Organometallics 1988, 7, 416–422

BHT groups are coordinated to each magnesium atom,[25] but the ionic radius of magnesium is 0.2 Å larger than aluminum. In the aluminum system, disproportionation of two Al(R)BHT_2 or H-BHT attack on Al(R)BHT_2 to give $AlBHT_3$ would require not three, but four-coordination with three BHT groups on a single center. Clearly, this is not a favored structure, even as a transition state along a reaction coordinate.

In the activation of heterogeneous Ziegler–Natta catalysts, the observed steric crowding is going to play a major role. The BHT-substituted aluminum alkyl will be restricted in its approach to the $TiCl_4$ or $TiCl_3$ surface species so only the most accessible will be able to react. The diminished reducing power of the BHT-substituted aluminum alkyls, reflected in their reaction with the ester Lewis bases, is also going to be a factor in their reactivity with titanium species on the catalyst. The catalyst is less likely to be overreduced to inactive $TiCl_2$ species.[31]

Conclusions about increased steric constraints and diminished reducing power are complicated by the observed disproportionation of the mono-BHT species. The less sterically hindered and more strongly reducing AlR_3 species will always be present unless 2 equiv of BHT are used. The observation that only 1 equiv of BHT is required in the aluminum alkyl activator indicates that the incorporation of H-BHT into the titanium center during the preparation of $MgCl_2$-supported catalysts apparently protects the active Ti centers from unwanted reduction by the Al_2Et_6 formed by disproportionation. Thus, $AlEt_2BHT$ is still capable of eliciting the observed[17] nonclassical behavior despite the disproportionation reactions observed here.

Acknowledgment. We wish to acknowledge the skilled technical assistance of Martin A. Cushing, Jr., Lou Lardeer, Elwood Conaway, and Wayne King. Discussion of the thermodynamic measurements with Patricia L. Watson were particularly helpful.

Registry No. H-BHT, 128-37-0; $AlEtBHT_2$, 61986-88-7; $AlEt_2BHT$, 61986-89-8; $AlMeBHT_2$, 56252-55-2; Al(*i*-Bu)BHT_2, 56252-57-4; $AlEt_2BHT$(MT), 111847-26-8; MT, 25567-11-7; $AlEt_3o$, 97-93-8; *t*-BuOH, 75-65-0; $AlMe_3$, 75-24-1; Al(*i*-Bu)$_3$, 100-99-2.

Supplementary Material Available: Data used for determination of equilibrium constants, plots of equilibrium constants as a function of BHT to aluminum ratios, and listings of anisotropic thermal parameters, hydrogen atom parameters, and additional bond distances and angles (13 pages); tables of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Ditungsten μ-Carbene Complexes: X-ray Crystal Structure of $W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)C{=}CH(CH_2)_5CH_2]$

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Received June 22, 1987

A series of ditungsten complexes, $W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)C(R^1){=}CHR^2]$ (**3**), containing μ-η^1,η^3-allylidene ligands have been prepared in moderate to excellent yields from Fischer-type α,β-unsaturated tungsten carbene complexes, $(CO)_5W[C(OCH_3)C(R^1){=}CHR^2]$ (**1**) and $(CO)_5W{\cdot}THF$ (**2**). These complexes (**3**) were purified on silica gel at −20 to −30 °C followed by crystallization to produce, in most cases, dark red crystalline materials. All new compounds were characterized by elemental analyses and ^1H and ^{13}C NMR spectroscopy. When $W_2(CO)_9[\eta^1,\eta^3\text{-}C(OCH_3)C{=}CH(CH_2)_2CH_2]$ (**3d**) was treated with CO in C_6D_6 solution, it was cleanly converted to the cyclopentenyl Fischer–carbene complex $(CO)_5W[C(OCH_3)C{=}CH(CH_2)_2CH_2]$ (**1d**) and $W(CO)_6$. $W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)C{=}CH(CH_2)_5CH_2]$ (**3f**), which contains a cyclooctene ring as part of the μ-η^1,η^3-allylidene ligand, was further characterized by variable-temperature ^{13}C NMR spectroscopy and single-crystal X-ray diffraction methods. Complex **3f** crystallizes in the monoclinic space group $P2_1/c$ with (at −150 °C) $a = 9.832$ (4) Å, $b = 10.424$ (3) Å, $c = 21.120$ (6) Å, $\beta = 93.37$ (3)°, and $D_{calcd} = 2.37$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 3394 independent observed $[F_o \geq 5\sigma(F_o)]$ reflections led to a final conventional R value of 0.038.

