

# Tungsten-Carbon, Carbon-Carbon, and Carbon-Hydrogen Bond Activations in the Chemistry of $W_2R_2(OR')_4(W \equiv W)$ Complexes.

## 3. Competitive $\alpha$ -Hydrogen versus $\beta$ -Hydrogen Eliminations and Ethylene-to-Acetylene Hydrogen Transfers

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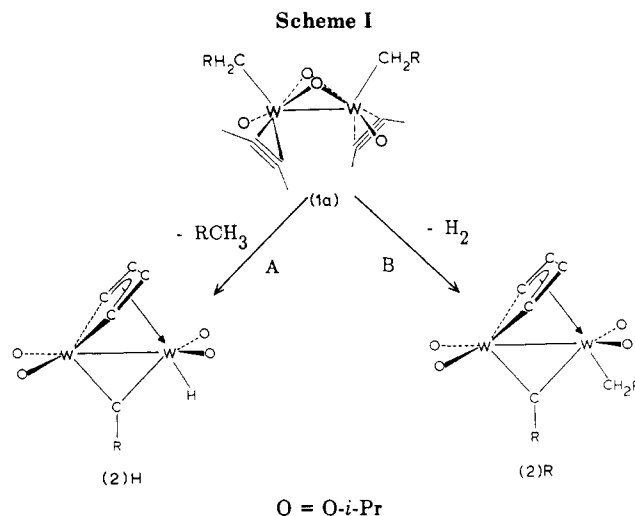
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Compounds of formula  $W_2(CH_2R)_2(MeCCMe)_2(O-i-Pr)_4$  (**1a**) (where  $R = Me$  or  $Et$ ) react thermally in hydrocarbon solutions to form 2:1 mixtures of  $W_4(\mu-CR)_2(\mu-C_2Me_2)(\eta^2-C_2Me_2)_2(O-i-Pr)_6$  (**4**) and  $W_2(\mu-MeCCMe)_2(O-i-Pr)_4$  (**3a**) via competitive  $\alpha$ - and  $\beta$ -hydrogen elimination pathways, respectively. The formation of **3a** involves elimination of 1 equiv of alkane and alkene. Compounds of formula  $W_2(CH_2-i-Pr)_2(R'CCR'')_2(O-i-Pr)_4$  ((**1**)(*i-Pr*)) (where  $R' = R'' = Me$ , (**1a**)(*i-Pr*);  $R' = Me$ ,  $R'' = Et$ , (**1b**)(*i-Pr*);  $R' = R'' = Et$ , (**1c**)(*i-Pr*)) react thermally in hydrocarbon solutions to produce the bis(alkyne)-bridged compounds  $W_2(\mu-R'CCR'')_2(O-i-Pr)_4$  (**3**) exclusively (where  $R' = R'' = Me$ , **3a**;  $R' = Me$ ,  $R'' = Et$ , **3b**;  $R' = R'' = Et$ , **3c**). No analogues of **4** with  $R = i-Pr$  have been detected. The rates of thermolysis of compounds **1a** are alkyl group dependent and follow the series  $k_{i-Bu} > k_{n-Pr} \sim k_{Et}$ . The rates of thermolysis of compounds (**1**)(*i-Pr*) are alkyne substituent dependent and follow the series  $k_{EtCCEt} < k_{EtCCMe} < k_{MeCCMe}$ . The data are suggestive of an olefin intermediate formed from an initial  $\beta$ -hydrogen elimination (possibly reversible) that is common to both  $\alpha$ - and  $\beta$ -hydrogen abstraction pathways. Compound **3a** reacts with ethylene in a 1:1 stoichiometry to form a metallacyclic complex of proposed formula  $W_2[MeC(Et)C(H)C(H)](\mu-MeCCMe)(O-i-Pr)_4$  (**5**). The formation of **5** requires a coupling of ethylene and acetylene functions and an ethylene-to-acetylene double-hydrogen transfer. In the solid state, compound **3a** possesses virtual  $D_{2h}$  symmetry with W-W and C-C(alkyne) bond distances of 2.611 (**3**) and 1.32 (**4**) Å, respectively. In solution, compound **3b** exists as a 1:1 mixture of syn and anti isomers, but the isomers do not interconvert in solution on the NMR time scale. The X-ray structure of (**4**)(*Et*) reveals a  $W_4$  chain with two W-W single bonds (W-W = 2.72 (**1**) Å) and an inner, nonbonding separation (W-W = 3.5 Å). The bridging alkyne ligands are twisted by 35° from a perpendicular position. The two  $W_2$  subunits are fused by virtue of weak, O-*i-Pr* bridges (W(2')-O(15) = 2.29 (**1**) Å). In toluene- $d_6$  solutions, compound (**4**)(*Et*) is involved in a rapid dimer-tetramer equilibrium that has been monitored by  $^1H$  NMR spectroscopy. Crystal data: (i) for  $W_2(\mu-C_2Me_2)_2(O-i-Pr)_4$  at -155 °C,  $a = 16.634$  (7) Å,  $b = 9.155$  (3) Å,  $c = 15.945$  (5) Å,  $Z = 4$ ,  $d_{calcd} = 1.95$  g  $cm^{-3}$ , and space group  $Pnam$ ; (ii) for  $W_4(\mu-C_2Me_2)_2(\mu-C_2Me_2)_2(\eta^2-C_2Me_2)_2(O-i-Pr)_6$  at -155 °C,  $a = 17.477$  (7) Å,  $b = 10.379$  (4) Å,  $c = 13.072$  (4) Å,  $\beta = 93.65$  (1)°,  $Z = 4$ ,  $d_{calcd} = 1.95$  g  $cm^{-3}$ , and space group  $P2_1/a$ .

### Introduction

In the previous paper,<sup>1</sup> we described the thermal  $\alpha$ -C-H activations of compounds  $W_2(CH_2R)_2(MeCCMe)_2(O-i-Pr)_4$  (**1a**) that contain alkyl ligands *without*  $\beta$ -hydrogen atoms in which reactions involving alkane ( $RCH_3$ ) and  $H_2$  eliminations were competitive. Mechanistic investigations indicated that a prior and rate-determining coupling of alkyne ligands initiated these processes. Scheme I summarizes these reactions. In both paths A and B, the terminal alkyne ligands are coupled and one alkyl ligand is stripped of two  $\alpha$ -hydrogens producing alkyldiene bridged complexes with  $MC_4$  metallacyclopentadiene rings. The rates of reactions shown in Scheme I are sensitive to the steric properties of the alkyl ligands.

In this paper, we describe the thermal chemistry of compounds **1a** that contain alkyl ligands with  $\beta$ -hydrogen atoms. In these systems,  $\alpha$ - and  $\beta$ -hydrogen activations are competitive and the chemistry is completely altered from that of Scheme I. The  $\alpha$ -hydrogen abstraction pathway in the present system produces compounds of molecular formula  $W_4(\mu-CR)_2(\mu-MeCCMe)_2(\eta^2-C_2Me_2)_2(O-i-Pr)_6$  with elimination of alkane and *i-PrOH*. The  $\beta$ -hydrogen abstraction reaction yields compounds of formula  $W_2(\mu-R'CCR'')_2(O-i-Pr)_4$  with the liberation of alkane and alkene. The latter reacts with ethylene in a 1:1 stoichiometry to produce the proposed compound  $W_2[MeC(Et)C(H)C(H)](\mu-MeCCMe)(O-i-Pr)_4$



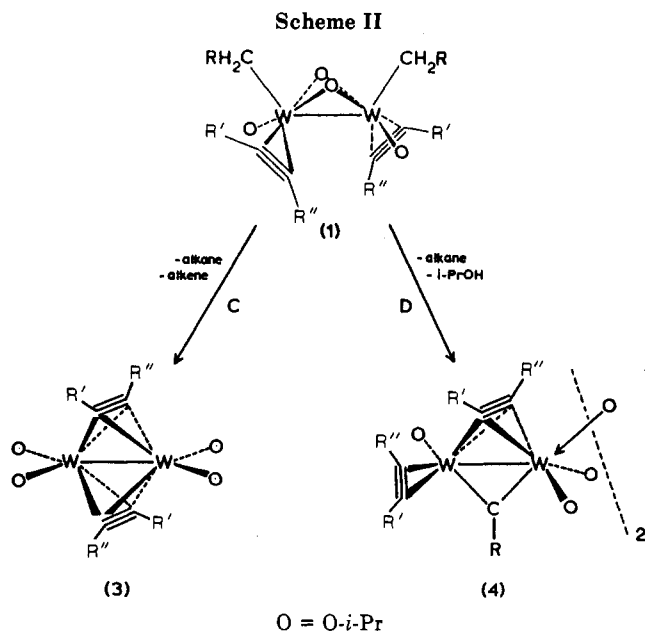
as a result of alkyne-ethylene coupling and ethylene-to-acetylene hydrogen transfer. A preliminary report of some of this work has appeared.<sup>2</sup>

### Synthesis and Reactivities

**Abbreviations for Compounds.** Drawings of compounds **1**, **3**, and **4** are shown in Scheme II. The sub-

(1) Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C. *Organometallics*, second of three papers in this issue.

(2) Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C. *Organometallics* 1987, 6, 2264.



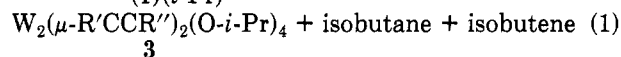
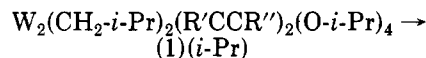
stituents on the alkyne ligands ( $R'$  and  $R''$ ) are systematically varied throughout this study as are the alkyl ligands ( $CH_2R$ ). The following nomenclature was developed to identify the individual compounds within the three classes of compounds. The compounds of formula  $W_2(CH_2R)_2(R'CCR'')_2(O-i-Pr)_4$  (1 in Scheme II) are referred to as **1a** when  $R' = R'' = Me$ , **1b** when  $R' = Me$  and  $R'' = Et$ , and **1c** when  $R' = R'' = Et$ . The abbreviation  $CH_2R$  where  $R = Me, Et, \text{ or } i\text{-Pr}$  corresponds to  $Et, n\text{-Pr}, \text{ and } i\text{-Bu}$  ( $CH_2CHMe_2$ ) ligands, respectively. Compounds of formula  $W_2(\mu-R'CCR'')_2(O-i-Pr)_4$  (**3** in Scheme II) are referred to as **3a** when  $R' = R'' = Me$ , **3b** when  $R' = Me$  and  $R'' = Et$ , and **3c** when  $R' = R'' = Et$ . Compounds of formula  $W_4(\mu-CR)_2(\mu-MeCCMe)_2(\eta^2-MeCCMe)_2(O-i-Pr)_6$  are referred to as **4**. When a unique compound is specified, the identity of  $R$  will immediately follow the compound number. For example,  $W_2(CH_2-i-Pr)_2(MeCCEt)_2(O-i-Pr)_4$  and  $W_4(\mu-CEt)_2(\mu-MeCCMe)_2(\eta^2-MeCCMe)_2(O-i-Pr)_6$  are defined by **(1b)**(*i*-Pr) and **(4)**(Et), respectively.

