05

[a] I = $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. [b] II = $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)\cdot{}^1/_2py$.

With the values of the $J_{^{13}C-^{13}C}$ derived from this experiment, the low temperature limiting ^{13}C NMR spectrum of the fully labeled species, Figure 5a, could successfully be simulated. The variable-temperature ^{13}C NMR data therefore provide evidence for two independent, but concurrent, fluxional processes: (1) Rapid rotation of the $\eta^2\text{-}C_2H_4$ ligand about the metal–olefin axis and (2) a fluxional process that generates a mirror plane containing the two metal atoms and bisects the metallacyclopentane ligand such that C_α is exchanged with $C_{\alpha'}$ and C_β is exchanged with $C_{\beta'}$. The two processes have different free energies of activation as determined from the coalescence temperatures of the ^{13}C resonances. The barrier, $\Delta G^{\ddagger}$, for ethylene rotation is 10.2 (±0.5) kcal mol^{-1} and the barrier for exchange of C_α and $C_{\alpha'}$ is 13.5 (±0.5) kcal mol^{-1}. Pseudorotation of the alkoxide ligands on W(2) (of VI) and bridge-terminal alkoxide exchange would satisfy the requirements of process 2.

The NMR data, however, do not unequivocally define the coordination of the $(CH_2)_4$ ligand. It could be part of a metallacyclopentane as shown in VI or the C_4 ring could span the M–M bond as seen in $M_2(CH_2)_4(NMe_2)_4$ (M≡M) compounds.[30] A single-crystal X-ray diffraction study was undertaken to distinguish between these possibilities.

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(28) For a listing of $^1J_{^{183}W-^{13}C}$ values for the various alkyl/alkylidene/alkylidyne/alkyne complexes, see Table VIII in ref 19.

(30) Chetcuti, M. J.; Chisholm, M. H.; Chiu, H.-T.; Huffman, J. C. *Polyhedron* **1985**, *4*, 1213.

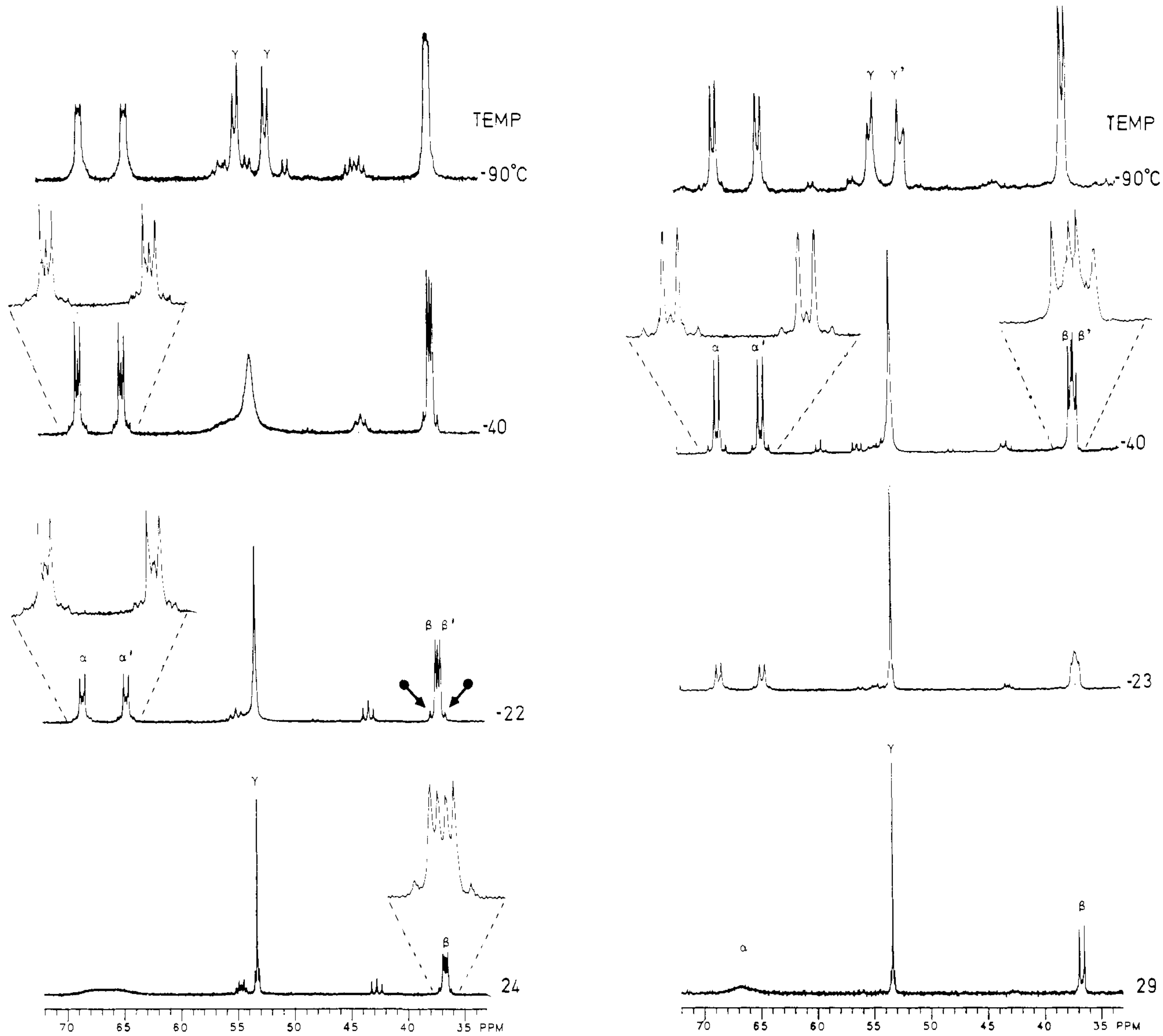

Figure 5. (a, top) Variable-temperature $^{13}C\{^1H\}$ NMR spectra (75.4 MHz, toluene-d_8) of $W_2(O\text{-}i\text{-}Pr)_6({*}CH_2)_4(\eta^2\text{-}{*}C_2H_4)$ generated in situ by addition of an excess of ${*}C_2H_4$ (where ${*}C$ = 99% ^{13}C enriched) to $W_2(O\text{-}i\text{-}Pr)_6$ at 0 °C. (b, bottom) Variable-temperature $^{13}C\{^1H\}$ NMR spectra (same conditions) of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ generated in situ by the addition of an excess of ethylene, ${*}C_2H_4$, and C_2H_4 in a 1:3 ratio, respectively. The dilution of the ^{13}C isotopically labeled ethylene results in a much simplified spin system within the metallocyclopentane ring, but does not affect the resonances of the coordinated ethylene ligand under the experimental conditions (see text).

Solid-State and Molecular Structure of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. A ball-and-stick drawing of the molecular structure of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ is shown in Figure 6 and a summary of crystal data is given in Table II. The metallacyclopentane ring is unequivocally established and the $\eta^2\text{-}C_2H_4$ ligand is bonded to the tungsten atom that is not a part of that ring. The local geometry about each tungsten atom may be viewed as pseudooctahedral if the $\eta^2\text{-}C_2H_4$ ligand is counted as a monodentate ligand. The W-to-W distance, 2.643 (1) Å is approaching that anticipated for a d^1-d^1 M–M single bond[31] and supports the view that the $(W{\equiv}W)^{6+}$ unit has been oxidized by (i) the coupling of the two ethylene ligands and (ii) the coordination of the π-acceptor ethylene ligand. By comparison, we note the W-to-W distance of 3.1 Å in $(i\text{-}PrO)_2(\eta^2\text{-}C_2(NMe_2))_2W(\mu\text{-}O\text{-}i\text{-}Pr)_3W(O\text{-}i\text{-}Pr)(CO)_2$.[32] Here the presence of one alkyl and two CO ligands effectively destroys the W-to-W bond by tungsten-to-ligand π back-bonding.

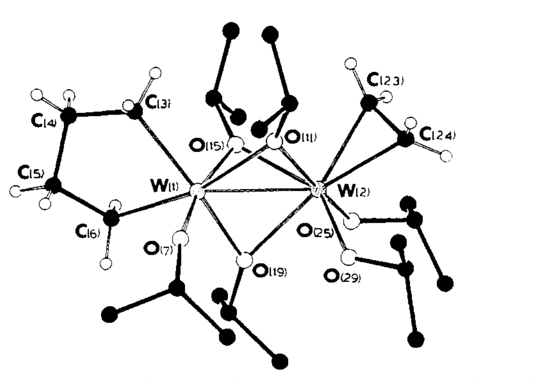

Figure 6. Ball-and-stick drawing of the molecular structure of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ together with the numbering scheme used in Tables IV and V, emphasizing the approximate confacial bioctahedral ligand environment of the metal atoms.

There is some evidence, from the structural data, that W(1) is more oxidized than W(2). Two of the three bridging isopropoxide ligands have significantly shorter W(1)–O than W(2)–O distances, and the terminal isopropoxide ligand bonded to W(1) has an angle at oxygen (164.7°) that is distinctly more linear than

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[31] For a listing of M–M distances in alkoxide bridged compounds, see: Reference 21.

[32] Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *J. Chem. Soc., Chem. Commun.* **1986**, 717. Chisholm, M. H.; Ho, D.; Huffman, J. C.; Marchant, N. S. *Organometallics*, in press.

Table III. Fractional Coordinates and Isotropic Thermal Parameters for the Molecule $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	2572.7 (5)	6209.8 (3)	8321.1 (3)	13
W(2)	1729.0 (4)	5391.0 (3)	7106.6 (3)	13
C(3)	4564 (12)	6330 (8)	8848 (7)	22
C(4)	4448 (14)	6566 (8)	9693 (7)	26
C(5)	3474 (15)	6006 (8)	10067 (7)	29
C(6)	2245 (12)	5966 (8)	9536 (7)	22
O(7)	2219 (7)	7249 (5)	8280 (4)	19
C(8)	2073 (12)	8051 (7)	8044 (7)	21
C(9)	2208 (14)	8110 (8)	7176 (8)	30
C(10)	3097 (16)	8534 (8)	8490 (8)	33
O(11)	3453 (7)	6139 (4)	7283 (4)	14
C(12)	4719 (11)	6294 (8)	6970 (7)	22
C(13)	5649 (12)	5616 (8)	7040 (8)	30
C(14)	4497 (13)	6553 (8)	6137 (7)	26
O(15)	2796 (7)	5027 (4)	8146 (4)	15
C(16)	3242 (13)	4369 (7)	8602 (7)	21
C(17)	2112 (15)	3922 (8)	8954 (8)	31
C(18)	4095 (15)	3861 (9)	8109 (8)	36
O(19)	633 (7)	5832 (4)	8024 (4)	15
C(20)	−681 (11)	5918 (7)	8256 (7)	21
C(21)	8987 (13)	5387 (9)	8919 (7)	28
C(22)	9044 (13)	6767 (9)	8478 (8)	32
C(23)	588 (12)	4330 (7)	7212 (7)	18
C(24)	9896 (12)	4841 (7)	6687 (7)	19
O(25)	1266 (8)	6265 (5)	6434 (4)	19
C(26)	219 (12)	6435 (7)	5879 (7)	21
C(27)	9065 (15)	6822 (8)	6268 (9)	34
C(28)	818 (14)	6951 (9)	5259 (7)	32
O(29)	2835 (8)	4827 (5)	6405 (4)	18
C(30)	2531 (11)	4323 (8)	5758 (7)	22
C(31)	2691 (15)	4778 (8)	5019 (8)	34
C(32)	3464 (14)	3636 (8)	5796 (8)	30

Table IV. Selected Bond Distances (Å) for the Molecule $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$

A	B	distance	A	B	distance
W(1)	W(2)	2.6426 (12)	W(2)	O(19)	2.092 (8)
W(1)	O(7)	1.806 (8)	W(2)	O(25)	1.938 (8)
W(1)	O(11)	2.024 (7)	W(2)	O(29)	1.923 (8)
W(1)	O(15)	2.051 (7)	W(2)	C(23)	2.151 (11)
W(1)	O(19)	2.108 (7)	W(2)	C(24)	2.179 (12)
W(1)	C(3)	2.191 (12)	C(3)	C(4)	1.523 (17)
W(1)	C(6)	2.173 (12)	C(4)	C(5)	1.522 (20)
W(2)	O(11)	2.169 (7)	C(5)	C(6)	1.524 (18)
W(2)	O(15)	2.162 (7)	C(23)	C(24)	1.428 (17)

Table V. Selected Bond Angles (Degrees) for $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$