Introduction

Over the past fifteen years there have been numerous reports concerning the preparation, reactivity, and structures of dimetallic complexes containing μ-η^1,η^3-allylidene ligands. Represented in Chart I are the four possible extreme bonding modes (A–D) for such complexes. For most of the reported complexes, M(1) and M(2) are the same, which include derivatives of molybdenum,[1] tungsten,[2]

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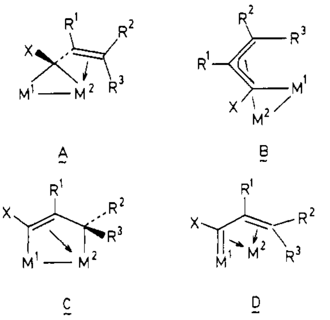
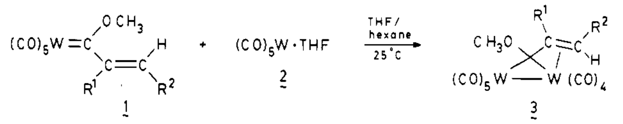
Chart I



rhenium,[3] iron,[4] ruthenium,[5] osmium,[6] cobalt,[7] and iridium.[8] Heterobimetallic complexes containing tungsten–cobalt (M(1) = Co, M(2) = W)[9a,b] as well as tungsten–iron (M(1) = W, M(2) = Fe)[9c] single bonds have also recently been reported. In addition to the above accounts, several homo- and heterodinuclear analogues containing μ-η^1,η^3-benzylidene ligands have been described in the literature.[9,10] Interest in studying the chemistry of these complexes A–D stems in part by their probable involvement in the C–H oxidative addition/reductive elimination of benzene[8b] and in the polymerization of alkynes.[2c,d,g,4d,5d] In this paper is described a straightforward synthetic procedure for the preparation of several ditungsten μ-carbene complexes (**3a–g**) starting from readily available α,β-unsaturated Fischer–carbene complexes. These new complexes have been characterized by analytical and spectroscopic techniques; moreover, the single-crystal X-ray structure of **3f** has also been determined.

Results and Discussion

Although there have been several ditungsten complexes containing μ-η^1,η^3-allylidene ligands reported in the literature,[2] there have been only two accounts of such complexes with X = OCH_3 (A–D).[2f,h] In these reports, a limited number of Fischer-type α,β-unsaturated tungsten carbene complexes (1) were treated with $(CO)_5W[CPh_2]$ in hexane at 40 °C to produce compounds having structure 3. Only one yield was reported for this reaction (49%), which was for 3 having R^1 = H and R^2 = CH_3. Furthermore, this same complex was obtained in 30% yield by irradiating a hexane solution of $W(CO)_6$ in the presence of $(CO)_5W[C(OC_2H_5)C(H){=}CHCH_3]$. We reasoned that $(CO)_5W{\cdot}THF$ (2), which is easily generated photochemically from $W(CO)_6$ in THF, could better serve as the source of the tungsten tetracarbonyl fragment in the synthesis of complexes **3**. Thus, stirring a solution of complexes **1** and **2** in hexane at 25 °C followed by removal of the solvent under vacuum and chromatography of the resulting residue produced complexes **3** in moderate to excellent yields (eq 1). These compounds were crystallized from hexane at 0 °C to afford dark red crystals that were slightly air-sensitive. It was also necessary to conduct the chromatographic purification of these compounds on silica gel at low temperatures (−20 to −30 °C) to avoid decomposition. For example, compound **3a** was obtained in 20% yield when chromatographed at 25 °C, whereas a 60% yield was obtained by chromatography at −30 °C. It is also interesting to note that upon reacting the *Z* isomer of **1c** with $(CO)_5W{\cdot}THF$ (**2**), none of the corresponding μ-carbene complex **3** was obtained. This may be in part due to an unfavorable steric interaction between the trans-methyl



	R^1	R^2	% Yield of 3
a	H	H	60
b	CH_3	H	68
c	CH_3	CH_3	21
d	—$(CH_2)_3$—		34
e	—$(CH_2)_4$—		21
f	—$(CH_2)_6$—		90
g	$SiMe_3$	H	78

(1)

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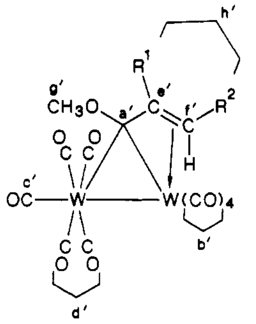
Table I. ^{13}C NMR Spectral Data (C_6D_6) for Complexes **3a–g**



3	a′	b′	c′	d′	e′	f′	g′	h′	R^1	R^2
a	232.56	205.10	201.24	196.14	80.92	56.15	59.00		H	H
b	231.13	206.12	199.64	195.77	107.61	63.45	63.92	22.67	CH_3	H
c	233.88	206.37	199.59	195.87	110.77	84.93	64.03	17.10, 15.69	CH_3	CH_3
d	230.63	205.98	200.16	195.94	118.52	89.12	63.54	34.42, 32.05, 21.15	$-(CH_2)_3-$	
e	233.73	206.53	199.33	195.76	113.30	90.74	63.87	29.65, 27.08, 21.45, 21.43	$-(CH_2)_4-$	
f	233.85	206.61	199.45	195.69	111.24	89.81	64.09	32.33, 30.91, 30.28, 29.65, 26.76, 26.13	$-(CH_2)_6-$	
g	235.78	206.75	199.41	195.51	102.11	63.61	63.38	26.06	$SiMe_3$	H

group attached to the terminal alkenyl carbon and the $W(CO)_4$ fragment which would result upon the formation of such a complex.