**Thermolyses.** Compounds of formula  $W_2(CH_2R)_2(MeCCMe)_2(O-i-Pr)_4$  (**1a**) (where  $R = Me, Et, \text{ or } i\text{-Pr}$ ) react thermally in hydrocarbon solutions at room temperature by competitive pathways outlined in Scheme II. The product of path C of Scheme II is a bis(alkyne)-bridged complex of formula  $W_2(\mu-MeCCMe)_2(O-i-Pr)_4$  (**3a**). The formation of **3a** represents a  $\beta$ -hydrogen atom initiated elimination of alkane and alkene and requires two terminal-to-bridge alkyne migrations. The product of path D of Scheme II is an alkylidyne-bridged complex of molecular formula  $W_4(\mu-CR)_2(\mu-MeCCMe)_2(\eta^2-MeCCMe)_2(O-i-Pr)_6$  (**4**). The formation of **4**, results from a double  $\alpha$ -hydrogen abstraction process occurring from one alkyl ligand with the formal elimination of alkane and *i*-PrOH. In addition, only one alkyne ligand migrates to a bridging position per  $W_2$  unit in contrast to path C. The  $\alpha$ -hydrogen abstraction process outlined in path D is clearly quite different from that of paths A and B of Scheme I. No hydride ligands or  $MC_4$  metallacycles have been detected in the thermolyses of **1a** when  $\beta$ -hydrogen atoms have been present.

The relative rates of thermolysis in Scheme II are alkyl group dependent and follow the series  $k_{i-Bu} > k_{n-Pr} \approx k_{Et}$ . The half-lives of these reactions at 25 °C are approximately 18 h for **(1a)**(*i*-Pr) and 40 h for **(1a)**( $R = Me \text{ or } Et$ ). The relative amounts of **3a** and **4** produced in Scheme II are also alkyl group dependent with the Et and *n*-Pr com-

pounds each yielding 2:1 mixtures of **4** to **3a** at 25 °C. However, the *i*-Bu compound **(1a)**(*i*-Pr) is converted to **3a** exclusively, and no analogue of **4** with  $R = i\text{-Pr}$  has been detected.

Compounds  $W_2(CH_2-i-Pr)_2(MeCCEt)_2(O-i-Pr)_4$  (**(1b)**(*i*-Pr)) and  $W_2(CH_2-i-Pr)_2(EtCCEt)_2(O-i-Pr)_4$  (**(1c)**(*i*-Pr)) also react thermally in hydrocarbon solutions to produce the corresponding bis(alkyne)-bridged compounds **3b** and **3c**, respectively, according to eq 1. No analogues of **4** were



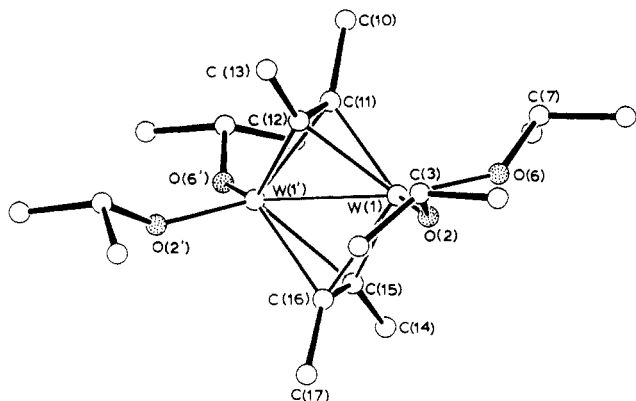
observed by  $^1H$  NMR spectroscopy in these reactions. The relative rates of reaction 1 decrease with increasing steric demands of the alkyne ligands such that  $k_{1a} > k_{1b} > k_{1c}$  ( $t_{1/2}$  for **(1c)**(*i*-Pr)  $\approx 36$  h and  $t_{1/2}$  for **(1b)**(*i*-Pr)  $\approx 24$  h at 25 °C). Thermolysis of  $W_2(CH_2Et)_2(MeCCEt)_2(O-i-Pr)_4$  (**(1b)**(Et)) produces mixtures of compounds that include two isomers (syn and anti) of **3b** and presumably two isomers of a compound related to **(4)**(Et). No compounds have been isolated in a pure form from this reaction, and the complex spin systems and isomeric distributions have hindered spectroscopic interpretation. The relative isomeric populations of **3b** in solution will be discussed in Spectroscopic Studies.

Compounds **3** were isolated in good yields from thermolyzed solutions of the appropriate **(1)**(*i*-Pr) precursors as dark, air-sensitive crystalline solids. Their solid-state and solution structures are represented by **3** in Scheme II and will be discussed in detail in the following two sections. The crystalline solids are thermally stable for greater than 2 months under vacuum or  $N_2$  atmospheres. Compounds **3** are very hydrocarbon soluble forming extremely air- and moisture-sensitive green-brown solutions. The compounds have been characterized by  $^1H$  NMR,  $^{13}C$  NMR, and IR spectroscopic studies, and, for **3a**, elemental analysis, and single-crystal X-ray diffraction. The isobutane and isobutene byproducts were identified by  $^1H$  NMR spectroscopy.

Compound **(4)**(Et) was isolated from a thermolyzed hexane solution of **(1a)**(Et) as an impure crystalline material that was contaminated with **3a**. Subsequent fractional recrystallization from  $Et_2O$  afforded large pale orange cubes of analytically pure **(4)**(Et) in a low crystalline yield. Compound **(4)**(Et) is air-sensitive in the solid state and forms air-sensitive, pale yellow hydrocarbon solutions. It has been characterized by  $^1H$  NMR,  $^{13}C\{^1H\}$  NMR, and IR spectroscopic studies and single-crystal X-ray diffraction. The elemental analysis of **(4)**(Et) registered low in carbon content by one carbon atom per  $W_2$  unit (see Experimental Section). The "missing" carbon atom is presumably the alkylidyne  $\mu$ -CEt carbon that forms undetectable tungsten carbide during combustion. This phenomenon was well documented<sup>1</sup> for the  $HW_2(\mu-CR)(\mu-C_2Me_4)(O-i-Pr)_4$  compounds reported in the preceding paper. Propene, *n*-propane, and *i*-PrOH byproducts were identified by  $^1H$  NMR spectroscopy as the organic elimination products of a thermolyzed solution of **(1a)**(Et).

Compound **(4)**(Me) was unequivocally identified by  $^1H$  NMR spectroscopy but was never isolated in a pure form.

The presence of  $\beta$ -hydrogens in some way alters the course of  $\alpha$ -hydrogen abstraction in Scheme II (path D) relative to paths A and B of Scheme I. Intermediates containing coordinated olefins are clearly implicated in path C and could be responsible for the differences in  $\alpha$ -hydrogen abstraction between path D and Scheme I. An experiment designed to test for the presence of olefin in-

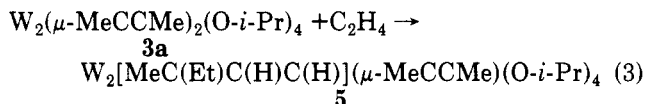


**Figure 1.** Ball-and-stick drawing of the  $W_2(\mu-C_2Me_2)_2(O-i-Pr)_4$  molecule.

intermediates that rapidly and reversibly coordinated alkene is outlined in eq 2. It was postulated that, if an intermediate containing a substitutionally labile isobutene ligand was present in the thermolysis of (1a)(i-Pr), an ethylene-for-butene exchange could occur in the presence of excess  $C_2H_4$ . Thus, if  $\alpha$ -hydrogen abstraction (path D) was occurring from such an intermediate, compound (4)(Me) may be formed. Experimentally, it was found that excess ethylene did not affect the course or rates of reaction in Scheme II. However, the resulting 3a that was produced in this experiment reacted with ethylene in a 1:1 stoichiometry to form a purple metallacyclic compound, formulated as  $W_2[MeC(Et)C(H)C(H)](\mu-MeCCMe)(O-i-Pr)_4$  (5), according to eq 3. The formation of 5 involves a



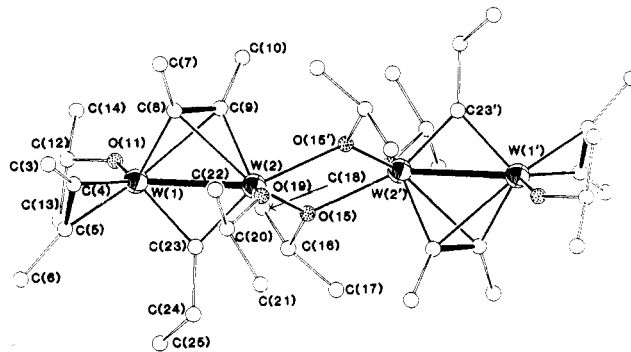
mediate containing a substitutionally labile isobutene ligand was present in the thermolysis of (1a)(i-Pr), an ethylene-for-butene exchange could occur in the presence of excess  $C_2H_4$ . Thus, if  $\alpha$ -hydrogen abstraction (path D) was occurring from such an intermediate, compound (4)(Me) may be formed. Experimentally, it was found that excess ethylene did not affect the course or rates of reaction in Scheme II. However, the resulting 3a that was produced in this experiment reacted with ethylene in a 1:1 stoichiometry to form a purple metallacyclic compound, formulated as  $W_2[MeC(Et)C(H)C(H)](\mu-MeCCMe)(O-i-Pr)_4$  (5), according to eq 3. The formation of 5 involves a



coupling of ethylene and acetylene ligands and two hydrogen transfers from ethylene to one acetylinic carbon. Thus one of the  $\mu-MeCCMe$  functions of 3a is transformed into a  $MeCCH_2Me$  fragment that is coupled to an ethylene-derived  $HCCH$  fragment in 5. The proposed structure of 5 is shown below by III but will be discussed in detail in a future publication if a suitable crystalline sample can be obtained. Reactions employing  $D_2CCH_2$  and 3a produced two isotopomers of 5 each having a deuterium in one of the methylene positions of the Et function. This indicates that one hydrogen atom is transferred from each ethylenic carbon (1,2-dihydride shift) versus an initial transfer of two hydrogens from one ethylenic carbon (1,1-dihydride shift) followed by a hydrogen atom rearrangement within the ethylenic fragment.

Compound 5 is thermally unstable in solution at room temperature but has been isolated from cold pentane solutions as a dark microcrystalline solid (>95% pure by  $^1H$  NMR analysis) that is very air-sensitive and thermally unstable. The compound has been characterized by  $^1H$  and  $^{13}C$  NMR spectroscopic studies involving a variety of labeled ethylenes.