A	B	C	angle
W(2)	W(1)	O(7)	115.27 (24)
W(2)	W(1)	O(11)	53.40 (20)
W(2)	W(1)	O(15)	53.05 (20)
W(2)	W(1)	O(19)	50.75 (20)
W(2)	W(1)	C(3)	130.7 (3)
W(2)	W(1)	C(6)	127.8 (3)
O(7)	W(1)	O(11)	96.5 (3)
O(7)	W(1)	O(15)	168.3 (3)
O(7)	W(1)	O(19)	96.3 (3)
O(7)	W(1)	C(3)	95.9 (4)
O(7)	W(1)	C(6)	101.0 (4)
O(11)	W(1)	O(15)	76.1 (3)
O(11)	W(1)	O(19)	100.9 (3)
O(11)	W(1)	C(3)	87.6 (4)
O(11)	W(1)	C(6)	157.7 (4)
O(15)	W(1)	O(19)	76.6 (3)
O(15)	W(1)	C(3)	92.9 (4)
O(15)	W(1)	C(6)	88.5 (4)
O(19)	W(1)	C(3)	164.3 (4)
O(19)	W(1)	C(6)	90.9 (4)
C(3)	W(1)	C(6)	77.0 (5)
W(1)	W(2)	O(11)	48.53 (20)
W(1)	W(2)	O(15)	49.30 (20)
W(1)	W(2)	O(19)	51.29 (20)
W(1)	W(2)	O(25)	97.96 (24)
W(1)	W(2)	O(29)	125.77 (22)
W(1)	W(2)	C(23)	122.6 (3)
W(1)	W(2)	C(24)	138.1 (3)
O(11)	W(2)	O(15)	70.87 (28)
O(11)	W(2)	O(19)	96.8 (3)
O(11)	W(2)	O(25)	79.2 (3)
O(11)	W(2)	O(29)	84.8 (3)
O(11)	W(2)	C(23)	155.3 (4)
O(11)	W(2)	C(24)	165.5 (4)
O(15)	W(2)	O(19)	74.58 (28)
O(15)	W(2)	O(25)	145.7 (3)
O(15)	W(2)	O(29)	95.6 (3)
O(15)	W(2)	C(23)	86.8 (4)
O(15)	W(2)	C(24)	123.6 (4)
O(19)	W(2)	O(25)	93.1 (3)
O(19)	W(2)	O(29)	168.8 (3)
O(19)	W(2)	C(23)	86.8 (4)
O(19)	W(2)	C(24)	87.0 (4)
O(25)	W(2)	O(29)	98.1 (3)
O(25)	W(2)	C(23)	125.1 (4)
O(25)	W(2)	C(24)	86.6 (4)
O(29)	W(2)	C(23)	87.2 (4)
O(29)	W(2)	C(24)	94.2 (4)
C(23)	W(2)	C(24)	38.5 (5)
W(1)	O(7)	C(8)	164.7 (7)
W(1)	O(11)	W(2)	78.07 (25)
W(1)	O(11)	C(12)	137.9 (7)
W(2)	O(11)	C(12)	141.1 (7)
W(1)	O(15)	W(2)	77.65 (26)
W(1)	O(15)	C(16)	136.1 (7)
W(2)	O(15)	C(16)	145.4 (7)
W(1)	O(19)	W(2)	77.96 (26)
W(1)	O(19)	C(20)	140.8 (7)
W(2)	O(19)	C(20)	140.8 (7)
W(2)	O(25)	C(26)	135.8 (7)
W(2)	O(29)	C(30)	132.4 (7)
W(1)	C(3)	C(4)	109.4 (8)
C(3)	C(4)	C(5)	107.9 (10)
C(4)	C(5)	C(6)	107.2 (10)
W(1)	C(6)	C(5)	115.6 (8)
W(2)	C(23)	C(24)	71.8 (6)
W(2)	C(24)	C(23)	69.7 (7)

the other terminal alkoxide ligands. This species could therefore be considered to contain a $[W^V = W^{III}]^{8+}$ dinuclear core in which there is, in addition to the W–W σ bond, a donor bond from W(2) → W(1).

The C–C distance of the η^2-C_2H_4 ligand, 1.43 (2) Å, is notably lengthened from the value of 1.34 (1) Å in free ethylene,[33] and the W–C distances to the η^2-C_2H_4 ligand are essentially identical with the W–η^1-C distances in the metallacyclopentane ligand. The W–η^2-C_2H_4 moiety could be viewed as a metallacyclopropane as a result of extensive Wd_π to C_2 π^* bonding. However, based on the magnitude of the $J_{^{13}C-^{13}C}$ value for the W–η^2-C_2H_4 ligand of 35 Hz, the back-bonding is not quite as extensive as in $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$. See Table I. Note also that there is facile rotation about the W–η^2-C_2H_4 bond that this is only frozen out at low temperatures.

A listing of fractional coordinates for the $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ molecule is given in Table III and selected bond distances and bond angles are given in Tables IV and V, respectively.

b. $W_2(O\text{-}c\text{-}C_5H_9)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. Hydrocarbon solutions of $W_2(O\text{-}c\text{-}C_5H_9)_6$ (W≡W) react with an excess of ethylene very slowly at 0 °C but faster at room temperature to form $W_2(O\text{-}c\text{-}C_5H_9)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, which exhibits variable-temperature ^1H and ^{13}C NMR spectra similar to those of the isopropoxide analogue (see Experimental Section). From the spectroscopic data it is likely that $W_2(O\text{-}c\text{-}C_5H_{11})_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ has a structure similar to that of VI. The barrier to ethylene rotation in this case is 10.3 (±0.5) kcal mol^{-1} and the barrier to exchange between C_α and $C_{\alpha'}$ is 13.9 (±0.5) kcal mol^{-1}.

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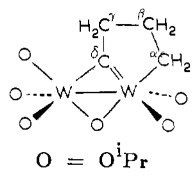
(33) Kuchitsu, K. *MTP Int. Rev. Sci., Phys. Chem., Ser. One* **1972**, *11*, 221.



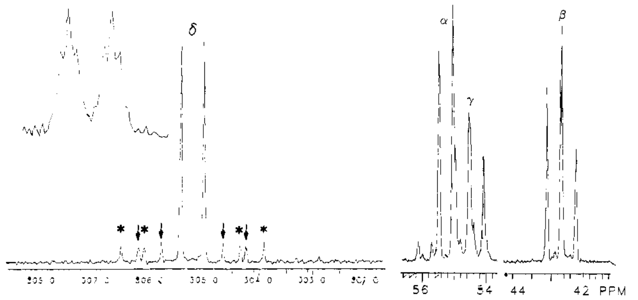
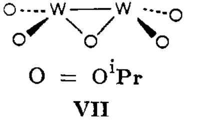


Figure 7. $^{13}C\{^1H\}$ NMR spectrum (75.4 MHz, 23 °C, toluene-d_8) of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}{*C}{*CH_2}{*CH_2}{*CH_2})$, where *C represents 99 mol % ^{13}C, showing the multiplicities of the resonances due to carbon–carbon coupling and the ^{183}W satellites of resonances α and δ; C_δ exhibits coupling to two different tungsten atoms of 117 and 165 Hz, whereas C_α exhibits coupling to only one tungsten atom of 97 Hz. Inset is the ^1H-coupled ^{13}C spectrum of C_δ showing it possesses no directly attached protons, but that it is bonded to a methylenic group, $^2J_{C\text{-}H}$ = 7 Hz.

c. $W_2(OCH_2\text{-}t\text{-}Bu)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. In the presence of an excess of ethylene, solutions of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ react to form $W_2(OCH_2\text{-}t\text{-}Bu)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ as well as other species. In contrast to the analogues described above, $W_2(OCH_2\text{-}t\text{-}Bu)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ shows no evidence of any dynamic process on the NMR time scale at room temperature. All the ^{13}C resonances of the metallacyclopentane ring are sharp and distinct, and the resonances ascribed to the coordinated ethylene are observed as two AB coupled doublets. C_α and $C_{\alpha'}$ carbon resonances exhibit large (70 and 86 Hz, respectively) couplings to ^{183}W, and the resonances ascribed to the coordinated ethylene ligand, C_γ and $C_{\gamma'}$ exhibit smaller couplings of 33 and 37 Hz. A 2D ^{13}C chemical shift correlated experiment confirmed that the connectivity was consistent with a structure such as VI where C_α is connected to C_β, $C_{\alpha'}$ is connected to $C_{\beta'}$, and C_γ is connected to $C_{\gamma'}$. A 2D heteronuclear ^{13}C–^1H chemical shift correlated experiment was used to locate the ^1H NMR resonances of $W_2(OCH_2\text{-}t\text{-}Bu)_6\text{-}(CH_2)_4(\eta^2\text{-}C_2H_4)$. They were observed over a ^1H NMR chemical shift region from 3.8 to 1.2 ppm, consistent with the values observed in the low temperature limiting ^1H NMR spectrum for the isopropoxide analogue.

$W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ and $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)\cdot{}^1/_2py$. The final products in the reaction between $W_2(OR)_6$ compounds and ethylene are the compounds $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$, where R = c-$C_6H_{11}$, c-$C_5H_9$, *i*-Pr, and CH_2-*t*-Bu. Regrettably, at this time we have been unable to obtain single crystals for any of these compounds that were suitable for a single-crystal X-ray diffraction study, though the solid-state characterization of a pyridine adduct, $W_2(O\text{-}i\text{-}Pr)_6\text{-}(\mu\text{-}CCH_2CH_2CH_2)\cdot py\cdot{}^1/_2py$, coupled with NMR spectroscopic data leave little doubt about the authenticity of this class of new compounds.

$W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ compounds are fluxional on the NMR time scale but at −90 °C in toluene-d_8 the ^1H signals of the alkoxy groups coupled with those of the metallacycle are consistent with a structure of the type depicted by VII.



VII

Table VI. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)\cdot{}^1/_2py$

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	1724.4 (3)	3279.1 (2)	1419.0 (3)	12
W(2)	2867.6 (3)	2069.0 (2)	1199.2 (3)	11
C(3)	3307 (7)	3067 (4)	2381 (8)	13
C(4)	4457 (8)	3320 (5)	3465 (9)	20
C(5)	4887 (8)	2565 (5)	3812 (9)	17
C(6)	4695 (8)	2041 (5)	2391 (9)	18
O(7)	1120 (5)	2269 (3)	138 (5)	17
C(8)	−101 (9)	1893 (6)	−535 (11)	31
C(9)	−744 (9)	2454 (6)	−1272 (12)	33
C(10)	−20 (9)	1180 (6)	−1463 (12)	36
O(11)	317 (5)	2907 (3)	2366 (6)	18
C(12)	−406 (7)	3280 (5)	3249 (9)	17
C(13)	−1764 (9)	3020 (6)	2674 (11)	30
C(14)	−106 (10)	3072 (6)	4775 (10)	30
O(15)	1869 (5)	4265 (3)	2525 (5)	17
C(16)	2740 (8)	4736 (5)	3644 (10)	23
C(17)	3888 (10)	5139 (6)	3079 (12)	37
C(18)	2074 (12)	5311 (8)	4339 (14)	54
O(19)	1992 (5)	3836 (3)	−205 (6)	17
C(20)	1990 (8)	4622 (5)	−512 (9)	18
C(21)	3191 (11)	4956 (6)	−1077 (15)	45
C(22)	832 (11)	4607 (7)	−1581 (13)	43
O(23)	3571 (5)	2295 (3)	−506 (5)	16
C(24)	4202 (9)	2896 (5)	−1255 (10)	24
C(25)	5470 (11)	2701 (7)	−1466 (14)	46
C(26)	3379 (11)	2959 (6)	−2611 (10)	34
O(27)	1973 (5)	1408 (3)	2409 (6)	15
C(28)	1377 (8)	1403 (5)	3679 (8)	16
C(29)	−8 (9)	1038 (5)	3262 (11)	26
C(30)	1991 (9)	946 (6)	4753 (10)	28
N(31)	3021 (6)	786 (4)	240 (7)	14
C(32)	3116 (8)	220 (5)	1101 (9)	19
C(33)	3309 (8)	−496 (5)	643 (10)	22
C(34)	3356 (8)	−669 (5)	−764 (11)	25
C(35)	3237 (9)	−100 (5)	−1706 (10)	25
C(36)	3078 (8)	626 (5)	−1164 (9)	19
C(37)	7103 (9)	1388 (5)	5421 (10)	27
N(38)	6559 (5)	582 (4)	5426 (7)	12
C(39)	5229 (8)	442 (5)	5092 (10)	24

Evidence for the alkylidyne ring moiety comes from both ^1H and ^{13}C NMR experiments. In the ^1H NMR spectrum, two triplets (2.7 and 4.7 ppm) and a pentet (3.6 ppm) were observed. The ^{13}C NMR spectrum of the ring carbon resonances derived from 99% ^{13}C enriched ethylene in $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}{*C}{*CH_2}{*CH_2}{*CH_2})$ are shown in Figure 7. C_α is directly bonded to one tungsten atom ($J_{C\text{-}W}$ = 97 Hz) and one carbon atom. C_δ is bonded asymmetrically to two tungsten nuclei and one other carbon atom. C_α, C_β, and C_γ have two attached protons (from ^1H-coupled ^{13}C NMR experiments), and C_δ has no attached protons. A 2D ^{13}C chemical shift correlated experiment confirmed the connectivity, and a 2D ^{13}C–^1H heteronuclear chemical shift correlated experiment completed the assignments (see Experimental Section for details). The methylene protons of the alkylidyne ring are nondiastereotopic even at low temperatures, which is consistent with the presence of a mirror plane passing through the $\mu\text{-}CCH_2CH_2CH_2$ carbons and the tungsten atoms.

In VII each W atom possesses a distorted trigonal-bipyramidal geometry and the μ-alkylidyne carbon atom occupies a common equatorial site. It is not clear which tungsten atom should carry the formal W–C double bond, but the marked inequivalence of the $^1J_{^{183}W\text{-}^{13}C}$ coupling constants, 117 and 165 Hz, is consistent with an asymmetric bridge.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)\cdot{}^1/_2py$. Though no suitable crystals of a compound of formula $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ were obtained, a pyridine adduct of the isopropoxide compound did yield a crystalline sample suitable for an X-ray study. A summary of the crystal data is given in Table II.

A ball-and-stick drawing of the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)$ molecule is given in Figure 8. Fractional coordinates are given in Table VI and selected bond distances and bond angles are given in Tables VII and VIII.

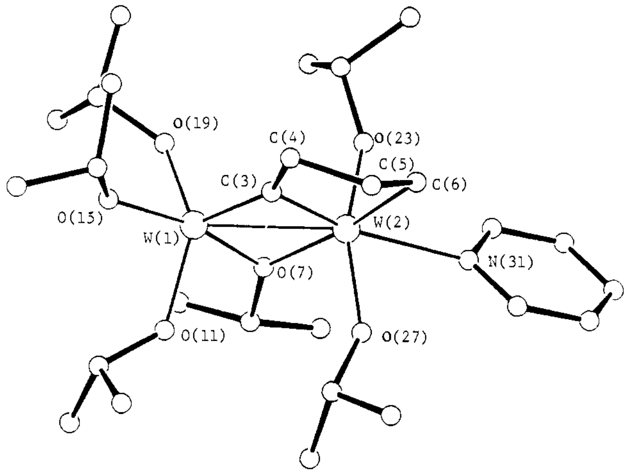


Figure 8. Ball-and-stick drawing of the molecular structure of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)\cdot{}^1/_2py$ together with the numbering scheme used in Tables VII and VIII.