Compounds **3a–g** were characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopic techniques. Electron-impact mass spectral analyses of these compounds provided limited structural information. Parent molecular ions were not observed for most compounds, which is probably due to decomposition at the temperatures required for their volatilization. All compounds except **3g**, which is a liquid, decomposed (80–100 °C) without melting. The products from these decompositions have not been characterized, although tungsten carbonyl fragments were always observed in the mass spectra of **3a–g**.

The ^{1}H NMR spectra of complexes **3a–g** are consistent with their assigned structures. The chemical shifts of the vinylic protons in complexes **3a–g** all appear at substantially higher field relative to those in the starting carbene complexes **1a–g**. This upfield shift of the vinylic resonances upon coordination of an alkene to tungsten carbonyl fragments in an η^2-manner has previously been observed.[11] Furthermore, the chemical shifts of the methoxy resonances for **3a–g** are also upfield relative to those of **1a–g**. For example, the methoxy resonances for **3a** and **1a** appear at δ 3.10 and 3.72 (C_6D_6) in their respective ^{1}H NMR spectra. This upfield chemical shift for **3a**, as compared to **1a**, is probably due to a reduction in partial positive charge on the methoxy oxygen atom in **3a** relative to **1a**.

The ^{13}C NMR spectral data for complexes **3a–g** are summarized in Table I. In some cases (**3a,b,g**) the chemical shift assignments were made by using gated-decoupled ^{13}C NMR spectroscopy. For example, the gated-decoupled ^{13}C NMR spectrum of **3g** exhibited a quartet at δ 63.38 (J_{CH} = 144 Hz) for $C_{f'}$ and a triplet at δ 63.61 (J_{CH} = 162 Hz) for $C_{g'}$. The μ-carbene carbon resonances for complexes **3a–g** (ca. δ 230) appear at substantially higher field than their terminal carbene counterparts **1a–g** (ca. δ 320). The chemical shift values of the μ-carbene carbons ($C_a{}'$) are somewhat downfield of the 100–200 ppm range commonly observed for other dimetallic bridging carbene complexes.[12] These downfield shifts are probably due to the electronegative methoxy group directly bonded to the μ-carbene carbon. There have, however, been similar chemical shift values observed for other μ-carbene complexes containing methoxy groups.[13] The chemical shifts of the vinylic carbons ($C_{e'}$) and ($C_{f'}$) in complexes **3a–g** occur at considerably higher field than the uncoordinated vinylic carbons in the starting α,β-unsaturated carbene complexes **1a–g**. For example, in complex **3g**, the resonances for $C_{e'}$ and $C_{f'}$ occur at δ 102.11 and 63.61, respectively, whereas in **1g**, the resonances of the corresponding carbons could be found at δ 172.13 and 125.17 in C_6D_6 solution. The magnitudes of these upfield shifts are within the range observed in other complexes upon π-coordination of alkenes to transition-metal systems.[14] Furthermore, the chemical shift values of these vinylic carbons ($C_{e'}$, $C_{f'}$) in **3a–g** are similar to other ditungsten complexes containing μ-η^1,η^3-allylidene ligands.[2]

The carbonyl region of complexes **3a–g** exhibits three resonances in the ^{13}C NMR spectra at 25 °C. The $W(CO)_5$ fragment gives rise to two resonances at ca. δ 196 (4 CO) and ca. 200 (1 CO); moreover, the $W(CO)_4$ fragment exhibits one broad resonance at ca. δ 206. The broad resonance observed in the ^{13}C NMR spectra of complexes **3a–g** was suggestive of carbonyl site exchange occurring on the $W(CO)_4$ fragment. Thus, a variable-temperature ^{13}C NMR experiment was performed on complex **3f** in CD_2Cl_2 solution (Figure 1). The ^{13}C NMR spectrum of **3f** exhibits a broad single peak at δ 207.16 at 25 °C. Upon cooling, this peak broadens, coalesces at −40 °C, and re-forms into four new sharp resonances at 210.31, 208.61, 206.15, and 205.05 ppm at −80 °C. This result clearly indicates the carbonyl ligands of the $W(CO)_4$ fragment are magnetically nonequivalent at low temperatures. The stereochemical nonequivalence of these four carbonyl ligands is also readily seen in the solid-state structure of **3f** (vide infra). It can also be seen (Figure 1) that fast scrambling of the carbonyl ligands of the $W(CO)_5$ fragment occurs because