It is interesting to note that the thermolysis of (1a)(Me) in an NMR tube fitted with a septum cap produces 3a and (4)(Me) according to Scheme II, but compound 5 is not observed. The septum cap acts as an "ethylene sponge" that effectively removes the ethylene as it is formed, thus blocking the conversion of 3a  $\rightarrow$  5. Apparently, the initial release of ethylene precedes the final step in the formation



**Figure 2.** Ball-and-stick drawing of the  $W_4(\mu-CEt)_2(\mu-C_2Me_2)_2(\eta^2-C_2Me_2)_2(O-i-Pr)_6$  molecule.

**Table I.** Selected Bond Distances (Å) and Angles (deg) for  $W_2(\mu-MeCCMe)_2(O-i-Pr)_4$

Bond Distances			
W(1)-W(1')	2.611 (3)	O(2)-C(3)	1.398 (24)
W(1)-O(2)	1.920 (14)	O(6)-C(7)	1.390 (24)
W(1)-O(6)	1.871 (14)	C(10)-C(11)	1.54 (4)
W(1)-C(11)	2.108 (24)	C(11)-C(12)	1.36 (4)
W(1)-C(12)	2.100 (20)	C(12)-C(13)	1.55 (3)
W(1)-C(15)	2.164 (24)	C(14)-C(15)	1.47 (4)
W(1)-C(16)	2.197 (22)	C(15)-C(16)	1.28 (4)
		C(16)-C(17)	1.50 (4)
Bond Angles			
O(2)-W(1)-O(6)	101.8 (8)	C(11)-C(12)-C(13)	130.9 (25)
W(1)-O(2)-C(3)	142.4 (13)	W(1)-C(15)-W(1)'	74.2 (10)
W(1)-O(6)-C(7)	144.9 (14)	C(14)-C(15)-C(16)	132.6 (27)
W(1)-C(11)-W(1)'	76.5 (10)	W(1)-C(16)-W(1)'	72.9 (9)
C(10)-C(11)-C(12)	131.9 (27)	C(15)-C(16)-C(17)	138.2 (27)
W(1)-C(12)-W(1)'	76.9 (9)		

**Table II.** Selected Bond Distances (Å) and Angles (deg) for  $W_4(\mu-CEt)_2(\mu-MeCCMe)_2(\eta^2-MeCCMe)_2(O-i-Pr)_6$

Bond Distances			
W(2)-W(2')	3.504 (1)	W(2)-O(15)	1.998 (7)
W(1)-W(2)	2.7208 (10)	W(2)-O(15')	2.291 (7)
W(1)-O(11)	1.885 (7)	W(2)-O(19)	1.919 (8)
W(1)-C(4)	2.028 (12)	W(2)-C(8)	2.476 (12)
W(1)-C(5)	2.209 (12)	W(2)-C(9)	2.002 (11)
W(1)-C(8)	2.104 (11)	W(2)-C(23)	1.925 (11)
W(1)-C(9)	2.509 (11)	C(4)-C(5)	1.303 (18)
W(1)-C(23)	1.995 (10)	C(8)-C(9)	1.396 (16)
		C(23)-C(24)	1.515 (15)
Bond Angles			
W(2)-W(1)-C(4)	121.2 (4)	W(1)-O(11)-C(12)	142.1 (7)
W(2)-W(1)-C(5)	132.6 (3)	W(2)-O(15)-W(2)'	109.7 (3)
W(2)-W(1)-C(8)	60.9 (3)	W(2)-O(15)-C(16)	126.0 (6)
W(2)-W(1)-C(9)	44.77 (26)	W(2)-O(19)-C(20)	132.0 (7)
W(2)-W(1)-C(23)	45.0 (33)	C(3)-C(4)-C(5)	136.1 (13)
W(1)-W(2)-C(23)	47.1 (3)	C(4)-C(5)-C(6)	135.2 (13)
O(15)-W(2)-O(15)'	70.3 (3)	C(7)-C(8)-C(9)	125.6 (11)
O(15)-W(2)-O(19)	81.3 (3)	C(8)-C(9)-C(10)	130.1 (11)

of 3a or is faster than the coupling reaction outlined in eq 3.

### Solid-State Structures and Bonding

Ball-and-stick drawings of the  $W_2(\mu-MeCCMe)_2(O-i-Pr)_4$  and  $W_4(\mu-CEt)_2(\mu-MeCCMe)_2(\eta^2-MeCCMe)_2(O-i-Pr)_6$  molecules are shown in Figures 1 and 2, respectively. Selected bond distances, bond angles, and fractional coordinates are listed in Tables I through IV. Summaries of the crystallographic data are given in Table V.

$W_2(\mu-MeCCMe)_2(O-i-Pr)_4$ . Compound 3a possesses virtual  $D_{2h}$  symmetry in the solid state with one crystallographically imposed mirror plane defined by the eight MeCCMe carbon atoms. The geometry about the tungsten atoms in 3a is distorted tetrahedral with each alkyne ligand occupying a single coordination site at each metal center.

Table III. Atomic Positional Parameters for  $W_2(\mu-C_2Me_2)_2(O-i-Pr)_4$ 

atom	$10^4x$	$10^4y$	$10^4z$	$10B_{iso}, \text{\AA}^2$
W(1)	3544.8 (4)	228 (1)	1681.2 (5)	16
O(2)	3934 (10)	-1237 (18)	922 (10)	45
C(3)	4627 (13)	-2007 (21)	698 (13)	22
C(4)	4608 (15)	7825 (30)	9752 (14)	46
C(5)	4639 (16)	6595 (26)	1139 (18)	50
O(6)	3129 (12)	1623 (15)	942 (11)	56
C(7)	3177 (14)	3068 (22)	679 (14)	26
C(8)	3093 (14)	3140 (26)	-235 (12)	34
C(9)	2532 (15)	3923 (23)	1117 (14)	35
C(10)	4493 (18)	3217 (32)	2500*	28
C(11)	4160 (19)	1649 (31)	2500*	24
C(12)	4532 (16)	324 (31)	2500*	17
C(13)	5436 (16)	-81 (32)	2500*	30
C(14)	1669 (19)	530 (31)	2500*	37
C(15)	2511 (18)	52 (32)	2500*	39
C(16)	2841 (16)	-1217 (31)	2500*	32
C(17)	2584 (19)	-2783 (28)	2500*	30

Table IV. Atomic Positional Parameters for  $W_4(\mu-CEt)_2(\mu-C_2Me_2)_2(\eta^2-C_2Me_2)_2(O-i-Pr)_6$ 

atom	$10^4x$	$10^4y$	$10^4z$	$10B_{iso}, \text{\AA}^2$
W(1)	9603.2 (2)	1534.6 (4)	6961.3 (3)	16
W(2)	9555.7 (2)	270.6 (4)	8779.6 (3)	14
C(3)	8500 (7)	132 (14)	5029 (10)	35
C(4)	8875 (7)	1073 (13)	5747 (9)	29
C(5)	8774 (6)	2280 (13)	5977 (9)	26
C(6)	8266 (7)	3357 (15)	5549 (12)	44
C(7)	9980 (7)	-1480 (12)	6422 (10)	32
C(8)	9968 (6)	-305 (11)	7061 (9)	22
C(9)	10449 (6)	-60 (11)	7932 (9)	22
C(10)	11282 (7)	-349 (14)	8145 (11)	36
O(11)	10446 (4)	2633 (8)	6804 (6)	26
C(12)	10709 (7)	3596 (11)	6173 (9)	24
C(13)	10401 (8)	4898 (13)	6478 (12)	38
C(14)	11559 (9)	3542 (14)	6219 (15)	55
O(15)	9986 (4)	1192 (7)	10019 (6)	20
C(16)	10085 (7)	2591 (10)	10076 (10)	27
C(17)	9986 (8)	3074 (12)	11139 (11)	36
C(18)	10832 (8)	2992 (12)	9621 (10)	34
O(19)	8737 (4)	-949 (8)	8651 (6)	25
C(20)	7994 (7)	-902 (13)	8114 (9)	30
C(21)	7413 (8)	-679 (17)	8894 (13)	51
C(22)	7854 (8)	-2123 (15)	7529 (11)	41
C(23)	9023 (6)	1757 (10)	8215 (8)	17
C(24)	8370 (6)	2603 (11)	8527 (9)	23
C(25)	8499 (7)	4049 (12)	8333 (11)	31

The W-W and C-C(alkyne) bond distances of 2.611 (3) and 1.32 (4) Å, respectively, are indicative of extensive metal-to-alkyne  $\pi^*$  back-bonding.<sup>3</sup> Compound **3a** is virtually isostructural with the crystallographically characterized compound  $W_2(\mu-PhCPh)_2(O-t-Bu)_4$ , reported by Cotton et al.,<sup>4</sup> that has a W-W bond distance of 2.677 (1) Å and a C-C(alkyne) distance of 1.45 (2) Å (average). The differences in bond distances between the two compounds may reflect the greater  $\pi$ -donating ability<sup>5</sup> of O-*t*-Bu versus O-*i*-Pr and the greater  $\pi$ -accepting capacity of PhC≡CPh versus MeC≡CMe, but the precision is such that the C-C distances fall within  $3\sigma$  of one another.

$W_4(\mu-CEt)_2(\mu-MeCCMe)_2(\eta^2-MeCCMe)_2(O-i-Pr)_6$ . The solid-state structure of (4)(Et), shown in Figure 2, comprises a chain of four tungsten atoms with two W-W single bonds (W(1)-W(2) = 2.721 (1) Å) and an inner,

Table V. Summary of Crystallographic Data

	I	II
empirical formula	$W_2C_{20}H_{40}O_4$	$W_4C_{40}H_{76}O_6$
color of cryst	black	orange
cryst dimens (mm)	$0.072 \times 0.060$ $\times 0.08$	$0.04 \times 0.15$ $\times 0.12$
$T_{max}/T_{min}$	0.567/0.442	0.675/0.296
space group	<i>Pnam</i>	<i>P2<sub>1</sub>/a</i>
cell dimens		
temp (°C)	-155	-155
<i>a</i> (Å)	16.634 (7)	17.477 (7)
<i>b</i> (Å)	9.155 (3)	10.379 (4)
<i>c</i> (Å)	15.945 (5)	13.072 (4)
$\beta$ (deg)		93.65 (1)
<i>Z</i> (molecules/cell)	4	4
<i>V</i> (Å <sup>3</sup> )	2427.95	2366.54
<i>d</i> (calcd) (g/cm <sup>3</sup> )	1.948	1.945
wavelength (Å)	0.71069	0.71069
mol wt	712.23	1388.44
linear abs coeff (cm <sup>-1</sup> )	98.812	99.383
detector to sample dist (cm)	22.5	22.5
sample to source dist (cm)	23.5	23.5
av $\omega$ scan width at half-height	0.25	0.25
scan speed (deg/min)	4.0	4.0
scan width (deg + dispersion)	2.0	2.0
individual bkgd (s)	8	4
aperture size (mm)	$3.0 \times 4.0$	$3.0 \times 4.0$
$2\theta$ range (deg)	6-45	6-45
total no. of reflctns collected	3622	4241
no. of unique intensities	1659	3110
no. of <i>F</i> > 2.33 $\sigma$ ( <i>F</i> )	1088	3110
<i>R</i> ( <i>F</i> )	0.0459	0.0363
<i>R<sub>w</sub></i> ( <i>F</i> )	0.0409	0.0365
goodness of fit for last cycle	0.847	1.140
max $\Delta/\sigma$ for last cycle	0.05	0.05

<sup>a</sup> I,  $W_2(\mu-C_2Me_2)_2(O-i-Pr)_4$ ; II,  $W_4(\mu-CEt)_2(\mu-C_2Me_2)_2(\eta^2-C_2Me_2)_2(O-i-Pr)_6$ .

nonbonding W-W separation (W(2)-W(2)') = 3.504 (1) Å. The bridging alkyne ligands are skewed<sup>6,7</sup> away from a perpendicular position by 35° as evidenced by the tungsten-alkyne distances W(1)-C(8) = 2.01 (1) Å, W(1)-C(9) = 2.48 (1) Å, W(2)-C(8) = 2.48 (1) Å, and W(2)-C(9) = 2.00 (1) Å. The C(8)-C(9) bond distance of 1.40 (2) Å in the bridging alkyne moiety is indicative of a highly reduced alkyne ligand.<sup>3</sup> The C(4)-C(5) bond distance of 1.30 (2) Å in the terminal alkyne ligand is similar to those observed for compounds **1a**.<sup>8</sup> The outer tungsten atoms are in distorted tetrahedral geometries if the alkyne ligands are assumed to occupy a single coordination site. The inner tungsten atoms are in trigonal-bipyramidal coordination environments with the alkylydine and one O-*i*-Pr ligand occupying axial sites. The two dinuclear units are fused along a common axial-equatorial edge by virtue of weak O-*i*-Pr bonds [W(2)-O(15)'] = 2.29 (1) Å].

### Spectroscopic Studies and Solution Structures

The <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR data for compounds **3**, **4**, and **5** are listed in Table VI. The IR data are listed in the Experimental Section.