Table VII. Selected Bond Distances (Å) for the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)$ Molecule

A	B	distance	A	B	distance
W(1)	W(2)	2.6742 (7)	O(11)	C(12)	1.429 (10)
W(1)	O(7)	2.028 (5)	O(15)	C(16)	1.433 (10)
W(1)	O(11)	1.900 (5)	O(19)	C(20)	1.424 (10)
W(1)	O(15)	1.929 (5)	O(23)	C(24)	1.418 (10)
W(1)	O(19)	1.887 (5)	O(27)	C(28)	1.431 (9)
W(1)	C(3)	1.974 (8)	N(31)	C(32)	1.332 (11)
W(2)	O(7)	2.156 (5)	N(31)	C(36)	1.348 (11)
W(2)	O(23)	1.896 (5)	N(38)	C(37)	1.420 (11)
W(2)	O(27)	1.895 (5)	N(38)	C(39)	1.424 (10)
W(2)	N(31)	2.414 (6)	C(3)	C(4)	1.500 (11)
W(2)	C(3)	1.956 (7)	C(4)	C(5)	1.529 (12)
W(2)	C(6)	2.190 (8)	C(5)	C(6)	1.545 (12)
O(7)	C(8)	1.425 (10)			

The molecular structure of the pyridine adduct is related to that shown in VII by the addition of a pyridine ligand trans to the W–C double bond. In this way one tungsten atom, W(2), becomes octahedrally coordinated, while the other, W(1), remains in a trigonal-bipyramidal environment. The W–W distance, 2.674 (1) Å, is consistent with a W–W single bond in a W_2^{10+} dinuclear compound, supported by an alkylidyne and an alkoxide bridge.[34]

The W–W distances to the bridging alkylidyne carbon atom are essentially identical, 1.974 (8) and 1.956 (7) Å, and do not reflect the asymmetry predicted by the valence bond description shown in VII. However, the W–O(7) distances associated with the bridging alkoxide are markedly asymmetric W(1)–O(7) = 2.028 (5) Å versus W(2)–O(7) = 2.156 (5) Å. The W(2)–C(6) distance, 2.190 (8) Å, is well within the range expected for a tungsten–C_{sp^3} bond distance.[35] The C–C distances within the metallacycle are as expected for C_{sp^3}–C_{sp^3} or C_{sp^2}–C_{sp^3} distances,[33] and there is a slight twist of the metallacyclopentene ring such that the C–H bonds of neighboring methylene groups are not eclipsed.

The variable-temperature ^1H and ^{13}C NMR spectra of the pyridine adduct have been recorded in toluene-d_8 and in neat pyridine-d_5. The spectra are essentially identical with those obtained for $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$. The ^{13}C NMR spectra recorded at low temperatures indicate the molecule retains the virtual mirror plane of symmetry and it appears that the pyridine ligation does not significantly alter the asymmetry of the W_2–μ-C bridge, as evidenced by the two distinct sets of tungsten satellites.

Table VIII. Selected Bond Angles (Degrees) for the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ Molecule

A	B	C	angle
W(2)	W(1)	O(7)	52.41 (15)
W(2)	W(1)	O(11)	104.63 (16)
W(2)	W(1)	O(15)	141.27 (16)
W(2)	W(1)	O(19)	106.71 (16)
W(2)	W(1)	C(3)	46.85 (22)
O(7)	W(1)	O(11)	84.42 (22)
O(7)	W(1)	O(15)	165.63 (22)
O(7)	W(1)	O(19)	90.19 (22)
O(7)	W(1)	C(3)	99.26 (26)
O(11)	W(1)	O(15)	86.46 (23)
O(11)	W(1)	O(19)	135.34 (23)
O(11)	W(1)	C(3)	113.21 (27)
O(15)	W(1)	O(19)	88.51 (22)
O(15)	W(1)	C(3)	94.53 (27)
O(19)	W(1)	C(3)	111.41 (27)
W(1)	W(2)	O(7)	48.20 (13)
W(1)	W(2)	O(23)	98.36 (16)
W(1)	W(2)	O(27)	99.11 (16)
W(1)	W(2)	N(31)	153.39 (15)
W(1)	W(2)	C(3)	47.40 (22)
W(1)	W(2)	C(6)	123.80 (23)
O(7)	W(2)	O(23)	87.88 (21)
O(7)	W(2)	O(27)	89.82 (22)
O(7)	W(2)	N(31)	105.19 (20)
O(7)	W(2)	C(3)	95.59 (26)
O(7)	W(2)	C(6)	171.88 (26)
O(23)	W(2)	O(27)	154.28 (22)
O(23)	W(2)	N(31)	78.20 (22)
O(23)	W(2)	C(3)	103.96 (27)
O(23)	W(2)	C(6)	92.52 (27)
O(27)	W(2)	N(31)	77.71 (22)
O(27)	W(2)	C(3)	101.76 (27)
O(27)	W(2)	C(6)	93.29 (28)
N(31)	W(2)	C(3)	159.19 (27)
N(31)	W(2)	C(6)	82.81 (27)
C(3)	W(2)	C(6)	76.4 (3)
W(1)	O(7)	W(2)	79.39 (17)
W(1)	O(7)	C(8)	131.3 (5)
W(2)	O(7)	C(8)	144.1 (5)
W(1)	O(11)	C(12)	133.7 (5)
W(1)	O(15)	C(16)	137.1 (5)
W(1)	O(19)	C(20)	133.9 (5)
W(2)	O(23)	C(24)	144.7 (5)
W(2)	O(27)	C(28)	143.7 (5)
W(1)	C(3)	W(2)	85.8 (3)
W(1)	C(3)	C(4)	149.3 (6)
W(2)	C(3)	C(4)	125.0 (6)
C(3)	C(4)	C(5)	105.1 (7)
C(4)	C(5)	C(6)	107.2 (7)
W(2)	C(6)	C(5)	109.3 (5)

The W(2)–N(pyridine) distance is very long, 2.414 (6) Å, and it seems unlikely that the presence or absence of this weak bond will significantly influence the rest of the molecule. We conclude that the marked difference in $J_{^{183}W-^{13}C}$ values may not, in this instance, be a measure of a valence bond asymmetry of the μ-alkylidyne ligand as depicted by VII. Since carbon–tungsten bonds involve extensive W 6s orbital contributions, the more carbon–tungsten bonds that a given tungsten atom forms, the lower the average value of $J_{^{183}W-^{13}C}$. In $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)_x$ compounds, $x = 0$ or 1, W(1) forms only one W–C bond whereas W(2) forms two, and so the larger $J_{^{183}W-^{13}C}$ could well involve W(1).

Mechanistic Aspects of the Reactions between $W_2(OR)_6$ Compounds and Ethylene. Though $W_2(OR)_6$ compounds react with ethylene to give $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ compounds, eq 2, where R = *i*-Pr, c-C_6H_{11}, c-C_5H_9, and CH_2-*t*-Bu, there are competing reactions for R = CH_2-*t*-Bu. In the latter case an ethylidyne bridged complex is also formed. This is clearly evident from studies using ^{13}C-enriched ethylene that show the formation of a $W_2(\mu\text{-}{}^*C^*CH_3)$ moiety in the ^{13}C NMR spectra.

At the present time we do not know much about the reaction leading to the $W_2(\mu\text{-}CCH_3)$-containing compound that is seen for

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[34] (a) Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Klang, J. A. *Organometallics* **1988**, *7*, 1033.

[35] For a discussion of W–C distances as a function of carbon sp, sp^2, sp^3 hybridization, see: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

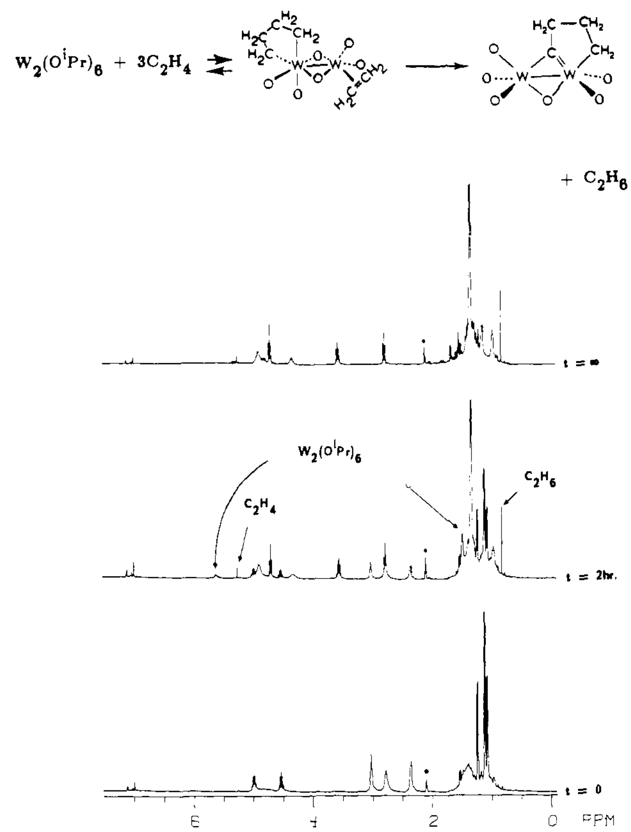


Figure 9. ^1H NMR spectra (360 MHz, 23 °C, toluene-d_8) showing the conversion of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ (t = 0) to $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ ($t = \infty$, ~24 h). At intermediate times (t = 2 h) resonances are observed (as indicated) consistent with the formation of $W_2(O\text{-}i\text{-}Pr)_6$ and C_2H_4.

R = $CH_2\text{-}t\text{-}Bu$. This reaction is surpressed by added ethylene and it seems likely that this involves either a competeing reaction of the bis(ethylene) complex, $W_2(OCH_2\text{-}t\text{-}Bu)_6(C_2H_4)_2$, or an independent reaction of a monoethylene adduct that is present in a small equilibrium concentration. In the presence of an excess of C_2H_4 (>10 equiv) the formation of the ethylidyne species is surpressed. An analogous species can be isolated for the isopropoxide derivative from the reaction of $W_2(O\text{-}i\text{-}Pr)_6 + C_2H_4 + H_2$. The mechanism by which these species are formed and their full characterization is under study and will be reported elsewhere.[36]

The relative rates of formation of the $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ compounds follow the order of alkoxide ligands R = i-Pr > c-C_5H_9 > c-C_6H_{11} > $CH_2\text{-}t\text{-}Bu$. This apparently reflects the relative rates of formation of a $W_2(OR)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ complex. In the case of R = $CH_2\text{-}t\text{-}Bu$, the successive formation of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ and $W_2(OCH_2\text{-}t\text{-}Bu)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ can be seen in the ^1H and ^{13}C NMR spectra, while for R = i-Pr and c-C_5H_9, the formation of $W_2(OR)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ is rapid and no $W_2(OR)_6(\eta^2\text{-}C_2H_4)_2$ compound is observed. For $W_2(O\text{-}c\text{-}C_6H_{11})_6$, the reaction with ethylene is relatively slow and proceeds to $W_2(O\text{-}c\text{-}C_6H_{11})_6(\mu\text{-}CCH_2CH_2CH_2)$ without the detection of any intermediates (by ^{13}C NMR spectroscopy employing $^{13}C_2H_4$).

These observations can qualitatively be understood in terms of steric pressure at the tungsten centers which follows the order R = c-C_6H_{11} > c-C_5H_9 > i-Pr > $CH_2\text{-}t\text{-}Bu$. (1) For reaction to proceed according to eq 2 two molecules of ethylene must coordinate to the W_2 center and couple. Apparently steric pressure at the W_2 centers favors C–C coupling R = i-Pr > $CH_2\text{-}t\text{-}Bu$, but if the steric requirements of R are too great then coordination of ethylene cannot occur, thus leading to the observed rate R = i-Pr > c-C_5H_9 ≫ t-Bu.[37]

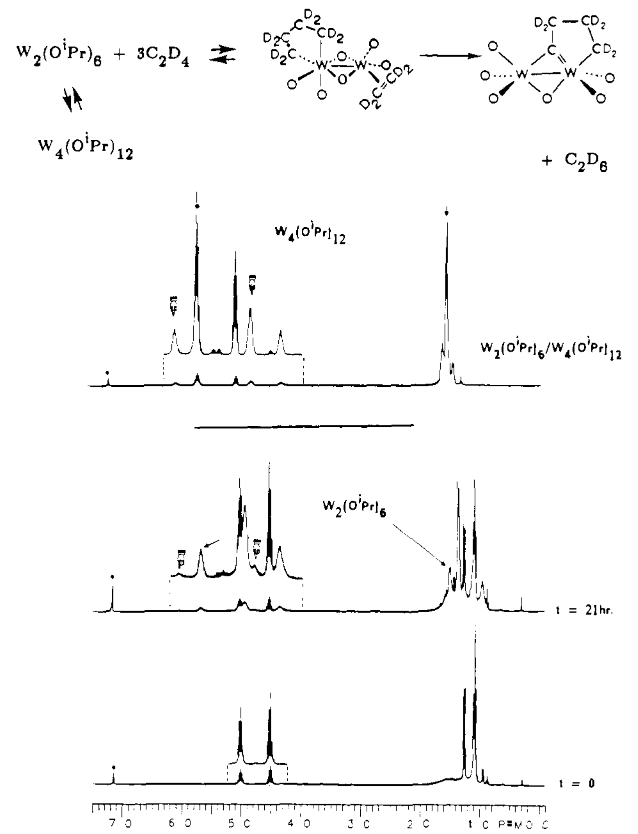
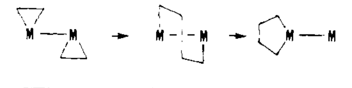
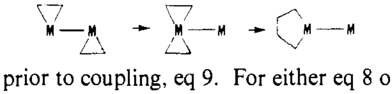


Figure 10. ^1H NMR spectra (300 MHz, 23 °C, benzene-d_6) showing the conversion of $W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$ (t = 0) to $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCD_2CD_2CD_2)$. After 21 h, resonances consistent with the presence of both $W_2(O\text{-}i\text{-}Pr)_6$ and $W_4(O\text{-}i\text{-}Pr)_{12}$ are observed, as can be seen by the comparison with the control experiment (top spectrum) which contains a mixture of these two species. The arrows (↓) indicate the position of the ^1H NMR resonances of $W_2(O\text{-}i\text{-}Pr)_6$ and the *hands* the signals associated with $W_4(O\text{-}i\text{-}Pr)_{12}$.