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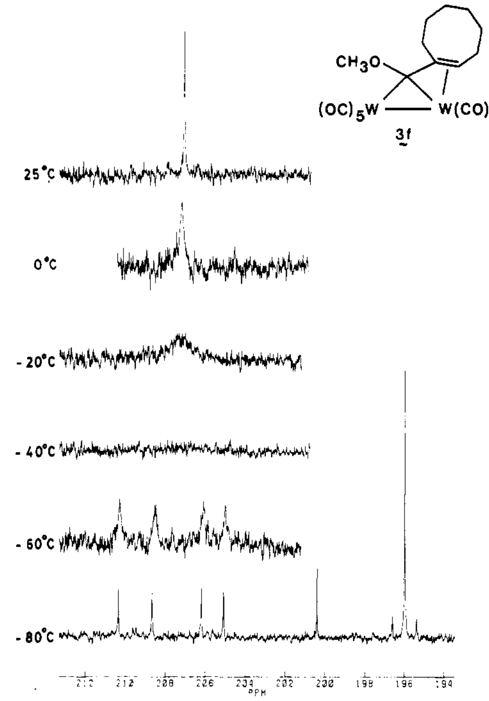


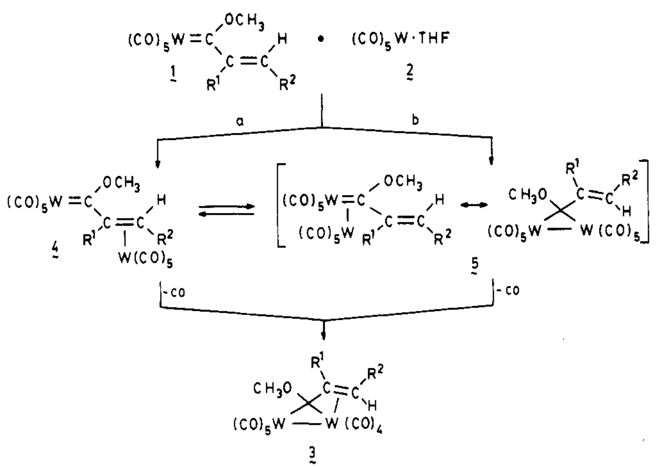
Figure 1. Variable-temperature ^{13}C NMR spectral study of the carbonyl region of complex **3f** in CD_2Cl_2 solution.

the resonances for these ligands remain sharp down to −80 °C (δ 200.36, 195.97). Apparently a steric interaction between the cyclooctene moiety and the carbonyl ligands of the $W(CO)_4$ fragment increases the activation energy of the carbonyl site-exchange process for the $W(CO)_4$ fragment relative to the $W(CO)_5$ fragment. The mechanism for these site-exchange processes probably involves local scrambling of the carbonyl ligands within each tungsten carbonyl fragment.[15]

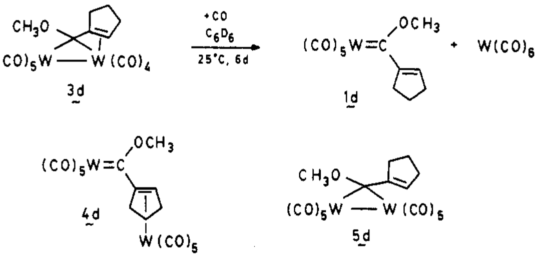
The formation of complexes **3a–g**, from **1a–g** and $(CO)_5W{\cdot}THF$ (**2**), could occur in several steps by two major pathways (Scheme I). In pathway a, the $W(CO)_5$ fragment first complexes to **1** to form **4**. Dissociative loss of a carbonyl ligand from the $W(CO)_5$ fragment complexed to the alkenyl group in **4** could occur next, followed by insertion of this coordinatively unsaturated species into the tungsten–carbon carbene bond, resulting in the formation of **3**. In pathway b, direct insertion of $(CO)_5W{\cdot}THF$ into the tungsten–carbon carbene bond of **1** could occur first to form **5**. In a subsequent step, the alkenyl group in **5** could then coordinate to one of the $W(CO)_5$ fragments with loss of a carbonyl ligand to afford **3**. Furthermore, it may be possible for these two reaction pathways to crossover by the interconversions of complexes **4** and **5**.

Although there is literature evidence to support both pathways depicted in Scheme I, the key compounds **4** and **5** have thus far been too elusive for us to detect or isolate. Literature support for the proposed conversion of complexes **1** to **5** (pathway b) is provided by the work of Stone and co-workers.[16] In these reports, several Fischer-type tungsten carbene complexes were treated with coordinatively unsaturated transition-metal species to produce heterobimetallic μ-carbene complexes containing W–Pt or W–Cu single bonds. Likewise, structural analogues of **5** have been prepared and characterized by X-ray crystallographic methods.[17] These latter ditungsten μ-carbene complexes do not, however, have heteroatom substituents directly bonded to the μ-carbene carbons as in complex **3** or **5**. Rudler and co-workers have also reported that $W_2(CO)_{10}[\mu\text{-}C(H)CH{=}C(CH_3)_2]$, which is a structural analogue of **5**, readily loses a carbonyl ligand in solution to form $W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(H)CH{=}C(CH_3)_2]$, which is a structural analogue of **3**.[2a,g] This observation supports the second step of pathway b, in which complex **5** is proposed to undergo loss of a carbonyl ligand to produce **3**.