$W_2(\mu-R'CCR'')_2(O-i-Pr)_4$ . The NMR data for compounds **3a** and **3c** are consistent with the solid-state structure of **3a** described in the previous section. The  $\mu-C_2Me_2$  methyl resonance of **3a** appears at 2.67 ppm in the <sup>1</sup>H NMR spectrum and displays a three-bond <sup>183</sup>W-<sup>1</sup>H coupling of 3.8 Hz (<sup>3</sup>*J*<sub>183W-1H</sub> = 3.8 Hz, 24% total satellite

(3) (a) Chisholm, M. H.; Conroy, B. K.; Clark, D. L.; Huffman, J. C. *Polyhedron* 1988, 7, 903. (b) Conroy, B. K. Ph.D. Thesis, Indiana University, 1987.

(4) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* 1983, 2, 1167.

(5) Blower, P. J.; Chisholm, M. H.; Clark, D. L.; Eichhorn, B. W. *Organometallics* 1986, 5, 2125.

(6) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Organometallics* 1986, 5, 2171.

(7) Hoffman, R.; Calhorda, M. J. *Organometallics* 1986, 5, 2181.

(8) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C. *Organometallics*, first of three papers in this issue.

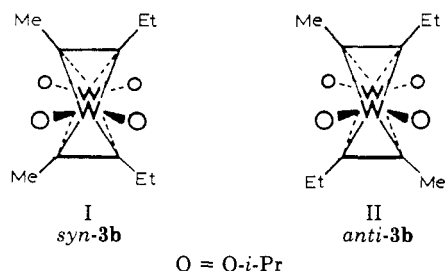
Table VI. NMR Data<sup>a</sup>

compound	<sup>1</sup> H NMR <sup>b</sup>	<sup>13</sup> C{ <sup>1</sup> H} NMR
W <sub>2</sub> (μ-MeCCMe) <sub>2</sub> (O- <i>i</i> -Pr) <sub>4</sub> (benzene- <i>d</i> <sub>6</sub> , 22 °C)	OCHMe <sub>2</sub> (4.58, sept, 1 H, 6.1); μ-C <sub>2</sub> Me <sub>2</sub> (2.67, s, 3 H, <sup>3</sup> J <sub>183W-1H</sub> = 3.8, ~24% total satellite intensity); OCHMe <sub>2</sub> (1.22, d, 6 H, 6.1)	μ-C <sub>2</sub> Me <sub>2</sub> (165.7, <sup>1</sup> J <sub>183W-13C</sub> = 44 Hz, 24% total satellite intensity); OCHMe <sub>2</sub> (74.1, <sup>2</sup> J <sub>183W-13C</sub> = 7, 14% total satellite intensity); OCHMe <sub>2</sub> (26.6); μ-C <sub>2</sub> Me <sub>2</sub> (19.9)
W <sub>2</sub> (μ-MeCCEt) <sub>2</sub> (O- <i>i</i> -Pr) <sub>4</sub> <sup>c</sup> (benzene- <i>d</i> <sub>6</sub> , 22 °C)	OCHMe <sub>2</sub> (4.58, sept, 4 H, 6.1); μ-C <sub>2</sub> (CH <sub>2</sub> Me)(Me) (3.03, q, 4 H, 7.5); μ-C <sub>2</sub> (CH <sub>2</sub> Me)(Me) (2.76, s, 3 H), (2.74, s, 3 H); μ-C <sub>2</sub> (CH <sub>2</sub> Me)(Me) (1.33, t, 6 H, 7.5); OCHMe <sub>2</sub> (1.24, d br, ~24 H, 6.0) [note: the <sup>1</sup> H NMR spectrum recorded at -95 °C (toluene- <i>d</i> <sub>8</sub> ) was virtually identical]	μ-C <sub>2</sub> MeEt (170.9), (170.5), (165.7, <sup>1</sup> J <sub>183W-13C</sub> ≈ 44, ~24% total satellite intensity); (164.8, <sup>1</sup> J <sub>183W-13C</sub> ≈ 44, 24% total satellite intensity); OCHMe <sub>2</sub> (74.3), (74.1), (74.0), relative intensities of 1:2:1, respectively; μ-C <sub>2</sub> (CH <sub>2</sub> Me)(Me) (29.0), (28.9); OCHMe <sub>2</sub> (26.6), (26.5), (26.4), (26.3); μ-C <sub>2</sub> (CH <sub>2</sub> Me)(Me) (20.7); μ-C <sub>2</sub> (CH <sub>2</sub> Me)(Me) (16.4), (16.3)
W <sub>2</sub> (μ-EtCCEt) <sub>2</sub> (O- <i>i</i> -Pr) <sub>4</sub> (benzene- <i>d</i> <sub>6</sub> , 22 °C)	OCHMe <sub>2</sub> (4.58, sept, 1 H, 6.5); μ-CCH <sub>2</sub> Me (3.08, q, 2 H, 7.4); μ-CCH <sub>2</sub> Me (1.31, t, 3 H, 7.4); OCHMe <sub>2</sub> (1.27, d, 6 H, 6.0)	μ-C <sub>2</sub> Et <sub>2</sub> (170.9, <sup>1</sup> J <sub>183W-13C</sub> = 44, 24% total satellite intensity); OCHMe <sub>2</sub> (74.3, <sup>2</sup> J <sub>183W-13C</sub> = 9, 14% total satellite intensity); μ-C <sub>2</sub> CH <sub>2</sub> Me (29.4); OCHMe <sub>2</sub> (26.5); μ-CCH <sub>2</sub> Me (16.6)
W <sub>4</sub> (μ-CEt) <sub>2</sub> (μ-MeCCMe) <sub>2</sub> (η <sup>2</sup> -MeCCMe) <sub>2</sub> (O- <i>i</i> -Pr) <sub>6</sub> (benzene- <i>d</i> <sub>6</sub> , 22 °C)	μ-CCH <sub>2</sub> Me (5.18, m, 1 H), (4.76, m, 1 H); OCHMe <sub>2</sub> (4.36, sept, 1 H, 6.1), (3.84, sept, 1 H, 6.1), (3.57, sept, 1 H, 6.1); μ-C <sub>2</sub> Me <sub>2</sub> (3.25, s, 3 H), (3.09, s, 3 H); η <sup>2</sup> -C <sub>2</sub> Me <sub>2</sub> (2.96, s, 6 H); μ-CCH <sub>2</sub> Me (1.89, t, 3 H, 7.4); OCHMe <sub>2</sub> (1.06, d, 3 H, 6.1), (0.92, d, 3 H, 6.1), (0.88, d, 3 H, 6.1), (0.78, d, 3 H, 6.1), (0.49, d, 3 H, 6.1), (0.43, d, 3 H, 6.1)	μ-CCH <sub>2</sub> Me (310.6); μ-C <sub>2</sub> Me <sub>2</sub> , η <sup>2</sup> -C <sub>2</sub> Me <sub>2</sub> (216.2), (195.1), (179.4); OCHMe <sub>2</sub> (77.2), (74.8), (73.7); μ-CCH <sub>2</sub> Me (42.6); μ-CCH <sub>2</sub> Me, μ-C <sub>2</sub> Me <sub>2</sub> , η <sup>2</sup> -C <sub>2</sub> Me <sub>2</sub> , OCHMe <sub>2</sub> (27.1), (26.5), (26.1), (26.0), (25.9), (24.7), (23.6), (20.2), (18.4)
W <sub>4</sub> (μ-CMe) <sub>2</sub> (μ-MeCCMe) <sub>2</sub> (η <sup>2</sup> -MeCCMe) <sub>2</sub> (O- <i>i</i> -Pr) <sub>6</sub> <sup>d</sup> (benzene- <i>d</i> <sub>6</sub> , 22 °C)	μ-CMe (4.81, s, 3 H); OCHMe <sub>2</sub> (3.89, sept, 1 H, 6.1), (3.34, sept, 1 H, 6.1); μ-C <sub>2</sub> Me (3.19, s, 3 H), (3.08, s, 3 H); η <sup>2</sup> -C <sub>2</sub> Me <sub>2</sub> (2.98, s, 6 H); OCHMe <sub>2</sub> (0.45, d, 3 H, 6.1), (0.52, d, 3 H, 6.1)	N/R
W <sub>2</sub> [MeC(Et)C(H)C(H)]-(μ-MeCCMe)(O- <i>i</i> -Pr) <sub>4</sub> (benzene- <i>d</i> <sub>6</sub> , 22 °C)	MeC(Et)C(H)C(H) (4.98, d, 1 H, 7.0), (4.76, d, 1 H, 7.0); OCHMe <sub>2</sub> (4.83, sept, 1 H, 6.1), (4.62, sept, 1 H, 6.1), (4.43, sept, 1 H, 6.1), (4.14, sept, 1 H, 6.1); MeC(CH <sub>2</sub> Me)C(H)C(H) (3.20, m, 1 H), (2.69, m, 1 H); MeC(Et)C(H)C(H), μ-C <sub>2</sub> Me <sub>2</sub> (2.86, s, 3 H), (2.58, s, 3 H), (2.10, s, 3 H); MeC(CH <sub>2</sub> Me)C(H)C(H) (1.62, t, 3 H, 7.2) OCHMe <sub>2</sub> (1.46, d, 3 H, 6.1), (1.34, d, 3 H, 6.1), (1.31, d, 3 H, 6.1), (1.27, d, 3 H, 6.1), (1.20, d, 3 H, 6.1), (1.10, d, 3 H, 6.1), (1.06, d, 3 H, 6.1)	MeC(Et)C(H)C(H), μ-C <sub>2</sub> Me <sub>2</sub> (209.2), (149.6), (111.9); MeC(Et)C(H)C(H) (191.7, <sup>1</sup> J <sub>183W-13C</sub> = 76, 19), (103.2, <sup>1</sup> J <sub>183W-13C</sub> = 18); OCHMe <sub>2</sub> (79.4), (77.7), (74.3), (73.6); MeC(Et)C(H)C(H), μ-C <sub>2</sub> Me <sub>2</sub> , OCHMe <sub>2</sub> (53.6), (39.9), (27.5), (26.8), (25.8), (25.7), (25.66, relative intensity 2), (25.58), (25.2), (22.4), (17.6), (15.5)

<sup>a</sup><sup>1</sup>H NMR data are reported as follows: assignment (chemical shift in ppm, multiplicity, relative intensity, H-H coupling constant in Hz, heteronuclear coupling constants in Hz). <sup>13</sup>C{<sup>1</sup>H} NMR data are reported as follows: assignment (chemical shift in ppm, heteronuclear coupling constants in Hz). <sup>b</sup>Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broad. <sup>c</sup>Assignments were based on the spectral similarities of this compound and **3a** and **3c**. <sup>d</sup>Because (4)Me was only observed in situ, some of the O-*i*-Pr resonances were obscured by the co-products. One set of O-*i*-Pr resonances appeared to be broadened due to exchange with free *i*-PrOH formed in the reaction. These broad resonances appeared at 4.4 and 1.1 ppm and are not listed above.

intensity). The acetylenic carbons of **3a** and **3c** appear at 166 and 171 ppm in the respective <sup>13</sup>C{<sup>1</sup>H} NMR spectra with <sup>183</sup>W-<sup>13</sup>C couplings of 44 Hz (<sup>1</sup>J<sub>183W-13C</sub> = 44 Hz, 24% total satellite intensity). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3a** is shown in Figure 3.