According to our proposed general scheme (Scheme I), the metallacyclopentane ligand is formed from the successive addition of two ethlene molecules to the W_2 center. The exact nature of the coupling remains speculative. In particular, we cannot comment on whether or not the C–C coupling occurs across the M–M bond to form a 1,2-dimetallacyclohexane ring which then undergoes a ring contraction by alkyl group migration, as shown in eq 8, or whether the two olefin ligands are present at the same metal center prior to coupling, eq 9. For either eq 8 or 9, alkoxide ligand migration from one metal to the other could occur, and it is easy to see how a vacant coordination site could be generated at the dimetal center to accommodate another moelcule of ethylene.



(8)



(9)

From our studies of the reactivity of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, we conclude that (i) this species is an intermediate in the formation of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ and (ii) it is formed *reversibly* from $W_2(O\text{-}i\text{-}Pr)_6$ and ethylene. We present the evidence for these conclusions below:

1. When toluene-d_8 solutions of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ are allowed to react in an NMR tube, ^1H resonances consistent with the formation of free ethylene and $W_2(O\text{-}i\text{-}Pr)_6$ are observed during the formation of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$, according to eq 10. See Figure 9. When the related reaction involving

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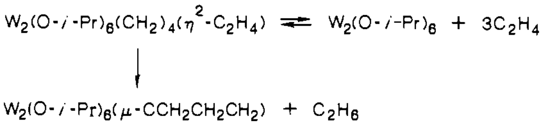
[36] Chisholm, M. H.; Hampden-Smith, M. J., unpublished results.

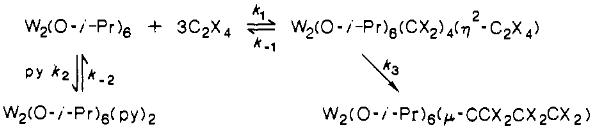
[37] The equilibria for Lewis base binding to $W_2(OR)_6$ compounds as defined by eq 5 follow the order $CH_2\text{-}t\text{-}Bu$ > i-Pr > c-C_5H_9 > c-C_6H_{11} > t-Bu. See: Reference 21.



$$\begin{tikzcd} W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4) \arrow[r, shift left] \arrow[d] & W_2(O\text{-}i\text{-}Pr)_6 + 3C_2H_4 \arrow[l, shift left] \\ W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2) + C_2H_6 & \end{tikzcd} \quad (10)$$

$W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$ is followed by ^1H NMR spectroscopy, the formation of the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCD_2CD_2CD_2)$ compound becomes sufficiently slow that resonances consistent with the formation of $W_4(O\text{-}i\text{-}Pr)_{12}$ can be detected. See Figure 10. Also, the rearrangement of the deuterium-labeled species is sufficiently slow such that, on heating a toluene-d_8 solution of $W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$ to 64 °C, the original deep red-brown solution turned bright yellow and the major species observed by ^1H NMR spectroscopy was $W_2(O\text{-}i\text{-}Pr)_6$. On cooling the solution the metallacyclopentane ring species was reformed, before final conversion to $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCD_2CD_2CD_2)$.

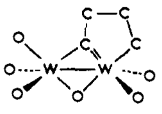
2. The conversion of $W_2(O\text{-}i\text{-}Pr)_6(CX_2)_4(\eta^2\text{-}C_2X_4)$ to $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCX_2CX_2CX_2)$, X = H or D, has been carried out in pyridine-d_5 *as a solvent* and monitored by ^1H NMR spectroscopy. Under these conditions, the larger excess of pyridine present essentially traps $W_2(O\text{-}i\text{-}Pr)_6$ as $W_2(O\text{-}i\text{-}Pr)_6(py\text{-}d_5)_2$. This is represented schematically by eq 11.



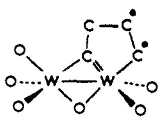
$$\begin{tikzcd} W_2(O\text{-}i\text{-}Pr)_6 + 3C_2X_4 \arrow[r, shift left, "k_1"] \arrow[d, shift right, "py\ k_2"'] & W_2(O\text{-}i\text{-}Pr)_6(CX_2)_4(\eta^2\text{-}C_2X_4) \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_3"] \\ W_2(O\text{-}i\text{-}Pr)_6(py)_2 \arrow[u, shift right, "k_{-2}"'] & W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCX_2CX_2CX_2) \end{tikzcd} \quad (11)$$

3. The compound $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ undergoes exchange with $^*C_2H_4$ ($^*C$ = 99 mol % ^{13}C). The exchange with the coordinated olefin is rapid to give $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}^*C_2H_4)$. Once again, though the NMR parameters and structural parameters for the $W\text{-}\eta^2\text{-}C_2H_4$ ligand indicate an activated or extensively rehybridized olefin, it is labile to dissociation.

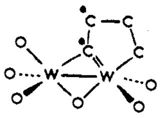
In addition, $^*C$ is ultimately incorporated into the alkylidyne ring in a pairwise manner as a result of dissociation of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ according to eq 10 to give a mixture of four isotopomers, VIII–XI.



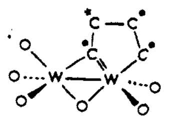
VIII



IX



X



XI

Note isotopomer VIII contains natural-abundance ^{13}C and in these experiments will give rise to singlets in the ^{13}C NMR for the α, β, γ, and δ carbon atoms, although the natural abundance of the ^{13}C isotope (1.1%) is expected to make VIII effectively invisible under the experimental conditions employed. Since no singlet resonances were observed (i.e., derived from labeled ^{13}C), this also indicates that no mischievous ethylene-metathesis reactions are occurring.

A comparison of the level of ^{13}C incorporation into the $W_2(\mu\text{-}CCH_2CH_2CH_2)$ compounds was made as a function of the amount of added $^*C_2H_4$ employing 3, 12, and 18 equiv of the latter. Incorporation of the label decreases with increasing added $^*C_2H_4$: For an added 3 equiv of $^*C_2H_4$ incorporation into the $\mu\text{-}CCH_2CH_2CH_2$ ligand was ca. 30%, but with 18 equiv of $^*C_2H_4$ incorporation was only ca. 10%. This is entirely consistent with the stepwise dissociation of C_2H_4 units from $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, as shown in eq 12. The reaction 12ii presumably involves the reverse of eq 8 or 9, the decoupling of the metallacyclopentane to two ethylene ligands followed by stepwise loss of ethylene.

$$W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4) \rightleftarrows W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4 + C_2H_4 \quad (12i)$$

$$W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4 \rightleftarrows W_2(O\text{-}i\text{-}Pr)_6 + 2C_2H_4 \quad (12ii)$$

Table IX. Rate Constants Obtained under Pseudo-First-Order Conditions for the Reaction $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4) \rightarrow W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2) + C_2H_6$ in the Presence of 20 Equiv of Ethylene

temp/°C	rate constant	temp/°C	rate constant
21	0.24×10^{-4}	40	0.35×10^{-3}
25	$0.53 \times 10^{-4} \pm 0.5 \times 10^{-6}$	45	0.55×10^{-3}
30		50	0.18×10^{-2}
35[a]	0.14×10^{-3}	55	0.34×10^{-2}
37	0.21×10^{-3}		

[a] This measurement was made at a different concentration than the other measurements. See Experimental Section.

In the case of ethylene addition to $W_2(OCH_2\text{-}t\text{-}Bu)_6$, no mono(ethylene) intermediate is detectable in the formation of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$, which implies that the mono(ethylene) must be a reactive intermediate present at low concentrations compared to $W_2(OCH_2\text{-}t\text{-}Bu)_6$ and $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$. A memory of this situation is apparently still present in the reaction between $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ and $^*C_2H_4$ (18 equiv), for although the overall level of $^*C$ incorporation is smaller than when 3 equiv of $^*C_2H_4$ is used, the presence of isotopomer XI is greater relative to IX and X than that expected from statistics by ca. 2:1.

4. The rate of formation of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ from $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ has been followed in toluene-d_8 in the presence of excess C_2H_4 (3, 10, and 20 equiv) by NMR spectroscopy. The data are given in Table IX and show that, with 20 equiv of C_2H_4 present, the formation of the alkylidyne ring complex is first order in $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ concentration. This is consistent (a) with the reversible formation of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ and (b) with the fact that this compound is an intermediate or precursor complex in the reaction yielding $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$. The possibility that $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ is formed as a result of dissociation of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ can therefore be eliminated.

The evidence gained from the above experiments rules out the possibility that the alkylidyne ring is formed from the coupling of a $W_2(\mu\text{-}C{=}CH_2)$ moiety with ethylene as we originally speculated.[18]

There is one other experiment that we mention that reflects on the conversion of the metallacyclopentane–ethylene complex to the alkylidyne ring, eq 7.

A reaction was carried out between $W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$ and added $^*C_2H_4$ (3 equiv) in toluene-d_8 and monitored by ^{13}C NMR spectroscopy. In addition to noting $^*C$ incorporation into the alkylidyne ring, the presence of ethylene and ethane was monitored. Formation of $^*C_2H_4D_2$ occurred and significantly the unreacted ethylene that was labeled showed the incorporation of deuterium: $^*C_2H_nD_{4-n}$. [It should be noted that once $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ is formed, there is no exchange with added labeled ethylenes.] The formation of $^*C_2H_{4-n}D_n$ implies that a σ-ethyl ligand is formed *reversibly* from the metallacyclopentane–ethylene complex. The hydride–deuteride necessary for the ethyl group formation comes from the metallacyclopentane ring. Thus there is an implied stepwise α-hydrogen abstraction from the metallacyclopentane to give an equilibrium involving (a) alkylidene–hydride/ethylene ⇄ alkylidene/ethyl or (b) alkylidyne–bis(hydride)/ethylene ⇄ alkylidyne–hydride/ethyl, from which reductive elimination by C–H bond formation yields ethane and the $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ compound. The elimination of ethane and the formation of an alkylidyne have a parallel with a number of recent studies in this laboratory involving 1,2-$R_2W_2(OR')_4(M{\equiv}M)$ compounds in their reactions with alkynes[27,38] and neutral donor ligands such as PMe_3.[39]

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(38) Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C. *Organometallics* **1989**, *8*, 49, 67, 80.

(39) Blau, R. J.; Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C., results to be published.

Comparison with Ethylene Activation in Other Organometallic Systems. (a) Dinuclear and Polynuclear Carbonyl Clusters. The now classic example of ethylene activation in carbonyl cluster chemistry involves the reactions employing $Os_3(CO)_{12}$.[40] Originally the reaction was observed at elevated temperatures (125 °C, 1 atm ethylene) leading to the μ-vinylidene complex $Os_3(H)_2(CCH_2)(CO)_9$.[41] Under these conditions, no intermediates were detected: the loss of three CO ligands occurs with C–H activation to give two Os–H groups and the μ-CCH_2 ligand. Subsequently, the substitutionally labile compound $Os_3(CO)_{11}(MeCN)$ was shown[42] to react with ethylene at 25 °C to give the first example of a simple olefin adduct of a trimetallic carbonyl cluster $Os_3(CO)_{11}(C_2H_4)$ that could be converted to $Os_3(H)_2(CCH_2)(CO)_9$. The intermediacy of a hydrido vinyl compound $Os_3(H)(CHCH_2)(CO)_{10}$[43] was established by other syntheses of $Os_3(H)_2(CCH_2)(CO)_9$ from the reactions between $Os_3(H)_2(CO)_{10}$ and ethyne, C_2H_2,[44] and ethylene (2 equiv).[44,45]

Subsequently, Brown and Nubel[46] investigated simple olefin activation by $Re_2(CO)_{10}$. The use of photolysis allowed for the formation of $Re_2(\mu\text{-}H)(\mu\text{-alkenyl})(CO)_{10}$ complexes at 25 °C in hydrocarbon solvents.

Very recently the reaction between $Cp'_2Ta_2X_4(M{=}M)$ and ethylene has been noted to lead to C–H oxidative addition with the formation of $Cp'_2TaX_4(\mu\text{-}H)(\mu\text{-}CH{=}CH)$, where Cp' = η^5-C_5H_4Me or C_5H_4Et and X = Cl or Br.[47] Though this example does not involve a carbonyl cluster, it is worthy of specific mention being the first example of ethylene activation by a M–M double bond.

Undoubtedly the most closely related work comes from the detailed studies of Norton and co-workers of the *reversible* addition of ethylene to $Os_2(CO)_8$[48] and $Os_2(\mu\text{-}CH_2)(CO)_8$.[49] In the former case addition of ethylene occurs *across* a Os–Os double bond [the structure of $Os_2(CO)_8$ is not known and the Os–Os double bond is formulated on the basis of the EAN rule] to give a 1,2-dimetallacyclobutane.[48] This reversible reaction occurs with retention of stereochemistry at ethylene, as is the case in the present work.

(b) Metal Surfaces. A number of reactions involving ethylene and metal surfaces have been shown to proceed to give μ_3-CCH_3 ligands.[50] Studies show that the reaction proceeds in a stepwise sequence involving initial π complexation followed by C–H activation. A μ-CCH_2 ligand was recently identified as an intermediate in the formation of the μ_3-CCH_3 ligand on a ruthenium metal surface.[51]

(c) Mononuclear Complexes. Coordinatively unsaturated mononuclear metal centers have been found to undergo a variety of reactions with ethylene, including reversible 1:1 adduct formation, e.g., with $L_2Pt(0)$,[22] and C–C coupling to give metallacyclopentanes as in reactions with $(PPh_3)_nNi$.[52] In the latter examples, the coupling of two ethylene molecules is reversible but is complicated by elimination processes involving cyclobutane and 1-butene.