Scheme I



Insight into pathway a (Scheme I) comes from an observation previously made by us[18] as well as Rudler and co-workers[2h] involving the chemistry of complexes **3a** and **4a**. It was found that when a benzene-d_6 solution of **3a** was treated with carbon monoxide, it was readily converted into **4a**. Moreover, heating a toluene solution of **4a** at 45 °C converted it back to **3a** in good yield. These findings led us to investigate the reactivity of other ditungsten μ-carbene complexes (**3**). Thus, complex **3d** was treated with carbon monoxide in benzene-d_6 solution in an NMR tube (eq 2). The progress of this reaction was periodically



(2)

monitored by ^1H NMR spectroscopy over a 6-day period. At the end of this time interval only the α,β-unsaturated tungsten carbene complex **1d** was observed. Furthermore, the ^{13}C NMR spectrum of this solution exhibited resonances for **1d** as well as $W(CO)_6$ (δ 191.09). At no time during the course of this reaction (eq 2) were any new resonances attributable to complex **4d** or **5d** observed by ^1H NMR spectroscopy. This result suggested that if **4d** or **5d** are intermediates in this conversion, their lifetimes are too short for detection by NMR spectroscopy at 25 °C. Moreover, complex **4a**, which has been isolated and characterized,[2h,18] may have significantly greater thermal

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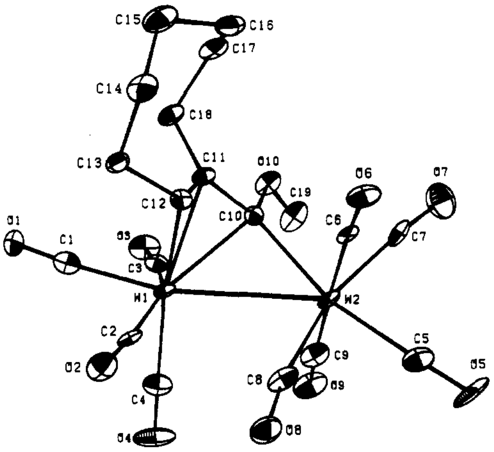

Figure 2. Molecular structure and atom-labeling scheme for $W_2(CO)_9[C(OCH_3)\overline{C{=}CH(CH_2)_5CH_2}]$ (**3f**). The atoms are represented by their 50% probability thermal ellipsoids.

stability over complexes **4b**–**g**.

The molecular structure and atom-labeling scheme for complex **3f** are presented in Figure 2, whereas bond distances and angles are presented in Table II. The overall structure reveals two tungsten atoms with a single-bond distance of 3.1909 (5) Å that are symmetrically bridged by the carbene carbon with distances of 2.296 (9) Å (W(1)–C(10)) and 2.293 (9) Å (W(2)–C(10)). The W(1)–W(2) separation of 3.1909 (5) Å is at the longer end of the range (3.049 (1)–3.189 (1) Å) found for complexes with similar structures.[2,17] Moreover, the tungsten–carbon(carbene) bond distances (W(1)–C(10), W(2)–C(10)) are shorter than the 2.34 (1) Å W–C single-bond distance in $[Et_4N^+][(CO)_5WCH(OCH_3)Ph^-]$[19] and are longer than the 2.17 (2) Å W–C double-bond distance in **4a**[18] and the 1.90 (5) Å W–C triple-bond distance in $I(CO)_4WCPh$.[20] The slightly longer C(10)–O(10) bond distance of 1.38 (1) Å, as compared to 1.32 (1) Å found in **4a**,[18] may be ascribed to the loss of multiple-bond character between these two atoms.[21] This 1.38 (1) Å separation in **3f** is similar to other μ-carbene–carbon oxygen bond distances. For example, a similar bond distance of 1.39 (2) Å was found in the heterobimetallic μ-carbene complex $(PMe_3)(CO)_4\overline{W[\mu\text{-}C(OCH_3)C_6H_4CH_3\text{-}4]Pt}(PMe_3)_2$.[16b]