Compound W<sub>2</sub>(μ-MeCCEt)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> (**3b**) can exist as syn and anti isomers that differ only in the arrangement of the alkyne ligands. Schematic drawings of the two isomers, I and II, viewed down the W-W vectors are de-



icted. Structure I has C<sub>2v</sub> symmetry and contains two types of O-*i*-Pr ligands with non-diastereotopic Me groups. Structure II possesses C<sub>2h</sub> symmetry and contains one type of O-*i*-Pr ligand, but the absence of a vertical plane of symmetry makes the O-*i*-Pr methyl groups diastereotopic. A 1:1 mixture of isomers I and II should show three O-*i*-Pr α-carbon resonances, with one signal being twice the relative intensity of the other two, and four equal intensity O-*i*-Pr methyl carbon resonances. Furthermore, four equal

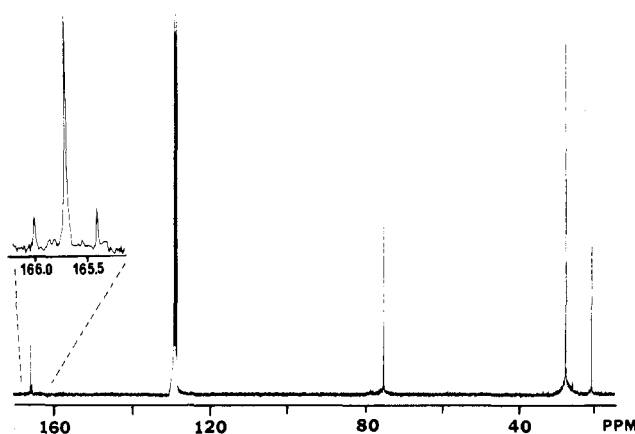
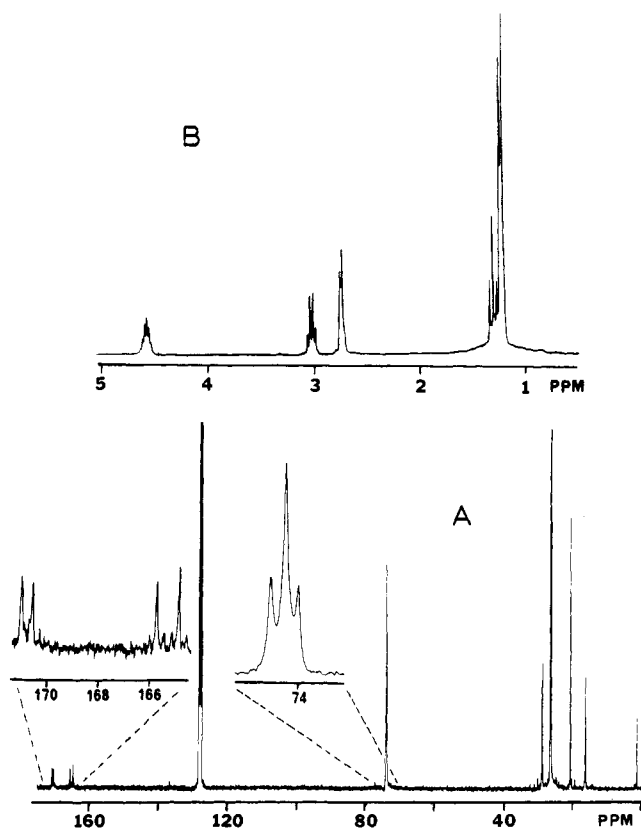


Figure 3. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of W<sub>2</sub>(μ-C<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> recorded in benzene-*d*<sub>6</sub> at 22 °C and 75 MHz. The resonances at 128 ppm arise from C<sub>6</sub>D<sub>6</sub>.

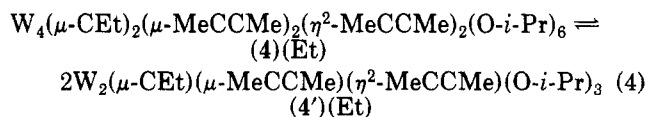
intensity acetylenic carbon resonances should be observed. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of a crystalline sample of **3b**, shown in Figure 4a, is consistent with these expectations. The methyl carbon resonances of the alkyne ligands are apparently accidentally degenerate in C<sub>6</sub>D<sub>6</sub> at 22 °C showing only one signal at 20.7 ppm. Tungsten-carbon coupling of 44 Hz (approximately 24% total satellite intensity) is observed on two of the four acetylenic carbons. These data leave little doubt that 1:1 mixtures of syn and



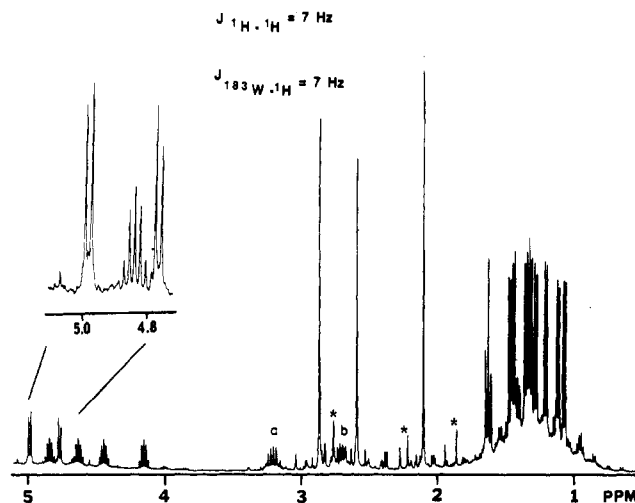
**Figure 4.** (a) The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $W_2(\mu\text{-MeCCEt})_2(\text{O-}i\text{-Pr})_4$  recorded in benzene- $d_6$  at 22 °C and 75 MHz. The resonances at 128 ppm arise from  $\text{C}_6\text{D}_6$ . (b) The  $^1\text{H}$  NMR spectrum of the same sample recorded in benzene- $d_6$  at 22 °C and 300 MHz.

anti isomers are present in  $\text{C}_6\text{D}_6$  solutions of **3b** and, moreover, show that the isomers are static and are not interconverting on the  $^{13}\text{C}$  NMR time scale. Curiously, the  $^1\text{H}$  NMR spectrum of the same sample is remarkably simple (Figure 4b). As expected, two alkyne methyl signals are seen at room temperature, but only one *O-i-Pr* methine septet, one *O-i-Pr* methyl doublet, and one set of alkyne Et resonances are observed by  $^1\text{H}$  NMR spectroscopy from -95 to 22 °C. On the basis of the symmetry arguments just presented, three *O-i-Pr* methyl doublets and two sets of alkyne Et resonances should be observed. Because of the sharpness of the two alkyne methyl resonances at room temperature and the small difference in their chemical shifts ( $\Delta\delta = 7.2$  Hz), a fluxional process involving isomer interconversion or exchange of ligand environments can be ruled out. Thus the simplicity of the  $^1\text{H}$  NMR spectrum of **3b** appears to result from a classic case of accidental degeneracies.

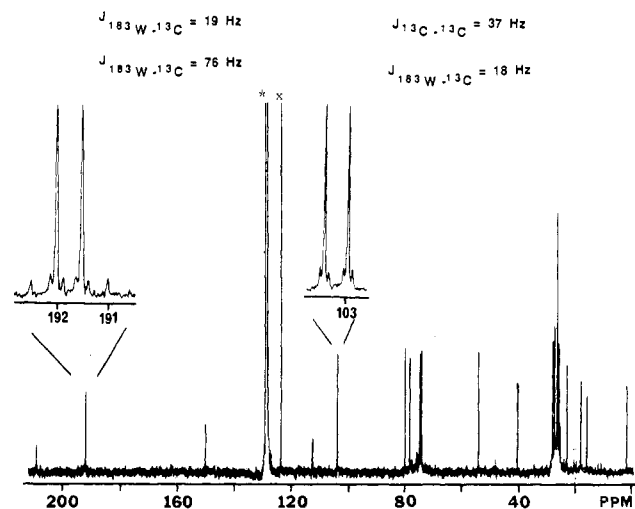
$W_4(\mu\text{-CEt})_2(\mu\text{-MeCCMe})_2(\eta^2\text{-MeCCMe})_2(\text{O-}i\text{-Pr})_6$ . Variable-temperature NMR studies of (4)(Et) are indicative of a dimer-tetramer equilibrium (eq 4) that is rapid



on the NMR time scale at room temperature but slow at temperatures below -40 °C. The room-temperature  $^1\text{H}$  NMR spectrum of (4)(Et) represents the weighted, time-averaged, signals of (4)(Et) and (4')(Et) although the position of the equilibrium is not known. The data are consistent with the solid-state structure of (4)(Et) described in the previous section except that the  $\eta^2\text{-MeCCMe}$  ligands are rapidly rotating on the NMR time scale pro-



**Figure 5.** The  $^1\text{H}$  NMR spectrum of  $W_2[\text{MeC}(\text{Et})\text{C}(\text{H})\text{C}(\text{H})](\mu\text{-C}_2\text{Me}_2)(\text{O-}i\text{-Pr})_4$  recorded in benzene- $d_6$  at 22 °C and 360 MHz. The resonances denoted by an asterisk arise from a subsequent rearrangement product.



**Figure 6.** The natural-abundance  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $W_2[\text{MeC}(\text{Et})\text{C}(\text{H})\text{C}(\text{H})](\mu\text{-C}_2\text{Me}_2)(\text{O-}i\text{-Pr})_4$  recorded in benzene- $d_6$  at 22 °C and 75 MHz. The spectrum was recorded in the presence of a 5-fold excess of  $\text{C}_2\text{H}_4$ . The insets are the resonances observed by using  $^*\text{C}_2\text{H}_4$  (where  $^*\text{C} = 99$  mol %  $^{13}\text{C}$ ) in eq 3 under otherwise identical experimental and spectroscopic conditions. The resonances denoted by the asterisk and  $\times$  represent  $\text{C}_6\text{D}_6$  and  $\text{C}_2\text{H}_4$ , respectively.

ducing a single, time-averaged methyl resonance. Attempts to monitor this process at low temperatures were hindered by unrelated resonance broadening caused by slowing the rate of (4)(Et)  $\rightleftharpoons$  (4')(Et) exchange (eq 4), and the barrier to alkyne rotation was not determined.

$W_2[\text{MeC}(\text{Et})\text{C}(\text{H})\text{C}(\text{H})](\mu\text{-MeCCMe})(\text{O-}i\text{-Pr})_4$ . The  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **5** are shown in Figures 5 and 6, respectively. The following observations aid in the structural characterization of the compound.

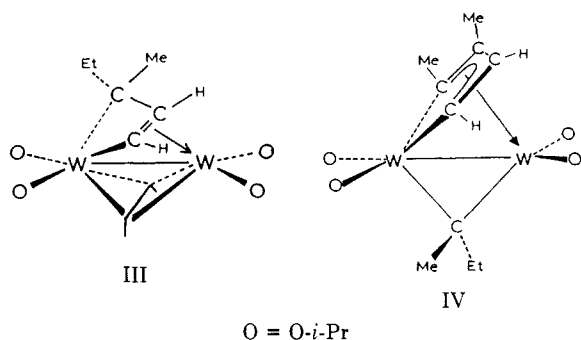
(A) The NMR spectra reveal four inequivalent *O-i-Pr* ligands each having diastereotopic methyl groups. This is best illustrated in the  $^1\text{H}$  NMR spectrum (Figure 5) by the four *O-i-Pr* methine septets between 4.0 and 5.0 ppm and eight *O-i-Pr* methyl doublets between 1.0 and 1.6 ppm. These data indicate that the compound has no molecular symmetry.