Other examples of ethylene activation involve dimerization to give 1-butene and polymerization.[53]

By contrast, the present study provides the first example of the reversible coupling of ethylene at a dinuclear metal center. Particularly noteworthy is the ability of the $W_2(OR)_6$ compounds to take up 3 equiv of ethylene in the formation of $W_2(OR)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ compounds. This occurs *without* loss of any ligand—in sharp contrast to carbonyl cluster chemistry or mononuclear chemistry. Two important electronic factors are at work in the present system. (1) The metal atoms are Lewis acidic and the alkoxide ligands are π buffers in their electron-donating ability. (2) The presence of the M–M triple bond provides a reservoir of electron density that may be tapped by a π-acidic ligand upon coordination to the M_2^{6+} center. As we have shown before, the orbital energetics are such that the $(W{\equiv}W)^{6+}$ moiety is a better reducing agent toward π-acidic ligands such as CO than is the $(Mo{\equiv}Mo)^{6+}$ unit.[54] At room temperature and 1 atm ethylene no reaction is observed between analogous $Mo_2(OR)_6$ compounds.

There are a number of interesting aspects of the present study that are clearly worthy of further attention. (1) The steric bulk of the alkoxide ligand influences the relative rates of the coupling of two ethylene ligands. Exactly how this coupling occurs is unknown at this stage. (2) The subsequent C–H activation process probably involves an α-CH bond leading to the novel $W_2(\mu\text{-}CCH_2CH_2CH_2)$ moiety. The ancillary bound ethylene in this reaction is involved in at least one reversible β-H insertion step before transfer of the other hydrogen to form ethane. This matter warrants further attention, as does the reactivity of the $W_2(OR)_6(\mu\text{-}CCH_2CH_2CH_2)$ compounds.

Concluding Remarks

The present study provides the first example of the activation of ethylene by a compound containing a M–M triple bond. The reversible formation of a bis(ethylene) complex and $W_2(OR)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ is particularly noteworthy and provides a rare if not unique example of C–C bond activation and coupling of ethylenes at a dinuclear or polynuclear metal center. These processes occur reversibly and without loss of alkoxide ligands. The latter move freely between terminal and bridging positions to accommodate the electronic and steric changes that occur upon substrate activation and release.

Further studies are in progress.

Experimental Section

General Procedures. All preparations were carried out under an inert atmosphere, generally of nitrogen, but also of ethylene where appropriate by using standard Schlenk techniques in conjunction with a Dri-lab System (Vacuum Atmosphere Co.). Aromatic and aliphatic hydrocarbon solvents, diethyl ether, 1,2-dimethoxyethane, and THF were dried and distilled from sodium benzophenone ketyl and stored over 4-Å molecular sieves. NMR solvents, benzene-d_6, toluene-d_8, and pyridine-d_5 were dried over molecular sieves and degassed with dry nitrogen. Dimethyl ether-d_6 was prepared by the method reported in the literature,[55] then dried, and distilled from molecular sieves in vacuo. Freon-12 was purchased from Matheson Chemical Co. and degassed twice before use. A convenient low-temperature NMR solvent system was obtained by mixing Freon-12 and toluene-d_8 in a ratio of approximately 70:30. Alcohols were purchased from Aldrich Chemical Co. 2-Propanol and cyclohexanol were dried and distilled from magnesium turnings and stored over 4-Å molecular sieves. Cyclopentanol and toluene solutions of neopentyl alcohol were degassed with dry nitrogen and dried over 4-Å molecular sieves. Ethylene was purchased from Air Products and used without purification. Labeled ethylene isotopomers, $^{13}C_2H_4$ (99% ^{13}C), *gem*-$C_2H_2D_2$, *cis*-

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(55) Sandstrom, J. *Dynamic NRM Spectroscopy*; Academic Press: New York, 1982; p 66.

$C_2H_2D_2$, and *trans*-$C_2H_2D_2$ were purchased from MSD Isotopes and used without further purification. $W_2(O\text{-}t\text{-}Bu)_6$[13a,56a] and $W_2(NMe_2)_6$[56] were prepared by literature procedures, and base-free $W_2(OR)_6$, R = cyclohexyl (c-C_6H_{11}), cyclopentyl (c-C_5H_9), neopentyl (CH_2-*t*-Bu), and isopropyl (*i*-Pr) were prepared by our recently developed procedure[13b] or were generated in situ and used directly. Elemental analysis were performed by Alfred Bernhardt Microanalytical Labs, Elbach, West Germany, and the samples were handled under inert atmosphere. Thermally sensitive samples were sent by express mail and maintained at −78 °C (dry ice).

Spectroscopic Instrumentation and Interpretation. ^1H and ^{13}C NMR spectra were recorded on Varian XL300, Nicolet NT360, and Bruker AM500 NMR spectrometers. In some cases, ^1H and ^{13}C NMR assignments were made with the aid of a variety of two-dimensional NMR experiments on all three instruments. Typical acquisition parameters were as follows: COSY, [512W (8 or 16 scans) × 128]; XHCORR, [1k (84 scans) × 256]; COSYX, [512W (64 scans) × 128]. In some cases, the 2D ^{13}C–^1H heteronuclear chemical shift correlated experiment (XHCORR) using ^{13}C-enriched compounds was used to locate the position of directly attached hydrogens in the ^1H NMR spectrum, followed by examination of the ^1H NMR spectrum of unlabeled compounds to determine the connectivity of the ^1H resonances. Spectral simulations were carried out with the NICSIM program on the Nicolet instrument. Activation energies were approximated from coalescence temperatures by the method reported in the literature.[57] Infrared spectra were recorded on a Perkin-Elmer 283 spectrophtometer and were calibrated with polystyrene.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$. $W_2(O\text{-}t\text{-}Bu)_6$ (0.500 g, 0.62 mmol) was placed in a 30-mL Schlenk flask and 5 mL of pentane was added. The solution was cooled to 0 °C, and 10 mL (a slight excess) of a 0.926 M toluene solution of neopentyl alcohol was added. The solution was stirred rapidly with the aid of a magnetically controlled spin bar. After 2 h the volatile components were removed in vacuo, and a pale yellow solid was obtained. To the solid was added 1 mL of pentane, the suspension was frozen at liquid nitrogen temperature, and the flask was evacuated. The flask was transferred to a calibrated vacuum manifold, where 27 mL (at atmospheric pressure) of C_2H_4 was condensed into the flask. The solution was warmed to 0 °C, and the yellow suspension in the deep yellow-brown solution was stirred for 2 h in this temperature. Nitrogen gas was then admitted to restore a positive pressure of gas inside the flask, and then it was cooled to −25 °C for 18 h. During this time, yellow microcrystals grew. The crystals were filtered under an atmosphere of ethylene to give 392 mg of material. The filtrate was then cooled to −78 °C overnight, during which cubic yellow crystals formed. The solution was filtered to give another 80 mg of compound. Both samples were shown to be spectroscopically pure $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ in a combined yield of 80.5% based on $W_2(O\text{-}t\text{-}Bu)_6$. A sample of this material was used for elemental analysis.

OCH_2-*t*-Bu ^1H NMR (21 °C, 360 MHz, C_6D_6): methylenes, CH_2, 4.70 (d, 10.4 Hz, 2 H), 4.38 (d, 10.4 Hz, 2 H), 4.15 (d, 10.4 Hz, 2 H), 4.05 (d, 10.4 Hz, 2 H), 3.91 (d, 10.8 Hz, 2 H), 3.31 (d, 10.8 Hz, 2 H); methyls, CH_3, 1.11 (s, 18 H), 0.96 (s, 18 H), 0.83 (s, 18 H) ppm. η^2-C_2H_4 ^1H NMR (21 °C, 360 Hz, C_6D_6): H_a, 2.85 (m, 2 H), H_b, 2.70 (m, 2 H), H_c, 2.15 (m, 2 H), H_d, 1.69 (m, 2 H) ppm. OCH_2-*t*-Bu $^{13}C\{^1H\}$ NMR (+10 °C, 75.42 MHz, C_6D_6): methylenes, CH_2, 84.8, 82.4, 81.2; quaternary C's, 34.7, 34.3, 33.7; methyls, CH_3, 27.4, 26.9, 26.7 ppm. η^2-C_2H_4 $^{13}C\{^1H\}$ NMR (+10 °C, 75.42 MHz, C_6D_6): 63.8 (J_{C-W} = 38 Hz (13%)), 60.9 (J_{C-W} = 37 Hz (13%)) ppm. IR ν(cm^{-1}): (KBr disk) 2960 (s), 2900 (s), 2860 (s), 1475 (m), 1460 (m), 1440 (w), 1390 (m), 1382 (sh), 1360 (m), 1290 (w), 1256 (w), 1211 (w), 1102 (m), 1055 (s), 1032 (s), 1015 (s), 930 (w), 900 (w), 751 (w), 717 (m), 680 (m), 618 (m), 613 (m), 465 (w), 417 (w), 400 (w). (Nujol mull) 2860 (s), 1390 (m), 1370 (m), 1290 (w), 1255 (w), 1210 (w), 1102 (m), 1085 (m), 1056 (s), 1035 (s), 1018 (s), 930 (w), 902, 892 (w), 752 (w), 718 (m), 680 (m), 618 (m), 611 (m), 462 (w), 416 (w), 400 (w). (Fluorolube mull) 2948 (s), 2900 (m), 2858 (m), 1470 (m), 1451 (m), 1388 (m), 1357 (m). Anal. Calcd for $C_{34}H_{74}O_6W_2$: C, 43.12; H, 7.88. Found: C, 42.91; H, 7.69.

The isotopomers $W_2(OCH_2\text{-}t\text{-}Bu)_6(^{13}C_2H_4)_2$ and $W_2(OCH_2\text{-}t\text{-}Bu)_6(C_2D_4)_2$ and $W_2(OCH_2\text{-}t\text{-}Bu)_6$(*gem*-$C_2H_2D_2)_2$ were prepared on a preparative scale by a similar method to that reported above. Other isotopomers were prepared by addition of the appropriate isotope of ethylene to C_6D_6 solutions of $W_2(OCH_2\text{-}t\text{-}Bu)_6$ at −196 °C in NMR tube reactions. The additional spectroscopic data obtained for these compounds are as follows.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(^{13}C_2H_4)_2$ $^{13}C\{^1H\}$ NMR (+10 °C, 75.42 MHz, C_6D_6): $^{13}C_2H_4$, C^1, 63.8 (d, $J_{^{13}C-^{13}C}$ = 30 Hz); C^2, 60.9 (d) ppm. From a ^{13}C–^1H 2D XHCORR experiment, C_1 is directly bonded to H_b and H_d, and C_2 is directly bonded to H_a and H_c. From ^1H NMR spectra: $J_{C'-H_b}$ = 163 Hz, $J_{C^1-H_d}$ = 154 Hz, $J_{C^2-H_a}$ = 150 Hz, $J_{C^2-H_c}$ = 146 Hz. IR ν(cm^{-1}) (KBr disk): 2950 (s), 2900 (s), 2862 (s), 1480 (m), 1460 (m), 1391 (m), 1388 (m), 1360 (m), 1290 (w), 1260 (w), 1213 (w), 1117 (w), 1050 (s, br), 1012 (s), 931 (w), 900 (w), 752 (w), 715 (m), 681 (m, br), 615 (m), 465 (w), 400 (w); (Nujol mull) 1391 (s), 1360 (s), 1292 (m, sh), 1289 (m), 1212 (m), 1205 (m, sh), 1165 (m), 1075 (s), 1055 (s), 1032 (s), 1000 (s), 978 (s), 932 (s), 902 (m), 895 (m), 800 (w, br), 752 (m), 718 (s), 684 (s), 630 (m), 620 (s), 612 (s, sh), 550 (w), 467 (m), 430 (m, sh), 418 (w), 401 (w), 370 (w), 342 (w), 332 (w), 319 (w), 310 (w, sh), 297 (w), 282 (w), 272 (w), 240 (m), 220 (m).

$W_2(OCH_2\text{-}t\text{-}Bu)_6$(*trans*-$\eta^2$-$C_2H_2D_2)_2$ ^1H NMR (21 °C, 360 MHz, C_6D_6): *trans*-η^2-$C_2H_2D_2$, H_a trans to H_d, ($J_{H_a-H_d}$ = 8.5 Hz); H_b trans to H_c, ($J_{H_b-H_c}$ = 7.4 Hz).

$W_2(OCH_2\text{-}t\text{-}Bu)_6$(*gem*-$\eta^2$-$C_2H_2D_2)_2$ ^1H NMR (21 °C, 360 MHz, C_6D_6): *gem*-η^2-$C_2H_2D_2$, H_a *gem* to H_c, ($J_{H_a-H_c}$ = 6.6 Hz); H_b *gem* to H_d, ($J_{H_b-H_d}$ = 7.4 Hz).

$W_2(OCH_2\text{-}t\text{-}Bu)_6$(*cis*-$\eta^2$-$C_2H_2D_2)_2$ ^1H NMR (21 °C, 360 MHz, C_6D_6): *cis*-η^2-$C_2H_2D_2$, H_a cis to H_b, ($J_{H_a-H_b}$ = 12.0 Hz); H_c cis to H_d, ($J_{H_c-H_d}$ = 10.4 Hz).

$W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2D_4)_2$ IR ν(cm^{-1}): (KBr disk) 2950 (m), 2920 (m), 2900 (m), 2860 (m), 2700 (w), 2360 (w), 2270 (w), 2170 (w), 2142 (w), 1470 (m), 1460 (m), 1440 (m), 1390 (m), 1360 (m), 1298 (w), 1290 (w), 1260 (w), 1215 (w), 1195 (m), 1165 (w), 1098 (m, sh), 1030 (vs), 931 (m), 918 (w), 900 (w), 785 (w), 752 (m), 700 (m), 690 (m), 630 (m, sh), 615 (m), 598 (w), 502 (w), 465 (m), 418 (w), 405 (w), 370 (w), 332 (w), 275 (m). (Nujol mull) 2358 (w), 2265 (w), 2165 (w), 2140 (w), 1390 (s), 1360 (s), 1296 (w), 1289 (w), 1259 (m), 1212 (m), 1195 (m), 1160 (w), 1098 (m), 1055 (s), 1038 (s), 1018 (s), 975 (m), 932 (m), 918 (w), 900 (w), 892 (w), 795 (m, br), 752 (m), 702 (m), 692 (s), 661 (w), 629 (m), 619 (m), 612 (m), 502 (m), 465 (m), 418 (w), 400 (m, br), 370 (w), 342 (w), 332 (w), 318 (w), 297 (w), 282 (w), 273 (w), 241 (m), 220 (m). (Fluorolube mull) 2360 (w), 2262 (w), 2168 (w), 2142 (w), 1475 (m), 1460 (m), 1455 (m), 1438 (m), 1390 (m), 1360 (m). Anal. Calcd for $C_{34}H_{66}D_8O_6W_2$: C, 42.76; H + D, 7.81. Found: C, 42.51; H + D, 7.70.