Table II. Bond Distances (Å) and Angles (deg) for Complex 3f

	Bond Distances		
W(1)–W(2)	3.1909 (5)	W(1)–C(1)	1.99 (1)
W(1)–C(2)	2.06 (1)	W(1)–C(3)	2.03 (1)
W(1)–C(4)	2.01 (1)	W(1)–C(10)	2.296 (9)
W(1)–C(11)	2.339 (9)	W(1)–C(12)	2.383 (9)
W(2)–C(5)	2.03 (1)	W(2)–C(6)	2.07 (1)
W(2)–C(7)	2.07 (1)	W(2)–C(8)	2.04 (1)
W(2)–C(9)	2.06 (1)	W(2)–C(10)	2.293 (9)
O(1)–C(1)	1.13 (1)	O(2)–C(2)	1.13 (1)
O(3)–C(3)	1.13 (1)	O(4)–C(4)	1.15 (1)
O(5)–C(5)	1.14 (1)	O(6)–C(6)	1.11 (1)
O(7)–C(7)	1.13 (1)	O(8)–C(8)	1.14 (1)
O(9)–C(9)	1.14 (1)	O(10)–C(10)	1.38 (1)
O(10)–C(19)	1.42 (1)	C(10)–C(11)	1.44 (1)
C(11)–C(12)	1.42 (1)	C(11)–C(18)	1.50 (1)
C(12)–C(13)	1.50 (1)	C(13)–C(14)	1.56 (1)
C(14)–C(15)	1.53 (2)	C(15)–C(16)	1.54 (2)
C(16)–C(17)	1.52 (2)	C(17)–C(18)	1.53 (1)
	Bond Angles		
W(2)–W(1)–C(1)	166.3 (3)	W(2)–W(1)–C(2)	97.2 (3)
C(1)–W(1)–C(2)	82.7 (4)	W(2)–W(1)–C(3)	105.5 (3)
C(1)–W(1)–C(3)	77.5 (4)	C(2)–W(1)–C(3)	155.2 (4)
W(2)–W(1)–C(4)	94.5 (3)	C(1)–W(1)–C(4)	99.1 (4)
C(2)–W(1)–C(4)	83.7 (4)	C(3)–W(1)–C(4)	84.9 (4)
W(2)–W(1)–C(10)	45.9 (2)	C(1)–W(1)–C(10)	124.1 (4)
C(2)–W(1)–C(10)	126.9 (4)	C(3)–W(1)–C(10)	77.2 (4)
C(4)–W(1)C(10)	126.9 (4)	W(2)–W(1)–C(11)	72.9 (2)
C(1)–W(1)–C(11)	94.1 (4)	C(2)–W(1)–C(11)	108.8 (4)
C(3)–W(1)–C(11)	87.5 (4)	C(4)–W(1)–C(11)	163.0 (4)
C(10)–W(1)–C(11)	36.1 (3)	W(2)–W(1)–C(12)	77.6 (2)
C(1)–W(1)–C(12)	89.3 (4)	C(2)–W(1)–C(12)	73.7 (3)
C(3)–W(1)–C(12)	120.3 (4)	C(4)–W(1)–C(12)	154.8 (4)
C(10)–W(1)–C(12)	63.2 (3)	C(11)–W(1)–C(12)	35.0 (3)
W(1)–W(2)–C(5)	148.6 (3)	W(1)–W(2)–C(6)	100.4 (3)
C(5)–W(2)–C(6)	90.2 (4)	W(1)–W(2)–C(7)	127.0 (3)
C(5)–W(2)–C(7)	83.2 (4)	C(6)–W(2)–C(7)	83.7 (4)
W(1)–W(2)–C(8)	70.1 (3)	C(5)–W(2)–C(8)	80.6 (4)
C(6)–W(2)–C(8)	90.1 (4)	C(7)–W(2)–C(8)	162.6 (4)
W(1)–W(2)–C(9)	81.1 (3)	C(5)–W(2)–C(9)	88.7 (4)
C(6)–W(2)–C(9)	178.5 (4)	C(7)–W(2)–C(9)	95.1 (4)
C(8)–W(2)–C(9)	90.8 (4)	W(1)–W(2)–C(10)	46.0 (2)
C(5)–W(2)–C(10)	165.3 (4)	C(6)–W(2)–C(10)	86.9 (3)
C(7)–W(2)–C(10)	82.1 (4)	C(8)–W(2)–C(10)	113.9 (4)
C(9)–W(2)–C(10)	93.9 (4)	C(10)–O(10)–C(19)	121.5 (8)
W(1)–C(1)–O(1)	175.2 (9)	W(1)–C(2)–O(2)	173.8 (9)
W(1)–C(3)–O(3)	170.2 (9)	W(1)–C(4)–O(4)	177.8 (9)
W(2)–C(5)–O(5)	178 (1)	W(2)–C(6)–O(6)	176.2 (8)
W(2)–C(7)–O(7)	173.4 (9)	W(2)–C(8)–O(8)	169.2 (9)
W(2)–C(9)–O(9)	177 (1)	W(1)–C(10)–W(2)	88.1 (3)
W(1)–C(10)–O(10)	128.3 (6)	W(2)–C(10)–O(10)	120.9 (6)
W(1)–C(10)–C(11)	73.6 (5)	W(2)–C(10)–C(11)	126.6 (7)
O(10)–C(10)–C(11)	109.3 (8)	W(1)–C(11)–C(10)	70.3 (5)
W(1)–C(11)–C(12)	74.2 (5)	C(10)–C(11)–C(12)	118.0 (8)
W(1)–C(11)–C(18)	124.2 (7)	C(10)–C(11)–C(18)	120.2 (9)
C(12)–C(11)–C(18)	121.7 (9)	W(1)–C(12)–C(11)	70.8 (5)
W(1)–C(12)–C(13)	123.1 (6)	C(11)–C(12)–C(13)	122.6 (8)
C(12)–C(13)–C(14)	112.5 (8)	C(13)–C(14)–C(15)	115.1 (9)
C(14)–C(15)–C(16)	117.1 (9)	C(15)–C(16)–C(17)	115.7 (9)
C(16)–C(17)–C(18)	116.4 (8)	C(11)—C(18)–C(17)	109.0 (8)