(B) Three equal intensity methyl singlets are observed between 2.0 and 3.0 ppm in the  $^1\text{H}$  NMR spectrum due to the two inequivalent  $\mu\text{-C}_2\text{Me}_2$  methyl groups and the lone metallacycle methyl.

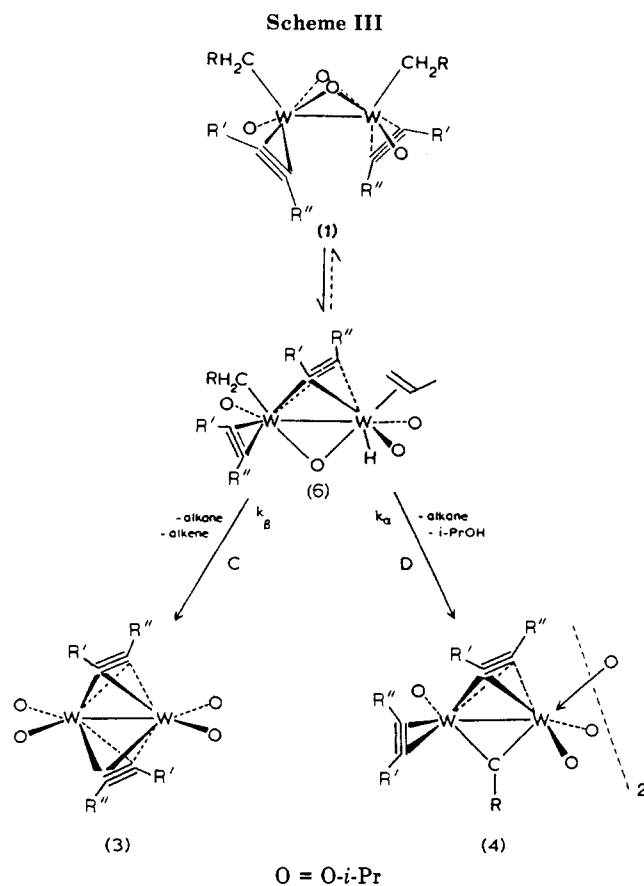
(C) The Et group gives rise to a typical ABX<sub>3</sub> spin pattern as evidenced by the ab multiplets in the <sup>1</sup>H NMR spectrum, marked a and b in Figure 5, and the ethyl triplet at 1.8 ppm. Selective decoupling experiments show that these resonances are mutually coupled. When the compound is prepared by using H<sub>2</sub>C=CD<sub>2</sub>, the methylene hydrogens become 50% deuteriated as evidenced by the appearance of a broad doublet at 1.8 ppm instead of the triplet for non-deuteriated **5**. These data reliably establish that the Et methylene hydrogens originate from the added ethylene in eq 3 and, moreover, that the Et moiety is derived from a double hydrogenation of one acetylenic carbon of **3a** [(i.e. MeC≡CMe + 2 H<sup>•</sup> → MeC-CH<sub>2</sub>Me). When <sup>13</sup>C<sub>2</sub>H<sub>4</sub> (where <sup>13</sup>C = 99 mol % <sup>13</sup>C) is used in eq 3, the Et resonances are unaffected.

(D) When <sup>13</sup>C<sub>2</sub>H<sub>4</sub> is employed in reaction 3, the resulting <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (insets of Figure 6) shows two mutually coupled doublets at 191.8 and 103.2 ppm with <sup>1</sup>J<sub><sup>13</sup>C-<sup>13</sup>C = 37 Hz. The signal at 191.8 ppm had two sets of <sup>183</sup>W satellites (<sup>1</sup>J<sub><sup>183</sup>W-<sup>13</sup>C = 76 and 19 Hz, each having 14% total satellite intensity) indicating that the corresponding carbon atom is bridging two inequivalent tungsten atoms. The resonance at 103.2 ppm has one set of <sup>183</sup>W satellites (<sup>1</sup>J<sub><sup>183</sup>W-<sup>13</sup>C = 18 Hz, 14% total satellite intensity). The proton-coupled <sup>13</sup>C NMR spectrum of the <sup>13</sup>C-enriched sample reveals doublets of doublets for the two resonances just described with <sup>1</sup>J<sub><sup>13</sup>C-<sup>1</sup>H = 142 and 170 Hz for the 191.8 and 103.2 ppm resonances, respectively. These data show that only *one* hydrogen atom remains on the ethylene-derived carbons of **5** consistent with the 1,2-dihydride shift described in C. The two remaining "ethylenic" hydrogens appear at 4.98 and 4.76 ppm as mutually coupled doublets of an AB quartet (<sup>1</sup>J<sub>H-H</sub> = 7 Hz) in the <sup>1</sup>H NMR spectrum. When compound **5** is prepared from <sup>13</sup>C<sub>2</sub>H<sub>4</sub>, these doublets split into doublets of doublets with <sup>13</sup>C-H coupling constants of ~138 and ~168 Hz for the 4.98 and 4.76 ppm resonances, respectively.</sub></sub></sub></sub>

Two viable structures for compound **5** are shown by III and IV. Both structures are consistent with the NMR



data just described. However, numerous compounds containing bridged MC<sub>4</sub> metallacyclopentadiene rings similar to that shown in IV have been prepared and fully characterized,<sup>1,9</sup> but couplings between the ring carbons and two tungsten atoms have never been observed. The <sup>13</sup>C resonance at 191.5 ppm clearly shows two types of <sup>183</sup>W couplings. Moreover, both of the "ethylenic" doublets show couplings to <sup>183</sup>W of ca. 7 Hz in the <sup>1</sup>H NMR spectrum which is inconsistent with the spectroscopic properties of similar MC<sub>4</sub> metallacycles previously studied.<sup>1,3b,9</sup> Thus, the data are most consistent with structure III.



### Mechanistic Considerations

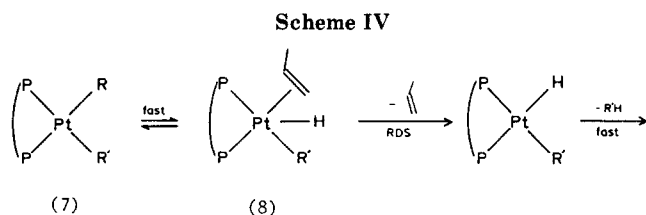
A proposed mechanism for thermal conversions of **1** to mixtures of **3** and **4** is shown in Scheme III. The reaction scheme involves an initial  $\beta$ -hydrogen activation step (possibly reversible) to produce a coordinated olefin complex of the type depicted by **6** in Scheme III. This step is then followed by either dissociation of alkene leading to the formation of **3** or by a complex  $\alpha$ -C-H activation pathway leading to the formation of **4**. Thus, the course of reaction is determined by the relative magnitudes of  $k_\alpha$  versus  $k_\beta$ . The mechanism of hydrogen transfer is not known and is not implied in Scheme III.

Several experimental observations are consistent with the formation of the proposed olefin intermediate **6**.

(1) The course of  $\alpha$ -hydrogen abstraction is altered by the presence of  $\beta$ -hydrogen atoms. When the alkyl ligands of **1a** do not contain  $\beta$ -hydrogens, subsequent thermolysis under identical reaction conditions leads to  $\alpha$ -C-H abstraction that is accompanied by an alkyne coupling process,<sup>1</sup> outlined in Scheme I. If  $\beta$ -hydrogen activation was not involved in the present  $\alpha$ -C-H abstraction process (path D, Scheme II), then the alkyne-coupled, alkylidyne complexes **2**, shown in Scheme I, should be the products of path D.

(2) The relative amounts of **3** and **4** produced in Scheme II are not a function of the number of  $\beta$ -hydrogen atoms present in **1a**. The *i*-Bu derivative of **1a**, which has only one  $\beta$ -hydrogen per alkyl ligand, reacts exclusively by  $\beta$ -hydrogen elimination whereas the Et complex, which has three  $\beta$ -hydrogens per alkyl ligand, favors  $\alpha$ -hydrogen elimination. Furthermore, the rate of thermolysis of the *i*-Bu complex is faster than that of the *n*-Pr or Et complexes. These data lead us to suggest that the rate and course of reaction in Scheme III is governed by the relative stabilities of the olefin complexes **6**. The larger, more sterically demanding olefins, such as isobutene, readily

(9) (a) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806. (b) Chisholm, M. H.; Conroy, B. K.; Huffman, J. C. *Organometallics* **1986**, *5*, 2384.



dissociate from 6 which leads (irreversibly) to the formation of 3. For smaller olefins, such as ethylene and propene, alkene elimination is not as rapid and  $\alpha$ -hydrogen abstraction becomes competitive (path D).

(3) Yamamoto and co-workers have proposed<sup>10</sup> that rate-determining alkene eliminations from olefin hydride intermediates direct the course of  $\beta$ -hydrogen elimination in nondissociative thermal decompositions of (LL)Pt(R)(R') compounds. They demonstrated that rapid and reversible  $\beta$ -hydrogen elimination preceded the rate-limiting olefin elimination, which in turn was followed by a rapid elimination of alkane. Scheme IV summarizes their conclusions. These studies showed<sup>10</sup> that the more sterically demanding alkyl ligand was eliminated as alkene and the less sterically demanding alkyl ligand as alkane for the asymmetric compounds 7 ( $R' \neq R$ ). The number of available  $\beta$ -hydrogens did not seem to effect the alkyl group disproportionation. Furthermore, the rates of thermolysis decreased as the steric demands of the alkyl ligands decreased such that  $k_{Bu} > k_{Pr} > k_{Et}$ . Yamamoto<sup>10</sup> proposed that the relative stability of the intermediate olefin complex 8 governed the rate of reaction and alkene/alkane distribution in the organic products. Apparently, the more sterically demanding olefin will preferentially dissociate in the rate-determining step when a choice exists. Moreover, the rates of reaction for the symmetrical complexes (compound 7 where  $R' = R$ ) increase with the ease of olefin dissociation which follows the order butene > propene > ethylene.

The findings of Yamamoto appear to parallel the results of the present study. A similar rate-limiting alkene dissociation could be operative in Scheme III. However, at present there is little direct experimental evidence to support such a proposal. It is interesting to note that the ethyl derivative of 1a yields 3a and ethylene as two of the reaction products. Yet, 3a reacts with ethylene to form 5 according to eq 3 which most likely proceeds via an initial ethylene adduct. This suggests that alkene elimination is not the final step in path C of Scheme III and is consistent with alkene elimination occurring prior to alkane elimination.

Selective deuteration of the  $\alpha$ -,  $\beta$ -, or  $\gamma$ -hydrogens of the alkyl ligands in 1a would provide valuable information concerning the operative processes in Scheme III. Unfortunately, H/D scrambling occurs during the synthesis of the precursors<sup>11</sup> to 1a, and these experiments are not currently possible. Mixed-alkyl complexes similar to those used by Yamamoto (Scheme IV)<sup>10</sup> are also not synthetically accessible at the present time.