$W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. $W_2(O\text{-}t\text{-}Bu)_6$ (1.000 g, 1.24 mmol) was placed in a 50-mL Schlenk flask together with 3 mL of pentane. The solution was cooled to −78 °C in a dry-ice/acetone bath, and then an excess of dry 2-propanol (1.5 mL) was added dropwise over ~5 min. The solution was stirred for 2 h at −78 °C, after which time the red color of $W_2(O\text{-}t\text{-}Bu)_6$ had disappeared and a pale yellow precipitate was present. The solution was filtered at −78 °C and washed with three 2-mL portions of hexane that had been precooled to −78 °C. The yellow solid that remained was dried in vacuo, first by pumping at −78 °C and then as it was warmed to room temperature to ensure the final traces of HO-*i*-Pr had been removed. The pale yellow $W_2(O\text{-}i\text{-}Pr)_6$ so obtained was suspended in 2 mL of hexane at −78 °C (dry-ice/acetone bath) and then cooled to −196 °C (liquid nitrogen). When the solution was frozen, the flask was evacuated and transferred to a calibrated vacuum manifold. The solution was warmed to −78 °C and ethylene gas was admitted to a pressure of 1 atm. With the flask still connected to the manifold (so that the pressure could be monitored), the solution was warmed to 0 °C. After the pressure had been readjusted to 1 atm, the flask was disconnected and the solution was stirred for 6 h at 0 °C. The yellow solid slowly dissolved to give a red-brown solution. The flask was then placed in a dry-ice/acetone bath for 10 h, during which time dark, red-brown crystals formed. The solution was filtered at −78 °C to give a first crop of 560 mg of pure material (by elemental analysis and ^1H and ^{13}C NMR spectroscopy). The volume of the filtrate was reduced by half at 0 °C in vacuo and then 1 atm of ethylene readmitted from the calibrated vacuum manifold. The flask was again cooled to −78 °C for 24 h. After filtration at −78 °C, a second crop of crystals (150 mg) was obtained. The supernatant from the filtration was replaced at −78 °C for 24 h and a third crop (50 mg) obtained as before. All three crops were shown to be identical by ^1H NMR spectroscopy. In total, 770 mg (0.99 mmol) of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ was collected, a yield based on $W_2(O\text{-}t\text{-}Bu)_6$ of 79.8%. The solid material was found to be unstable in the solid state as well as in solution (see Discussion) and a solid sample stored in a vial under N_2 rearranged (~80% completion by ^1H NMR) to $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ on standing for 7 days at 35 °C. This compound is best stored in the solid state at −20 °C.

O-*i*-Pr ^1H NMR (23 °C, 300.1 MHz, C_6D_6): methine, CH 5.02 (septet, J_{H-H} = 6 Hz), 4.53 (septet, J_{H-H} = 6 Hz), ~4.8 (v br); methyls, CH_3, 1.25 (d), 1.10 (d), 1.05 (d) ppm. $(CH_2)_4(\eta^2\text{-}C_2H_4)$ ^1H NMR (23

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(56) (a) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Ontiveros, C. D.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1987**, *26*, 3182. (b) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477.

(57) See ref 55, p 79, 109.

°C, 300.1 MHz, C_6D_6): methylenes, CH_2, C_α, 2.80 (s, v br); C_β, 3.05 (s, br); C_γ, 2.40 (s, br) ppm. From a COSY experiment, the septet at 5.02 ppm is part of a diastereotopic isopropoxide ligand, connected to the methyls at 1.25 and 1.05 ppm: H_α is coupled to H_β. ^1H NMR (−90 °C, 300.1 MHz, 70:30 Freon-12/toluene-d_8) methines, CH, 5.32 (septet, 1 H), 5.05 (septet, 1 H), 4.45 (septet, 1 H), 4.37 (septet, 1 H), 4.18 (septet, 1 H), 4.15 (septet, 1 H); methyls, CH_3, 1.62 (d, 3 H), 1.53 (d, 3 H); remaining methyl resonances overlapping doublets from 1.3 to 0.7; $(CH_2)_4(\eta^2\text{-}C_2H_4)$, 3.57 (m, 1 H), 3.40 (m, 1 H), 2.75 (m, 1 H), 2.60 (m, 2 H), 2.35 (overlapping m's, 4 H), 1.80 (m, 1 H), 1.46 (m, 1 H) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, toluene-d_8): Variable-temperature ^{13}C NMR data were recorded on the corresponding compound prepared from 99% ^{13}C enriched C_2H_4, $W_2(O\text{-}i\text{-}Pr)_6(^{13}CH_2)_4(\eta^2\text{-}^{13}C_2H_4)$, and from an isotope dilution experiment in which the species $W_2(O\text{-}i\text{-}Pr)_6$, C_2H_4, and $^{13}C_2H_4$ were mixed in a 5-mm NMR tube in the molar ratio 1:3:1, respectively. Under the conditions that the ^{13}C data were acquired (relaxation delay = 1 s), only the ^{13}C resonances due to the isotopically enriched carbon nuclei were observed. See Figure 5. 29 °C, C_α, $C_{\alpha'}$, 66.8 (v br), C_β, $C_{\beta'}$, 36.7 (m, $J_{C_\beta-C_{\beta'}} = 33$ Hz), C_γ, $C_{\gamma'}$, 53.3 (s, $J_{C_\gamma-W} = 29$ Hz) ppm. −40 °C, C_α, 67.9 (m, $J_{C_\alpha-C_\beta} = 29.1$ Hz, $J_{C_\alpha-W} = 88$ Hz), $C_{\alpha'}$, 64.1 (m, $J_{C_{\alpha'}-C_{\beta'}} = 33.2$ Hz, $J_{C_{\alpha'}-W} = 77$ Hz), C_β, 36.8 (m, $J_{C_\beta-C_{\beta'}} = 33$ Hz), $C_{\beta'}$, 36.4 ppm, (m), C_γ, $C_{\gamma'}$, 52.8 (s) ppm. −90 °C, C_γ, 67.2 (d, $J_{C_\gamma-C_{\gamma'}} = 35$ Hz), $C_{\gamma'}$, 64.6 (d) ppm. IR ν(cm^{-1}) (Nujol mull): 1370 (s), 1340 (m), 1328 (m), 1269 (w), 1172 (s), 1125 (s, br), 1040 (m), 1003 (s), 990 (s, br), 979 (s, sh), 965 (s, sh), 852 (m), 610 (m), 465 (w), 440 (w).

$W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. A 1.000-g sample of $W_2(O\text{-}t\text{-}Bu)_6$ was suspended in 3 mL of pentane in a 50-mL Schlenk flask at −78 °C, and 1 mL (an excess) of 2-propanol-d_8 was added. The solution was rapidly stirred at this temperature until the red color of $W_2(O\text{-}t\text{-}Bu)_6$ had completely disappeared and a pale yellow precipitate remained (~5 h). The solution was filtered at −78 °C and the pale yellow $W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6$ washed with three 2-mL portions of cold pentane and then dried in vacuo as the flask was slowly warmed to room temperature. The yellow solid was then suspended in 2 mL of pentane at −78 °C, and the contents of the flask were frozen and evacuated. The flask was transferred to a calibrated vacuum manifold and warmed to −78 °C and 1 atm of ethylene admitted. The flask was further warmed to 0 °C while a pressure of 1 atm of ethylene was maintained, with the flask connected to a calibrated vessel containing 75 mL of ethylene (i.e., an excess). After stirring for 4 h at 0 °C, the flask was cooled to −78 °C and the contents left to crystallize for 10 h. The first crop of dark red-brown crystals obtained in this way was filtered at −78 °C to give 680 mg of $W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, taking care to keep the filtrate cold. A second crop of 113 mg of crystals was obtained from the filtrate after standing for 24 h at −78 °C. The combined weight of $W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ recovered was 793 mg (0.93 mmol), a yield of 75.4% based on $W_2(O\text{-}t\text{-}Bu)_6$.

Anal. Calcd for $C_{24}H_{12}D_{42}O_6W_2$: C, 33.98; H + D, 6.42. Found: C, 34.26; H + D, 6.48.

$(CH_2)_4(\eta^2\text{-}C_2H_4)$ ^1H NMR (300 MHz, toluene-d_8): 21 °C, 2.32 (br, 4 H), 2.75 (v br, 4 H), 3.07 (br, 4 H) ppm. +2 °C, 2.32 (br, 4 H), 2.62 (v br, 2 H), 2.90 (v br, 2 H), 3.08 (br, 4 H) ppm. −14 °C, 2.32 (br, 4 H), 2.60 (br, 2 H), 2.93 (br, 2 H), 3.10 (br, 4 H) ppm. −49 °C, 2.60 (br), ~2.7 (v v br) ppm. ^1H NMR (−98 °C, 70:30, Freon-12/toluene-d_8): 3.55 (br, 1 H), 3.42 (br, 1 H), 3.23 (br, 1 H), 2.70 (q, 1 H), 2.50 (br, 2 H), 2.25 (overlapping m, 4 H), 1.70 (br, 1 H), 1.45 (q, 1 H) ppm. IR ν(cm^{-1}) (Nujol mull): 2238 (s), 2160 (m), 2130 (m), 2065 (m), 1266 (m), 1217 (s), 1170 (s), 1150 (s), 1101 (sh), 1085 (s), 1057 (s), 1010 (s), 982 (s), 975 (sh), 910 (m), 860 (s, br), 805 (sh), 732 (s), 610 (w), 558 (m), 430 (m, br), 370 (w).

$W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$. This isotopomer was prepared in a manner identical with the compounds above starting with 1.000 g (1.24 mmol) of $W_2(O\text{-}t\text{-}Bu)_6$ and using C_2D_4 in place of C_2H_4. On crystallization of the final material, the mass of the first crop was 284 mg and that of the second crop was 344 mg. The $W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$ obtained was spectroscopically and analytically pure. The combined mass of product was 628 mg (0.77 mmol), a yield of 61.9%. The ^1H NMR spectra of $W_2(O\text{-}i\text{-}Pr)_6(CD_2)_4(\eta^2\text{-}C_2D_4)$ were recorded at room temperature and at low temperature in toluene-d_8 and 70:30 Freon-12/toluene-d_8. See Figure 4. The NMR data obtained were consistent with that recorded for the other isotopomers.

Anal. Calcd for $C_{24}H_{42}D_{12}O_6W_2$: C, 35.21; H, 6.40. Found: C, 35.18; H, 6.64. IR ν(cm^{-1}) (Nujol mull): 2300 (w), 2280 (w), 2198 (m), 2175 (m, sh), 2097 (m), 1382 (s), 1341 (s), 1320 (m), 1268 (w), 1238 (m), 1172 (s), 1125 (s, br), 1040 (s), 1002 (s), 980 (s, br), 852 (3), 620 (m, sh), 610 (s), 590 (m), 500 (w), 466 (m), 435 (m), 375 (w), 352 (w).

$W_2(O\text{-}c\text{-}C_5H_9)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. Attempts to isolate this compound were unsuccessful. Addition of ethylene to pentane and toluene solutions of $W_2(O\text{-}c\text{-}C_5H_9)_6$ at 0 °C did not lead to any significant reaction. Pentane solutions of $W_2(O\text{-}c\text{-}C_5H_9)_6$ and ethylene that were stirred until all the yellow solid dissolved at room temperature resulted in formation of $W_2(O\text{-}c\text{-}C_5H_9)_6(\mu\text{-}CCH_2CH_2CH_2)$. Toluene solutions of $W_2(O\text{-}c\text{-}C_5H_9)_6$ and ethylene that were stirred at room temperature for 4 h did result in formation of mainly $W_2(O\text{-}c\text{-}C_5H_9)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$, but it could not be isolated as a solid from either pentane or toluene solutions at low temperatures (see later). $W_2(O\text{-}c\text{-}C_5H_9)(CH_2)_4(\eta^2\text{-}C_2H_4)$ was formed cleanly and quantitatively by mixing $W_2(O\text{-}c\text{-}C_5H_9)_6$ and ethylene in toluene-d_8 and could be spectroscopically characterized in solution by both ^{13}C and ^1H NMR spectroscopy.