The bonding associated with the bridging allylidene ligand (C(10), C(11), C(12)) is similar to that found in other ditungsten complexes.[2a,c,d,h] Structures A and B (Chart I) appear to be the best representations for these compounds as well as for **3f**. The nearly equal bond distances of 2.296 (9) (W(1)–C(10)) and 2.293 (9) Å (W(2)–C(10)), as well as the significantly longer W(1)–C(11) (2.339 (9) Å) and W(1)–C(12) (2.383(9) Å) bond distances, support the vinyl carbene structure A. Alternatively, the near equivalence of C(10)–C(11) (1.44 (1) Å) and C(11)–C(12) (1.42 (1) Å), which are between carbon–carbon single and double bonds, supports the delocalized allylic structure B. Furthermore, W(2), C(10), C(11), and C(12) are coplanar to 0.08 Å, which is also implied by structure B. It is interesting to note that unlike **3f**, $W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(1)(H)C(2)H{=}C(3)(CH_3)_2]$, which has a short C(1)–C(2) bond distance of 1.24 (3) Å, has a possible bonding contribution from structure C.[2a]

Experimental Section

General Data. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-400 instrument at 400.1 and 100.6 MHz, respectively. ^1H NMR data are reported as follows: chemical shift in parts per million referenced to residual solvent proton resonance (multiplicity, coupling constants in hertz, number of protons). Elemental analyses were performed by Microlytics, South Deerfield, MA. Column chromatography was conducted under nitrogen on E. Merck silica gel 60 (40–63 μm) using a modified low-temperature air-sensitive flash chromatography apparatus.[22]

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Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement $\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)\overline{C{=}CH(CH_2)_5C}H_2]}$ (3f)

color/shape	red/irregular
mol wt	772.0
space group	$P2_1/c$
temp, °C	−150
cell const	
a, Å	9.832 (4)
b, Å	10.424 (3)
c, Å	21.120 (6)
β, deg	93.37 (3)
cell vol, Å^3	2160.8
molecules/unit cell	4
D(calcd), g cm^{-3}	2.37
μ(calcd), cm^{-1}	109.2
range of relative transm factors	67%/100%
radiatn, graphite monochromator	Mo Kα (λ = 0.71073 Å)
max crystal dimens, mm	0.25 × 0.28 × 0.50
scan width	0.80 + 0.35 tan θ
std reflctns	700, 060, (0,0,22)
decay of stds	±2%
reflctns measd	4239
2θ range, deg	$2 < 2\theta < 50$
range of h,k,l	+11,+12,±25
reflctns obsd [$F_o \geq 5\sigma(F_o)$]	3394
no. of parameters varied	275
weights	unit
GOF	5.23
R	0.038
R_w	0.042

Tetrahydrofuran was distilled from sodium–benzophenone ketyl under nitrogen. Hexane and methylene chloride were distilled from CaH_2 under nitrogen.

Complexes **1a–g** were prepared according to literature procedures as follows: Complex **1a** was prepared by literature methods[18,23] from vinyllithium.[24] Complexes **1b** and **1c** were obtained by procedures similar to the chromium analogues[25] starting from 2-bromopropene[26] and 2-bromo-2-butene,[27] respectively. Complex **1d** was prepared according to the method described by Fischer and co-workers[28] from 1-cyclopentenyllithium.[29] Complex **1e** was obtained according to a procedure developed for the chromium analogue[30] starting from cyclohexanone 2,4,6-triisopropylbenzenesulfonyl hydrazone.[31] Complexes **1f** and **1g** were prepared according to the literature procedure described for **1d**,[28] from the corresponding lithium reagents,[32] which were in turn obtained from 1-bromo-1-cyclooctene[33] and 1-bromo-1-(trimethylsilyl)ethylene.[34]

X-ray Data Collection, Structure Determination, and Refinement for $\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)\overline{C{=}CH(CH_2)_5C}H_2]}$ (3f). A red single crystal of the title compound was mounted on a pin and transferred to the goniomenter. The crystal was cooled to −150 °C during data collection by using a stream of cold nitrogen gas. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections ($\theta > 21°$) accurately centered on the diffractometer are given in Table III. The space group was determined to be the centric $P2_1/c$ from the systematic absences.