### Conclusions

Compounds of formula W<sub>2</sub>(CH<sub>2</sub>R)<sub>2</sub>(MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> (1a) (where R = Me, Et, or *i*-Pr) react thermally in hydrocarbon solvents by competitive  $\alpha$ - and  $\beta$ -hydrogen activation pathways to produce new compounds of formula W<sub>4</sub>( $\mu$ -CR)<sub>2</sub>( $\mu$ -MeCCMe)<sub>2</sub>( $\eta^2$ -MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>6</sub> (4) and

W<sub>2</sub>( $\mu$ -MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> (3a). The formation of 4 is accompanied by the elimination of *i*-PrOH and RCH<sub>3</sub> whereas 3 is formed from the elimination of alkane and alkene. The product distributions and relative rates of reaction involving the thermolyses of 1a are alkyl group dependent. Compound (1a)(*i*-Pr) reacts the fastest ( $t_{1/2} \approx 18$  h at 25 °C) and produces 3a exclusively whereas compounds (1a)(R = Me or Et) react slower ( $t_{1/2} \approx 40$  h at 25 °C) and give 2:1 mixtures of (4)(R = Me or Et) and 3a. The number of  $\beta$ -hydrogen atoms present on the alkyl ligands of 1a apparently do not effect the course of reactions. These data suggest that an olefin intermediate, formed from an initial  $\beta$ -hydrogen elimination, is involved in both reaction pathways. The rate and course of reaction appear to correlate with the relative stability of the olefin intermediate with the more sterically demanding olefins dissociating faster (faster reaction rates) and producing more of the  $\beta$ -hydrogen-elimination product 3.

The formation of compound 4 in Scheme II represents a rare example of a W-O bond cleavage facilitating tungsten-carbon multiple bond formation. The structure of 4 comprises an unusual W<sub>4</sub> chain with a grossly distorted bridging alkyne ligand. The inherent stability of these and other  $\mu$ -CR functionalities in high oxidation state W<sub>2</sub> complexes is manifested by their chemical inertness and their resistance to combustion<sup>1</sup> (tungsten carbide formation during elemental analysis).

The preparations of 3a-c represent high-yield rational syntheses of a new class of compounds having the formula W<sub>2</sub>( $\mu$ -R'CCR'')<sub>2</sub>(alkoxide)<sub>4</sub>. The first member of this series W<sub>2</sub>( $\mu$ -PhCCPh)<sub>2</sub>(O-*t*-Bu)<sub>4</sub> was prepared by Cotton et al.<sup>4</sup> in very low yield and isolated by crystal separation from a reaction between W<sub>2</sub>(O-*t*-Bu)<sub>6</sub> and PhC≡CPh at 60 °C. Compound 3b exists as equal mixtures of syn and anti isomers in hydrocarbon solutions, but isomer interconversion is slow (undetectable) on the NMR time scale. The synthesis of compounds 3 represents a formal reductive elimination of alkane and alkene though the formation of two alkyne bridges during the reaction is clearly oxidative with respect to the W<sub>2</sub> center. Therefore, the net reaction results in little (if any) change in the oxidation state of the W<sub>2</sub> center as evidenced by the similarities of the W-W bond distances in 3a (W-W = 2.61 (1) Å) and compounds 1a (W-W = 2.66 (2) Å (average)).

Compound 3a reacts with 1 equiv of ethylene to form a metallacyclic compound formulated as W<sub>2</sub>[MeC(Et)C(H)C(H)]( $\mu$ -MeCCMe)(O-*i*-Pr)<sub>4</sub> (5). Compound 5 results from a coupling of ethylene and acetylene functions and an ethylene-to-acetylene double-hydrogen transfer. The detailed nature of the new compound 5 remains to be established by a single-crystal X-ray diffraction study.

### Experimental Section

**General Procedures.** Standard Schlenk procedures and Vacuum Atmospheres Co. Dri-Lab Systems were used for all syntheses and sample manipulations. Solvents were distilled under N<sub>2</sub> from Na/benzophenone and stored in solvent bottles over 4-Å molecular sieves.

The <sup>1</sup>H NMR spectra were recorded in dry and deoxygenated benzene-*d*<sub>6</sub> or toluene-*d*<sub>8</sub> by using either a Varian XL-300 (300 MHz) or a Nicolet NT-360 (360 MHz) spectrometer. The data were calibrated against the residual protio impurities set at 7.15 ppm (benzene-*d*<sub>6</sub>) or 2.09 ppm (toluene-*d*<sub>8</sub>). The <sup>13</sup>C NMR spectra were recorded on a Varian XL-300 spectrometer at 75 MHz. The data were calibrated against the central carbon resonances set at 128.0 ppm (benzene-*d*<sub>6</sub>) or 20.4 ppm (toluene-*d*<sub>8</sub>). The IR spectra were obtained as KBr pellets. The data were calibrated against the polystyrene absorbance at 1601 cm<sup>-1</sup>.

Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, and

(10) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* 1982, 1, 1528.

(11) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Tatz, R. J. *Organometallics* 1986, 5, 1599.



Schwarzkopf Microanalytical Laboratory, Woodside, NY.

**Chemicals.** Compounds 1a–c were prepared by published methods.<sup>8</sup> Isobutane, isobutene, propane, propene, and ethylene were purchased from the Matheson Co. <sup>13</sup>C<sub>2</sub>H<sub>4</sub> (99 mol % <sup>13</sup>C) and D<sub>2</sub>C=CH<sub>2</sub> were purchased from Cambridge Isotopes and MSD Isotopes, respectively.

**W<sub>2</sub>(μ-MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>4</sub>.** In a Schlenk reaction vessel, W<sub>2</sub>(*i*-Bu)<sub>2</sub>(MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> (309 mg, 0.47 mmol) was dissolved in hexane (10 mL) at room temperature producing an orange solution. The mixture was stirred at room temperature for 3 days during which time it slowly turned to a green-brown color. After 3 days, the solution was evaporated to dryness under dynamic vacuum and the resulting residue extracted into pentane (6 mL). The solution was then concentrated to ca. 3 mL and cooled to -20 °C. After 48 h, long dark brown rectangular prisms were harvested by removing the supernatant liquid via cannula and drying in vacuo (crystalline yield 183 mg, 67%).

IR data (KBr pellet, cm<sup>-1</sup>): 2960 (vs), 2905 (s), 2890 (sh), 2865 (m), 1455 (m), 1440 (m, br), 1365 (m), 1355 (m), 1320 (m), 1155 (m), 1110 (vs), 990 (vs), 980 (vs), 845 (s), 615 (m), 605 (m), 580 (m), 480 (w), 450 (w).

Anal. Calcd for W<sub>2</sub>O<sub>4</sub>C<sub>26</sub>H<sub>54</sub>: C, 33.73; H, 5.62. Found: C, 33.53; H, 5.48.

**W<sub>2</sub>(μ-MeCCEt)<sub>2</sub>(O-*i*-Pr)<sub>4</sub>.** In a Schlenk reaction vessel, W<sub>2</sub>(*i*-Bu)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> (400 mg, 0.61 mmol) was dissolved in hexane (12 mL) at room temperature. *i*-PrOH (4.1 equiv, 2.50 mmol, 190 μL) was added to the mixture by using a microliter syringe. The solution was stirred at room temperature for 1 h during which time it was degassed under reduced pressure on three separate occasions to remove the HNMe<sub>2</sub> liberated during the reaction. The orange-yellow solution slowly turned darker orange over the 1-h period. The reaction mixture was then cooled to 0 °C and MeC≡CEt (2.1 equiv, 1.28 mmol, 122 μL) added by using a microliter syringe causing a color change from orange to dirty green and then to burnt orange after ~8 s. The solution was stirred at 0 °C for 5 min, then warmed to room temperature, and stirred for an additional 7 days. The color of the reaction mixture slowly turned from orange to yellow-green after ca. 3 days at room temperature. The solution was then evaporated to dryness under dynamic vacuum and the resulting solid, dark green residue extracted into pentane (ca. 2 mL) and cooled to -20 °C. After 4 days, dark crystals were harvested by removing the supernatant liquid via cannula and drying in vacuo (crystalline yield ca. 50%).

IR data (KBr pellet, cm<sup>-1</sup>): 2985 (vs), 2920 (s), 2885 (m), 1455 (m), 1445 (m), 1365 (m), 1345 (m), 1320 (m), 1305 (m), 1160 (m), 1105 (vs), 975 (vs, br), 845 (m), 800 (m, br), 600 (m), 580 (sh), 450 (w).

**W<sub>2</sub>(μ-EtCCEt)<sub>2</sub>(O-*i*-Pr)<sub>4</sub>.** A procedure identical with that described for W<sub>2</sub>(μ-MeCCEt)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> was followed except using EtC≡CEt. W<sub>2</sub>(*i*-Bu)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> (507 mg, 0.77 mmol) produced a green microcrystalline powder (yield ca. 50%).

**W<sub>4</sub>(μ-CEt)<sub>2</sub>(μ-MeCCMe)<sub>2</sub>(η<sup>2</sup>-MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>6</sub>.** In a Schlenk reaction vessel, W<sub>2</sub>(*n*-Pr)<sub>2</sub>(MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> (350 mg, 0.56 mmol) was dissolved in hexane (10 mL) and stirred for 7 days at room temperature. The solution slowly turned from orange to brown during the reaction period. After 7 days, the mixture was evaporated to dryness under dynamic vacuum and the residue extracted into pentane (2 mL) and subsequently cooled to -20 °C. After 3 days, a crystalline material was isolated by removing the supernatant liquid via cannula and drying in vacuo. This isolated material (ca. 120 mg) was composed of long, dark rectangular prisms and pale orange-yellow cubes. The mixture was redissolved in Et<sub>2</sub>O (ca. 2 mL) and cooled to -20 °C. After 24 h, large pale orange-yellow cubes were isolated by removing the supernatant liquid via cannula and drying in vacuo (crystalline yield 33 mg, 9%).

IR data (KBr pellet, cm<sup>-1</sup>): 2960 (s), 2922 (s), 2895 (s), 2330 (w), 1460 (m), 1438 (m), 1382 (m), 1371 (m), 1361 (m), 1321 (w), 1293 (vw), 1161 (m), 1112 (s), 990 (s), 971 (vs), 909 (w), 848 (w), 797 (w), 609 (m).

Anal. Calcd for W<sub>4</sub>C<sub>40</sub>O<sub>6</sub>H<sub>76</sub> (correct molecular formula with mol wt 1388.4): C, 34.60; H, 5.52. Found: C, 32.91; H, 5.34. Anal. Calcd for W<sub>4</sub>O<sub>6</sub>C<sub>39</sub>H<sub>76</sub> (but with mol wt 1388.4): C, 32.87; H, 5.52. As we have found for other W<sub>2</sub>(μ-CR)-containing compounds, the analyses upon combustion suggest the retention of the alkylidyne carbon as W<sub>2</sub>C.<sup>1</sup>

**W<sub>4</sub>(μ-CMe)<sub>2</sub>(μ-MeCCMe)<sub>2</sub>(η<sup>2</sup>-MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>6</sub>.** The synthesis of this compound was only accomplished by the room-temperature thermolysis of W<sub>2</sub>(Et)<sub>2</sub>(MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> in benzene-*d*<sub>6</sub> in a 5-mm Pyrex NMR tube fitted with a septum cap. The compound was never isolated. The identity of the compound was determined by <sup>1</sup>H NMR spectroscopy by the distinctive 2:1:1 alkyne methyl resonances and the μ-CMe methyl resonance at 4.81 ppm. The general features of the <sup>1</sup>H NMR spectrum were virtually identical with those of (4)(Et).

**W<sub>2</sub>[MeC(Et)C(H)C(H)](μ-MeCCMe)(O-*i*-Pr)<sub>4</sub>.** In a 100-mL Schlenk reaction vessel, W<sub>2</sub>(μ-MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> (300 mg, 42 mmol) was dissolved in hexane (15 mL) at room temperature producing a yellow-green homogeneous solution. The reaction flask was then subjected to dynamic vacuum and backfilled with C<sub>2</sub>H<sub>4</sub> three times to introduce a large excess of ethylene. The mixture was stirred for 36 h under an ethylene atmosphere at room temperature during which time the color changed from yellow-green to bright purple. The solution was then evaporated to dryness under dynamic vacuum and the resulting dark solid extracted into pentane (~1 mL) and cooled to -78 °C. After 3 days, a dark precipitate (ca. 30 mg) was isolated by removing the supernatant liquid via cannula and drying in vacuo. The solid turned into an oily semisolid before it could be removed from the flask in the drybox. Attempted recrystallizations from Et<sub>2</sub>O and dimethoxyethane were unsuccessful. Elemental analyses were not attempted since the purity and authenticity of this compound are still under investigation.