^1H NMR (300 MHz, 22 °C, toluene-d_8): $OCH(CH_2)_4$, 5.33 (br, m), 4.78 (br, m); $OCH(CH_2)_4$, 2.2–1.2 (br overlapping m's); $(CH_2)_4(\eta^2\text{-}C_2H_4)$, H_α, 2.89 (br, m), 2.67 (br, m), H_β, 3.10 (br, m), H_γ, 2.42 (br, m) ppm. $^{13}C\{^1H\}$ NMR (75.42 MHz, toluene-d_8) $W_2(O\text{-}c\text{-}C_5H_9)_6(^*CH_2)_4(\eta^2\text{-}^*C_2H_4)$, * = 99% ^{13}C enriched: +50 °C, C_α, $C_{\alpha'}$, 67.2 (br s), C_γ, $C_{\gamma'}$, 54.5 (s), C_β, $C_{\beta'}$, 36.7 (br m) ppm. 21 °C, C_α, 69.9 (br s), $C_{\alpha'}$, 66.3 (br s), C_γ, $C_{\gamma'}$, 54.5 (s, $J_{C-W} = 27.$ Hz), C_β, $C_{\beta'}$, 36.7 (br s) ppm. 0 °C, C_α, 69.9 (d, $J_{C-C} = 31$ Hz), $C_{\alpha'}$, 66.3 (d, $J_{C-C} = 31$ Hz), C_γ, $C_{\gamma'}$, 54.6 (s, $J_{C-W} = 27$ Hz), C_β, 37.1 (dd, $J_{C-C} = 33, 36$ Hz), $C_{\beta'}$, 36.1 (dd, $J_{C-C} = 33, 36$ Hz) ppm. −40 °C, C_α, 69.7 (d, $J_{C-C} = 31$ Hz, $J_{C-W} = 88$ Hz), $C_{\alpha'}$, 66.2 (d, $J_{C-C} = 32$ Hz, $J_{C-W} = 76$ Hz), C_γ, $C_{q'}$, 54.6 (br s) ppm. −80 °C, C_α, 69.0 (d, $J_{C-C} = 30$ Hz), $C_{\alpha'}$, 65.3 (d, $J_{C-C} = 29$ Hz), C_γ, 55.3 (d, $J_{C-C} = 32$ Hz), $C_{\gamma'}$, 52.7 (d, $J_{C-C} = 30$ Hz), C_β, 37.0 (dd, $J_{C-C} = 33$ Hz), $C_{\beta'}$, 36.1 (dd, $J_{C-C} = 31$ Hz) ppm.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$. This species could be observed as an intermediate in the formation of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}CCH_2CH_2CH_2)$ from the reaction of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ and ethylene. No attempt was made to isolate it since it is formed while both the starting materials and products are still present. The compound was spectroscopically characterized and the NMR data provided below were recorded 12 h after the addition of C_2H_4 to a solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$ at room temperature.

The ^1H NMR chemical shift positions of the ethylene-derived protons were established by a 2D $^{13}C-^1H$ heteronuclear chemical shift correlated experiment using 99% ^{13}C enriched ethylene and the assignment was confirmed by a 2D ^1H NMR homonuclear chemical shift correlated experiment using unlabeled material.

^1H NMR (500.13 MHz, 23 °C, toluene-d_8) H_α, 2.98 (m), $H_{\alpha'}$, 2.73 (m), H_β, 2.32 (m), $H_{\beta'}$, 3.05 (m), $H_{\gamma a}$, 2.05 (m), $H_{\gamma b}$, 1.20 (m), $H_{\gamma c}$, 3.02 (m), $H_{\gamma d}$, 2.89 (m) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, 23 °C, toluene-d_8) $(^*CH_2)_4(\eta^2\text{-}^*C_2H_4)$, C_α, 81.1 (d, $J_{C-C} = 30.5$ Hz, $J_{C-W} = 70.2$ Hz), $C_{\alpha'}$, 74.9 (d, $J_{C-C} = 30.5$ Hz, $J_{C-W} = 85.5$ Hz), C_β, 37.3 (t, $J_{C-C} = 33.6$ Hz), $C_{\beta'}$, 36.7 (t, $J_{C-C} = 30.5$ Hz), C_γ, 63.9 (d, $J_{C-C} = 30.5$ Hz, $J_{C-W} = 30.4$ Hz), $C_{\gamma'}$, 55.3 (d, $J_{C-C} = 30.0$ Hz, $J_{C-W} = 30.0$ Hz) ppm.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$. Attempts to isolate this compound as a solid were unfruitful; however, it could be obtained quantitatively as an oil by rearrangement of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ in solution at room temperature. A 0.489-g (0.61 mmol) sample of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ was placed in a 30-mL Schlenk flask and 8 mL of hexane added at room temperature. The red-brown solution was stirred for 50 h and then the volatile components were removed in vacuo to give an oily dark brown residue. A ^1H NMR spectrum of a sample of the residue showed only the presence of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$. Attempts to crystallize the material from pentane at −20 and −78 °C were unfruitful. In every case an oil was obtained. It has been previously noted that crystalline samples of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ rearrange in the solid state to form $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$. A closed ampule containing 450 mg of crystalline $W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ was kept at 30 °C for 9 days. During this time some pressure built up inside the tube. A ^1H NMR spectrum of the solid material showed it to be spectroscopically pure $W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(\mu\text{-}CCH_2CH_2CH_2)$. This was the only method by which a solid sample of the alkylidyne species could be obtained. This sample was used to obtain elemental analysis and an infrared spectrum.

Upon the addition of pyridine to a pentane solution of $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$, the solution turned from dark brown to dark red-brown, and on cooling to −20 °C for 15 h, deep red-brown needles were obtained and were filtered at 0 °C. The filtrate was recooled to −20 °C and after 20 h another crop of smaller cubic red-brown crystals was obtained. ^1H NMR spectra of both crops of crystals, which had been dried in vacuo, contained pyridine in an integral ratio consistent with the formula $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)$. A sample of the second crop of crystalline material was submitted for an X-ray diffraction structure and elemental analysis. The ^{13}C-enriched compound $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}^*C^*CH_2{}^*CH_2{}^*CH_2)$ was obtained in NMR tube reactions between $W_2(O\text{-}i\text{-}Pr)_6$ and $^*C_2H_4$ on standing for 18 h. The ^{13}C-enriched compound $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}^*C^*CH_2{}^*CH_2{}^*CH_2)(py)$ was prepared by adding an excess of $^{13}C_2H_4$ to $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ in toluene-d_8 in an NMR tube which was then sealed in vacuo. On standing at −20 °C, deep red-brown crystals grew from this solution. The NMR tube was opened, the supernatant was removed, and the crystals were dried in vacuo. A

0.5-mL aliquot of fresh toluene-d_8 was added and the NMR tube resealed in vacuo. After shaking for some time, the crystalline material redissolved. A ^{1}H NMR spectrum indicated that pyridine was still present, and a low-temperature ^{13}C NMR spectrum was recorded.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ ^{1}H NMR (300 MHz, toluene-d_8): 21 °C, 4.90 (br s, 4 H, OC*H*Me$_2$), 4.30 (septet, 2 H, J_{H-H} = 6 Hz, OC*H*Me$_2$), 4.70 (t, 2 H, J_{H-H} = 6.0 Hz, CH_2^{γ}), 3.58 (p, 2 H, J_{H-H} = 6.0 Hz, CH_2^{β}), 2.80 (t, 2 H, J_{H-H} = 6.0, J_{H-W} = 8.6 Hz (14%), CH_2^{α}), 1.32 (br s 24 H, OCH*Me*$_2$), 1.12 (d, 6 H, OCH*Me*$_2$), 0.93 (d, 6 H, OCH*Me*$_2$) ppm. −90 °C, 5.96 (br septet, 1 H, OC*H*Me$_2$), 4.78 (br m 3 H, OC*H*Me$_2$ and CH_2^{γ}), 4.52 (br m 2 H, OC*H*Me$_2$), 4.25 (septet, 2 H, J_{H-H} = 6 Hz, CH_2^{β}), 3.74 (br m 2 H, OC*H*Me$_2$); 2.97 (br m 2 H, CH_2^{α}); 2.0–0.8 (br d's, OCH*Me*$_2$) ppm.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)$ ^{1}H NMR (300 MHz, 23 °C, benzene-d_6): OC*H*Me$_2$, 3.93 (br), 3.72 (br), CH_2^{α}, 2.60 (t, 2 H, J_{H-H} = 6 Hz, J_{H-W} = 10 Hz), CH_2^{β}, 3.76 (p, 2 H, J_{H-H} = 6 Hz), CH_2^{α}, 5.29 (t, 2 H, J_{H-H} = 6 Hz); OCH(C*H*$_3$)$_2$, 1.44 (br ~24 H), 0.98 (br ~12 H); py, ortho, 8.81 (m, 2 H), meta, 6.68 (m, 2 H), para, 6.98 (m, 1 H) ppm.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}{*C}{*CH_2}{*CH_2}{*CH_2})$ $^{13}C\{^1H\}$ NMR (75.42 MHz, 23 °C, benzene-d_6): 22 °C, 55.6 (d, J_{C-C} = 31 Hz, J_{C-W} = 99 Hz, C_{α}), 54.4 (dd, J_{C-C} = 33 Hz, C_{γ}), 42.6 (dd, J_{C-C} = 35 Hz, C_{β}), 305.5 (d, J_{C-C} = 33 Hz, J_{C-W} = 116 (14%), 165 Hz (14%), C_{δ}) ppm. $W_2(O\text{-}i\text{-}Pr)_6(CCH_2CH_2CH_2)$ $^{13}C\{^1H\}$ NMR (toluene-d_8, −90 °C) 77.9 (s), 76.4 (s), 75.9 (s), 72.5 (s, O*C*HMe$_2$), 55.4 (s, J_{C-W} = 97 Hz, C_{α}), 53.1 (s, C_{β}), 42.4 (s, C_{γ}), 28.2–24.5 (overlapping s's, OCH(*C*H$_3$)$_2$) ppm.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}{*C}{*CH_2}{*CH_2}{*CH_2})(py)$ $^{13}C\{^1H\}$ NMR (125.8 MHz, 28 °C, tolueen-d_8): 51.9 (d, J_{C-C} = 33 Hz, J_{C-W} = 107 Hz (14%), C_{α}), 43.6 (t, J_{C-C} = 33 Hz, C_{β} = 33 Hz, C_{β}), 56.1 (t, J_{C-C} = 34 Hz, C_{γ}), 314.5 (d, J_{C-C} = 31 Hz, J_{C-W} = 161 (14%), 119 Hz (14%), C_{δ}) ppm. Assignments confirmed by a COSYX experiment: C_{α} coupled to C_{β}, C_{β} coupled to C_{α} and C_{γ}, C_{γ} coupled to C_{δ}, C_{α} also exhibit small cross peaks ($^2J_{C-C}$) to C_{δ}.

$W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)(py)\cdot{}^1/_2py$ IR ν(cm^{-1}) (Nujol mull): 1610 (m), 1580 (w), 1490 (m), 1455 (sh), 1375 (sh), 1330 (s), 1270 (w), 1240 (w), 1222 (m), 1170 (s), 1130 (s, br), 1080 (m), 1048 (m), 1000 (s, br), 965 (s), 860 (s), 765 (m), 703 (m), 730 (w), 685 (w), 615 (s), 600 (s), 580 (s), 510 (w), 482 (m), 462 (m), 440 (m), 310 (m, br).

$W_2(O\text{-}i\text{-}Pr\text{-}d_7)_6(\mu\text{-}CCH_2CH_2CH_2)$ IR ν(cm^{-1}) (Nujol mull): 2240 (m), 2160 (w), 2132 (w), 2105 (w), 2070 (w), 1370 (m, sh), 1265 (w), 1120 (m, br), 1152 (s), 1074 (s), 1062 (s), 1053 (s), 1010 (m), 985 (s, br), 910 (w), 860 (s), 732 (m), 550 (m, br), 475 (w), 420 (w). Anal. Calcd for $C_{22}H_{48}O_6W_2$: C, 34.02; H, 6.23. Found: C, 33.86; H, 6.11.

$W_2(O\text{-}c\text{-}C_5H_9)_6(\mu\text{-}CCH_2CH_2CH_2)$. $W_2(O\text{-}c\text{-}C_5H_9)_6$ (1.007 g, 1.15 mmol) was placed in a 50-mL Schlenk flask and 5 mL of toluene was added at 0 °C. The flask was then frozen at liquid nitrogen temperature, evacuated, and transferred to a calibrated vacuum manifold. The flask was warmed to 0 °C, and an excess of ethylene gas was admitted to the flask. After stirring for 1 h at 0 °C, the solution was warmed to room temperature and the yellow solid slowly dissolved to form a red-brown solution. The solution was stirred for 4 h at room temperature and then cooled to −78 °C (dry-ice/acetone bath) for 48 h. No material crystallized during this time so the solvent was removed in vacuo to given an oily red-brown residue. The residue was redissolved in 3 mL of pentane at 0 °C and then frozen at liquid nitrogen temperature, and 1 atm of ethylene was admitted via a calibrated vacuum manifold. The solution was cooled to −20 °C for 14 h; during this time $W_2(O\text{-}c\text{-}C_5H_9)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ did not crystallize. The flask was then warmed to room temperature and stirred for 48 h. The volatile components were removed in vacuo to form a dark red-brown oily residue. A sample of this material was removed for ^{1}H NMR spectroscopy, which showed only the presence of $W_2(O\text{-}c\text{-}C_5H_9)_6(\mu\text{-}CCH_2CH_2CH_2)$. The residue was taken up in 3 mL of pentane and cooled to −78 °C (dry-ice/acetone bath) for 12 h, and brown crystals formed. The solid was filtered at −78 °C to give 602 mg of solid material, which had a ^{1}H NMR spectrum consistent with the formulation $W_2(O\text{-}c\text{-}C_5H_9)_6(\mu\text{-}CCH_2CH_2CH_2)$; 405 mg of the solid was stored and the remainder returned to the original flask. The filtrate was transferred to the flask containing some of the isolated brown solid, the filtrate flask was washed with 0.5 mL of pyridine, and the washings were transferred to the original flask. The solution turned from deep brown to green on addition of the pyridine, and the solution was cooled to −20 °C for 12 h. The green crystalline material formed was isolated by filtering the solution at 0 °C and dried in vacuo; 264 mg of sample was recovered. A ^{1}H NMR spectrum of this material showed that pyridine was present in a ratio (by integration) consistent with the formulation $W_2(O\text{-}c\text{-}C_5H_9)_6(\mu\text{-}CCH_2CH_2CH_2)(py)$. The volume of the filtrate was reduced by half and the solution replaced at −20 °C.