**NMR Tube Reactions and Half-Life Measurements.** The approximate half-life values were determined by monitoring the thermolyses of compounds 1a by <sup>1</sup>H NMR spectroscopy in sealed NMR tubes except where noted. A typical experiment involved ca. 15 mg of 1a dissolved in benzene-*d*<sub>6</sub> in a Pyrex NMR tube with a glass extension. The solution was then frozen to -198 °C the tube evacuated and then sealed with a torch. The rates of reaction were estimated by comparing the normalized C<sub>2</sub>R<sub>2</sub><sup>1</sup>H NMR resonances of reactants and products as a function of time. The reactions of W<sub>2</sub>(μ-MeCCMe)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> with ethylene were conducted in the same manner, except ca. 5 equiv of the appropriate ethylene (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>, \*C<sub>2</sub>H<sub>4</sub>) were condensed into the NMR tube prior to sealing with a calibrated vacuum manifold.

**Identification of Organic Byproducts.** The isobutane and isobutene liberated in the thermolyses of compounds (1)(*i*-Pr) were unambiguously identified in sealed NMR tube reactions (see above) by comparison of the <sup>1</sup>H NMR resonances in the thermolyzed solutions to those of authentic samples in the same solvent (C<sub>6</sub>D<sub>6</sub>). The two organic compounds were present in a ca. 1:1 molar ratio, but no attempt was made to rigorously quantify the yields.

Propane, propene, and *i*-PrOH were identified in the volatile components of a thermolyzed C<sub>6</sub>D<sub>6</sub> solution of (1a)(Et) by comparison of the NMR resonances with those of authentic samples in the same solvent (C<sub>6</sub>D<sub>6</sub>). The volatiles and C<sub>6</sub>D<sub>6</sub> solvent were vacuum transferred into an NMR tube for spectral analysis after complete thermolysis. The absolute yields of these products were not rigorously measured.

**Crystallographic Studies.** General operating procedures and listings of programs have been previously given.<sup>12</sup> A summary of crystallographic data is given in Table V.

**W<sub>4</sub>(μ-CEt)<sub>2</sub>(MeCCMe)<sub>4</sub>(O-*i*-Pr)<sub>6</sub>.** A suitable crystal was located and transferred to the goniostat by using 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 *P*<sub>2</sub><sub>1</sub>/*a* (alternate setting of *P*<sub>2</sub><sub>1</sub>/*c*, No. 14). Subsequent solution and refinement of the structure confirmed this choice. Data were collected in the usual manner by using a continuous  $\theta$ - $2\theta$  scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated  $\sigma$ s in the usual manner.

The structure was solved by using a combination of direct methods (MULTAN78) and Fourier techniques. All nonhydrogen atoms were allowed to vary anisotropically during refinement.

(12) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* 1984, 23, 1021.

Many of the hydrogen atom positions were visible in a difference Fourier phased on the non-hydrogen atoms. Positions were calculated for all hydrogens assuming idealized geometry (with  $d(\text{C-H}) = 0.95 \text{ \AA}$ ), and they were included as fixed atom contributors in the final cycles. A  $\psi$  scan indicated there was a significant absorption effect, and the data were thus corrected before the final cycles of refinement. A final difference Fourier was essentially featureless, with the largest peak being  $1.3 \text{ e/\AA}^3$  at the location of  $W(1)$ .

$W_2(\mu\text{-C}_2\text{Me})_2(\text{O-}i\text{-Pr})_4$ . Techniques identical with the above were used for handling and characterization of the crystal used and led to the assignment of the orthorhombic space group  $Pnam$  (alternate setting of  $Pnma$ , No. 62). An analytical absorption correction was applied to the data. Direct methods and Fourier techniques were again utilized, and hydrogen atoms were visible in a difference Fourier synthesis. For the final refinement, all non-hydrogen atoms were varied anisotropically, and hydrogen atoms were included as fixed atom contributors.

A final difference Fourier was featureless, the largest peak being  $0.62 \text{ e/\AA}^3$ .

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**Registry No.** 1a (*i*-Pr), 110456-68-3; 1a (Et), 110433-53-9; 1a (Me), 116563-29-2; 3a, 110456-67-2; *syn*-3b, 116784-33-9; *anti*-3b, 116839-39-5; 3c, 116784-34-0; 4 (Et), 110433-54-0; 4 (Me), 116840-29-0; 5, 116784-35-1;  $W_2(i\text{-Bu})_2(\text{NMe}_2)_4$ , 101860-16-6;  $\text{EtC}\equiv\text{CEt}$ , 928-49-4;  $\text{MeC}\equiv\text{CMe}$ , 627-21-4; ethylene, 74-85-1.

**Supplementary Material Available:** For  $W_4(\text{CET})_2(\text{MeCCMe})_4(\text{O-}i\text{-Pr})_6$  and  $W_2(\mu\text{-C}_2\text{Me})_2(\text{O-}i\text{-Pr})_4$ , tables of anisotropic thermal parameters and complete listings of bond distances and angles (7 pages); listings of  $F_o$  and  $F_c$  values (11 pages). Ordering information is given on any current masthead page.

## Metal Alkoxides: Models for Metal Oxides. 14.<sup>1</sup> Carbonylation of an Ethylidyne-Capped Tritungsten Alkoxide Cluster To Form $W_3(\mu\text{-CMe})(\text{O-}i\text{-Pr})_9(\text{CO})_2$ : Preparation, Properties, and Structure

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We have investigated the reactions between  $W_3(\mu_3\text{-CMe})(\mu\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$  and each of the alkynes ( $\text{MeC}\equiv\text{CMe}$ ,  $\text{PhC}\equiv\text{CH}$ ,  $\text{HC}\equiv\text{CH}$ ,  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ ), ethylene, molecular hydrogen, and carbon monoxide (separately) at 1 atm and room temperature. The tritungsten ethylidyne capped cluster failed to show reactivity toward ethylene,  $\text{H}_2$ , and the alkynes  $\text{MeC}\equiv\text{CMe}$  and  $\text{PhC}\equiv\text{CH}$ . With  $\text{HC}\equiv\text{CH}$  and  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  polymerization of the alkyne occurred, but no detectable reaction with the tritungsten cluster was observed. However, carbon monoxide (2 equiv) was rapidly taken up to give, upon crystallization, black crystals of a compound of formula  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9(\text{CO})_2$ . In the solid state an unusual structure is found involving a chain, or open triangle of W atoms ( $W\text{-}W\text{-}W = 150^\circ$ ), that may be best viewed as a  $d^1\text{-}d^1$  alkylidyne-bridged moiety linked by three *O-}i\text{-Pr} ligands to a distorted octahedral  $d^4$  *cis*- $W^{II}(\text{CO})_2$  center:  $(i\text{-PrO})_3W(\mu\text{-CMe})(\mu\text{-O-}i\text{-Pr})W(\text{O-}i\text{-Pr})(\mu\text{-O-}i\text{-Pr})_3W(\text{O-}i\text{-Pr})(\text{CO})_2$ . The  $W\text{-}W$  distance supported by the  $\mu\text{-CMe}$  and  $\mu\text{-O-}i\text{-Pr}$  ligands is  $2.658(1) \text{ \AA}$  comparable to that of the  $d^1\text{-}d^1$  compound  $(i\text{-PrO})_2W(\mu\text{-CSiMe})_2W(\text{O-}i\text{-Pr})_2$ . The other  $W\text{-}W$  distance is typical of a nonbonding distance. There is NMR evidence that the essential features of the solid-state structure are maintained in solution. NMR data for the  $^{13}\text{C}$ -labeled compounds  $W_3(*\text{CMe})(\text{O-}i\text{-Pr})_9(\text{CO})_2$  and  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9(*\text{CO})_2$  reveal  $\delta$  313 ( $J_{183\text{W-}^{13}\text{C}} = 150 \text{ Hz}$ ) (24% intensity) for  $W_2(\mu\text{-}^*\text{CMe})$  and  $\delta$  267 and 264 with  $J_{183\text{W-}^{13}\text{C}} = \text{ca. } 190 \text{ Hz}$  (15% intensity) and  $J_{13\text{C-}^{13}\text{C}} = 12.2 \text{ Hz}$ . Crystal data for  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9(\text{CO})_2$  at  $-140^\circ\text{C}$ :  $\alpha = 11.673(4) \text{ \AA}$ ,  $b = 18.640(8) \text{ \AA}$ ,  $c = 10.285(3) \text{ \AA}$ ,  $\alpha = 102.38(2)^\circ$ ,  $\beta = 103.04(2)^\circ$ ,  $\gamma = 72.43(2)^\circ$ ,  $Z = 2$ ,  $d_{\text{calcd}} = 1.887 \text{ g cm}^{-3}$ , and space group  $P\bar{1}$ .*

### Introduction

Ethylidyne ligands have been known to be present on the surface of various metals for a number of years now, and their formation can be monitored starting from a clean metal surface and ethylene.<sup>2,3</sup> Alkylidyne ligands are also well-known in carbonyl cluster chemistry, and the alkylidyne capped tricobalt nonacarbonyl compounds represent some of the earliest known and best studied examples of this class.<sup>4,5</sup> Our discovery of  $W_3(\mu_3\text{-CMe})(\text{O-}i\text{-Pr})_9$ <sup>6</sup>

and related  $W_3(\mu\text{-CR})(\text{OR}')_9$  compounds<sup>7</sup> provided the first examples of  $\mu_3$ -alkylidyne ligands supported entirely by oxygen donor ligands with coordinative unsaturation still present at the metal centers.<sup>8</sup> The square-based pyram-

(1) Chisholm, M. H.; Conroy, B. K.; Clark, D. L.; Huffman, J. C. *Polyhedron Symposium-in-Print, Reactivity of Bridging Hydrocarbyl Ligands*; 1988; Vol. 7, in press.

(2) E.g. on Pt surfaces, see: Somorjai, G. A. In *Chemistry in Two Dimensions: Surfaces*; Cornell University: Ithaca, NY, 1981; p 278.

(3) For a  $\mu$ -vinylidene to  $\mu$ -ethylidyne conversion see: Hills, M. M.; Parmeter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* 1987, 109, 597.

(4) Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* 1973, 6, 73.

(5) Seyferth, D. *Adv. Organomet. Chem.* 1976, 14, 97.

(6) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* 1984, 23, 3683. Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* 1985, 107, 1234.

(7) Chisholm, M. H.; Conroy, B. K.; Eichhorn, B. W.; Folting, K.; Hoffman, D. M.; Huffman, J. C.; Marchant, N. A. *Polyhedron* 1987, 6, 783.

(8) Alkylidyne-capped compounds of formula  $[\text{Mo}_3(\mu_3\text{-X})(\mu_3\text{-Y})(\text{OAc})_6(\text{H}_2\text{O})_3](\text{anion})\cdot\gamma\text{H}_2\text{O}$  have previously been obtained as products in the reactions between  $\text{Mo}(\text{CO})_6$  and carboxylic acids,  $\text{RCOOH}$ , where  $X, Y = \text{O}$  and/or alkylidyne: Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* 1981, 103, 234.