$W_2(O\text{-}c\text{-}C_5H_9)_6(\mu\text{-}CCH_2CH_2CH_2)$ ^{1}H NMR (300 MHz, 0 °C, toluene-d_8): OC*H*(CH$_2$)$_4$, 4.62 (m, 2 H), 5.08 (v br m, ~4 H), OCH(C*H*$_2$)$_4$, overlapping multiplets from 2.0 to 1.3 ppm; H_{α}, 2.90 (t, 2 H, J_{H-H} = 6.6 Hz, J_{C-W} = 6.4 Hz), H_{β}, 3.60 (p, 2 H, J_{H-H} = 6.3 Hz), H_{γ}, 4.73 (t, 2 H, J_{H-H} = 6.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.42 MHz, 23 °C, toluene-d_8): ($\mu\text{-}{*C}{*CH_2}{*CH_2}{*CH_2}$), C_{α}, 57.8 (d, J_{C-C} = 29 Hz, J_{C-W} = 96 Hz), C_{β}, 42.5 (t, J_{C-C} = 31 Hz), C_{γ}, 54.3 (t, J_{C-C} = 31 Hz), C_{δ}, 304.8 (d, J_{C-C} = 33 Hz, J_{C-W} = 170, 116 Hz) ppm. IR ν(cm^{-1}) (Nujol mull): 1372 (m), 1345 (m), 1269 (w), 1175 (s), 1080 (s, br), 1040 (s), 1020 (s, br), 945 (m), 900 (w, sh), 875 (m, br), 805 (w), 730 (w), 615 (w), 555 (m, br), 440 (w). Anal. Calcd for $C_{34}H_{60}O_6W_2$: C, 43.77; H, 6.48. Found: C, 43.58; H, 6.32.

$W_2(O\text{-}c\text{-}C_5H_9)_6(\mu\text{-}CCH_2CH_2CH_2)(py)$ ^{1}H NMR Data (300 MHz, −5 °C, toluene-d_8): OC*H*(CH$_2$)$_4$, 4.12 (br, m, 2 H), 5.48 (br, m, 4 H); OCH(C*H*$_2$)$_4$, overlapping multiplets from 2.10 to 1.30 ppm; ($\mu\text{-}CCH_2CH_2CH_2$), H_{α}, 2.50 (t, 2 H, J_{H-H} = 6.6 Hz), H_{β}, 3.73 (p, 2 H, J_{H-H} = 6.6 Hz), H_{γ}, 5.30 (t, 2 H, J_{H-H} = 6.0 Hz); py, H_{ortho}, 9.30 (dd, 2 H, J_{H-H} = 1.2, 4.8 Hz), H_{meta}, 6.81 (m, 2 H), H_{para}, 6.99 (m, 1 H) ppm. IR ν(cm^{-1}) (Nujol mull): 1630 (w), 1372 (m), 1350 (s), 1270 (w), 1220 (w), 1178 (s), 1080 (s, br), 1045 (s), 1020 (s, br), 942 (m), 900 (w), 870 (m), 801 (w), 760 (w), 700 (m), 628 (w), 610 (w), 545 (m), 444 (w), 422 (w). Anal. Calcd for $C_{39}H_{65}O_6NW_2$: C, 46.29; H, 6.47; N, 1.38. Found: C, 46.12; H, 6.34; N, 1.35.

$W_2(O\text{-}c\text{-}C_6H_{11})_6(\mu\text{-}CCH_2CH_2CH_2)$. In reactions between $W_2(O\text{-}c\text{-}C_6H_{11})_6$ and ethylene conducted in NMR tubes, no intermediate was observed in the formation of $W_2(O\text{-}c\text{-}C_6H_{11})_6(\mu\text{-}CCH_2CH_2CH_2)$. Attempts to isolate a crystalline material were unfruitful and only oils were obtained, quantitatively, as described above.

^{1}H NMR (300 MHz, 23 °C, toluene-d_8): OC*H*, 5.10 (m, 4 H), 4.62 (m, 2 H), CH_2^{α}, 2.87 (t, 2 H, J_{H-H} = 7 Hz, J_{H-W} = 8.9 Hz), CH_2^{β}, 3.58 (p, 2 H, J_{H-H} = 6 Hz), CH_2^{γ}, 4.72 (t, 2 H, J_{H-H} = 7 Hz); cyclohexyl protons overlapping multiplets from 2.2 to 1.2 ppm.

Kinetic Measurements. The conversion of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ to $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$ was studied in the absence as well as in the presence of various amounts of added ethylene. The reactions were monitored by ^{1}H NMR spectroscopy. The concentrations of the two species were measured by integration of the resonance due to the four equivalent (time-averaged) methylenic protons attached to C_{β} for $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ and the resonance due to the methylenic protons attached to C_{β} for $W_2(O\text{-}i\text{-}Pr)_6(\mu\text{-}CCH_2CH_2CH_2)$. Neither of these resonances is obscured by other resonances during the course of the reactions. The integrals were measured in the absolute intensity mode with identical spectrum phasing constants and identical integral slope, bias, and cutoff points within each kinetic run. Temperatures were calibrated with methanol standard immediately before and after each run.

Determination of Reaction Order in $[W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)]$. A 20-mg sample of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ was placed in an extended 5-mm NMR tube under nitrogen in an inert atmosphere glovebox. A Kontes valve adapter was placed over the open end of the tube and the apparatus was transferred to a standard double manifold. The tube was cooled to −78 °C (dry-ice/acetone bath), the Kontes tap replaced with a septum cap, and 0.5 mL of toluene-d_8 syringed in under a nitrogen atmosphere. The Kontes tap was replaced and closed, and the sample was frozen at −196 °C and then transferred to a calibrated vacuum manifold. Four samples were prepared in this way. One sample was sealed in vacuo, and into the other three were placed 3, 10, and 20 equiv of ethylene via the calibrated vacuum manifold. Each sample was warmed to room temperature immediately prior to placing it inside the magnet of an NMR instrument, which was equilibrated at +35 °C. ^{1}H NMR spectra were recorded at various times until the starting material had disappeared. From the integral values that corresponded to the concentration of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$([A]), each set of data was used to plot a graph of ln [A]/[A$_0$] vs time. Only in the presence of 20 equiv of added ethylene did the data fit this first-order plot. Under these conditions, the calculated pseudo-first-order rate constant was 0.144 × 10^{-3} s^{-1}.

Activation Parameters. The samples were prepared in an analogous manner to that described above. In this case the data were recorded under pseudo-first-order conditions by dissolving 15 mg of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ in 0.5 mL of toluene-d_8 and adding 20 equiv of ethylene from a calibrated vacuum manifold. The disappearance of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ was monitored until it was no longer detectable on a 500-MHz instrument over a temperature range of +21 to +55 °C. The rate constants obtained from the plot of ln [A]/[A$_0$] vs time, which are given in Table IX, were used to calculate the activation parameters from an Arrhenius plot of log k vs 1/*T*. See Figure 11. No account was taken of the different solubility and partition coefficient of ethylene in toluene-d_8 at the different temperatures of each experiment nor of the different pressures within the closed NMR tubes, which all contained essentially the same volume. This negligence may contribute to the errors of the experiment. The pseudo-first-order nature of the decomposition of $W_2(O\text{-}i\text{-}Pr)_6(CH_2)_4(\eta^2\text{-}C_2H_4)$ in the presence of 20 equiv of added ethylene is confirmed by the fact that the rate constant

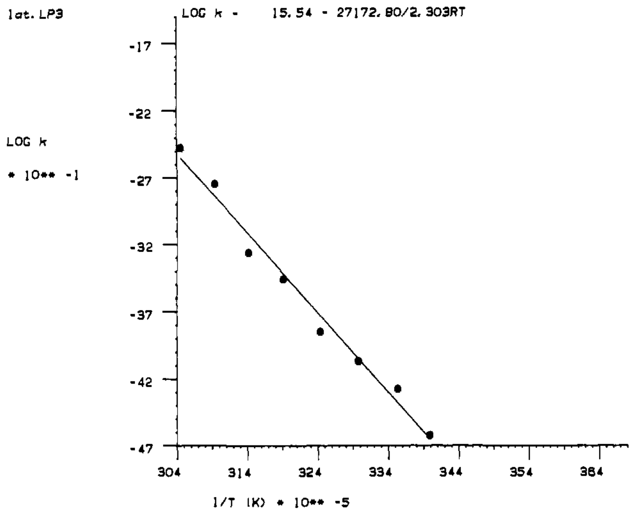

Figure 11. Plot of the logarithm of the pseudo-first-order rate constant versus reciprocal of absolute temperature for the conversion of W_2(O-*i*-Pr)$_6$(CH_2)$_4$(η^2-C_2H_4) → W_2(O-*i*-Pr)$_6$(μ-$CCH_2CH_2CH_2$) + C_2H_6 in the presence of 20 equiv of ethylene.

obtained above at a different concentration (20 mg/0.5 mL) falls on the Arrhenius plot (within experimental error).

Crystallographic Studies. General operating procedures and listing of programs have been reported previously.[58] A summary of the crystallographic data is given in Table II.

W_2(O-*i*-Pr)$_6$(CH_2)$_4$(η^2-C_2H_4). A suitable crystal was located and transferred to the goniostat by standard inert atmosphere handling techniques employed by the IUMSC and cooled to −155 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this choice. Data were collected in the usual manner using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atoms positions were therefore calculated by using idealized geometries and d(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement.

A final difference Fourier was featureless, with the largest peak being 0.85 e/Å^3. Based on a manual ψ scan no absorption correction was performed.

W_2(O-*i*-Pr)$_6$(μ-$CCH_2CH_2CH_2$)(py)·$^1/_2$py. A small crystal was selected by inert atmosphere handling techniques. The crystal was transferred to the goniostat, where it was cooled to −150 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited no symmetry (other than $\bar{1}$) and no systematic extinctions. The reflections were indexed by using a triclinic lattice, and the choice of the centrosymmetric space group $P\bar{1}$ (No. 2) was confirmed by the subsequent solution and refinement of the structure. Details of the data collection are given in Table II. After the usual data processing and averaging of equivalent reflections, a unique set of 4613 reflections was obtained. The R for the averaging was 0.034 for 69 reflections observed more than once. No correction for absorption was performed.

The structure was solved by standard heavy-atom techniques. The two W atoms were located by using a Patterson function. (Direct methods failed to solve the structure.) The remaining non-hydrogen atoms were located in a difference map phased with the W atoms. Hydrogen atoms were located in a difference map following initial refinement. The full matrix least-squares refinement was completed using anisotropic thermal parameters on all non-hydrogen atoms and individual isotropic thermal parameters on the hydrogen atoms. The final R was 0.031. The least-squares refinement was based on 4087 reflections considered observed by the crierion $F > 3.0\sigma(F)$.

The final difference map was essentially featureless. It contained two peaks of approximately 1.5 e/Å^3 in the immediate vicinity of the W atoms.

The asymmetric unit contains $^1/_2$ molecule of pyridine solvent per W_2-dimer.

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Registry No. W_2(OCH_2-*t*-Bu)$_6$(η^2-C_2H_4)$_2$, 110141-90-7; W_2(O-*t*-Bu)$_6$, 57125-20-9; W_2(OCH_2-*t*-Bu)$_6$($^{13}C_2H_4$)$_2$, 110141-91-8; W_2(OCH_2-*t*-Bu)$_6$(*trans*-η^2-$C_2H_2O_2$)$_2$, 110141-92-9; W_2(OCH_2-*t*-Bu)$_6$(*gem*-η^2-$C_2H_2O_2$)$_2$, 120608-67-5; W_2(OCH_2-*t*-Bu)$_6$(*cis*-η^2-$C_2H_2O_2$)$_2$, 120707-43-9; W_2(OCH_2-*t*-Bu)$_6$(η^2-C_2D_4)$_2$, 120608-68-6; W_2(O-*i*-Pr)$_6$(CH_2)$_4$(η^2-C_2H_4), 120608-69-7; W_2(OCH_2-*t*-Bu)$_6$, 110116-70-6; W_2(O-*i*-Pr)$_6$, 71391-16-7; W_2(O-*i*-Pr)$_6$(μ-$CCH_2CH_2CH_2$), 110241-92-4; W_2(O-*i*-Pr)$_6$($^{13}CH_2$)$_4$(η^2-$^{13}C_2H_4$), 120636-79-5; W_2(O-*i*-Pr-d_7)$_6$(CH_2)$_4$(η^2-C_2H_4), 120608-70-0; W_2(O-*i*-Pr-d_7)$_6$, 120608-71-1; W_2(O-*i*-Pr)$_6$(CO_2)$_4$(η^2-C_2D_4), 120608-72-2; W_2(O-c-C_5H_9)$_6$, 120608-73-3; W_2(O-c-C_5H_9)$_6$(μ-$CCH_2CH_2CH_2$), 120608-74-4; W_2(O-c-C_5H_9)$_6$(CH_2)$_4$(η^2-C_2H_4), 120608-75-5; W_2(OCH_2-*t*-Bu)$_6$(CH_2)$_4$(η^2-C_2H_4), 120608-76-6; W_2(OCH_2-*t*-Bu)$_6$(μ-$CCH_2CH_2CH_2$), 120608-77-7; W_2(O-i-Pr)$_6$(μ-$CCH_2CH_2CH_2$)(py), 120608-78-8; Wi$_2$(O-*i*-Pr)$_6$(μ-*C*CH_2*CH_2*CH_2), 110270-79-6; *C_2H_4, 51915-19-6; W_2(O-*i*-Pr)$_6$(μ-*C*CH_2*CH_2*CH_2)(py), 120636-80-8; W_2(O-*i*-Pr)$_6$(py)$_2$, 70178-75-5; W_2(O-*i*-Pr)$_6$(μ-$CCH_2CH_2CH_2$)(py)·$^1/_2$py, 120709-17-3; W_2(O-*i*-Pr-d_7)$_6$(μ-$CCH_2CH_2CH_2$), 120608-79-9; W_2(O-c-C_5H_9)$_6$(μ-$CCH_2CH_2CH_2$)(py), 120608-80-2; W_2(O-c-C_6H_{11})$_6$, 111835-58-6; W_2(O-c-C_6H_{11})$_6$(μ-$CCH_2CH_2CH_2$), 120636-81-9; neopentyl alcohol, 75-84-3; 2-propanol-d_8, 22739-76-0.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete listings of bond distances and bond angles, VERSORT drawings and steroviews for W_2(O-*i*-Pr)$_6$(CH_2)$_4$(η^2-C_2H_4) and W_2(O-i-Pr)$_6$(μ-$CCH_2CH_2CH_2$)(py)·$^1/_2$py (14 pages); listings of observed and calculated structure factors (20 pages). See any current masthead page for ordering information.

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