Table IV. Final Fractional Coordinates for Complex 3f

atom	x/a	y/b	z/c
W(1)	0.91746 (4)	0.79421 (4)	0.65379 (2)
W(2)	0.76607 (4)	0.74667 (4)	0.51802 (2)
O(1)	1.0050 (7)	0.8923 (7)	0.7896 (3)
O(2)	1.1383 (8)	0.9993 (7)	0.6152 (4)
O(3)	0.8109 (8)	0.5924 (7)	0.7503 (4)
O(4)	1.1551 (9)	0.5976 (8)	0.6311 (5)
O(5)	0.783 (1)	0.6921 (8)	0.3714 (4)
O(6)	0.6518 (7)	1.0253 (7)	0.4837 (3)
O(7)	0.4558 (9)	0.6701 (9)	0.4834 (4)
O(8)	1.0636 (8)	0.8399 (8)	0.4915 (4)
O(9)	0.8723 (9)	0.4599 (7)	0.5437 (4)
O(10)	0.5927 (7)	0.6998 (7)	0.6412 (3)
C(1)	0.979 (1)	0.857 (1)	0.7397 (5)
C(2)	1.056 (1)	0.926 (1)	0.6254 (4)
C(3)	0.845 (1)	0.6576 (9)	0.7113 (5)
C(4)	1.068 (1)	0.668 (1)	0.6403 (5)
C(5)	0.779 (1)	0.711 (1)	0.4243 (5)
C(6)	0.6945 (9)	0.930 (1)	0.4975 (4)
C(7)	0.564 (1)	0.695 (1)	0.4994 (5)
C(8)	0.960 (1)	0.8071 (9)	0.5075 (5)
C(9)	0.834 (1)	0.563 (1)	0.5366 (5)
C(10)	0.6931 (9)	0.7770 (9)	0.6180 (4)
C(11)	0.704 (1)	0.8931 (9)	0.6548 (4)
C(12)	0.7953 (9)	0.9895 (9)	0.6357 (4)
C(13)	0.824 (1)	1.1088 (9)	0.6736 (5)
C(14)	0.718 (1)	1.217 (1)	0.6575 (5)
C(15)	0.579 (1)	1.198 (1)	0.6852 (6)
C(16)	0.488 (1)	1.091 (1)	0.6563 (5)
C(17)	0.486 (1)	0.968 (1)	0.6943 (5)
C(18)	0.625 (1)	0.908 (1)	0.7132 (5)
C(19)	0.588 (1)	0.566 (1)	0.6286 (5)

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ-2θ scan technique. A summary of data collection parameters is given in Table III. The intensities were corrected for Lorentz, polarization effects, and absorption. The absorption correction (empirical using Ψ-scan data for seven χ–90° reflections) was hampered by the irregular shape of the crystal. As a result of this and the high value of μ (109.4 cm^{-1}), the refinement did not proceed as smoothly as expected. The inability to refine C(10) anisotropically may also be a result of an inadequate absorption correction. We were unable to find a more regularly shaped crystal and thus report the refinement in its present form. Higher than normal standard deviations and an inability to locate all hydrogen atoms also resulted.

Calculations were carried out with the SHELX system of computer programs.[35] Neutral atom scattering factors for W, O, C, and H were taken from ref 36, and the scattering was corrected for the real and imaginary components of anomalous dispersion.[36]

The positions of the tungsten atoms were revealed by using the direct methods program MULTAN.[37] A difference Fourier map phased on the tungsten atoms readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.096$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl hydrogen atoms could not be located. Refinement of the non-hydrogen atoms with anisotropic temperature factors, except for C(10), led to final values of $R = 0.038$ and $R_w = 0.042$. A final difference Fourier showed satellite peaks near each W position, but no other feature greater than 1.2 e/Å^3. The weighting scheme was based on unit weights no systematic variations of $w(|F_o| - |F_c|)$ vs $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional pa-

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rameters are given in Table IV.

$\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)CH{=}CH_2]}$ (3a). In a water-jacketed Schlenk tube were placed $\mathrm{W(CO)_6}$ (0.36 g, 1.0 mmol) and 50 mL of tetrahydrofuran. The solution was then irradiated with a medium-pressure mercury vapor-lamp under a slight $\mathrm{N_2}$ positive pressure for 4 h. This light yellow solution of $\mathrm{(CO)_5W\cdot THF}$[38] was transferred via cannula to a solution of **1a** (0.25 g, 0.63 mmol) in 10 mL of hexane. The reaction was allowed to stir for 15 min and then the solvent removed under vacuum. The resulting residue was chromatographed on silica gel at −30 °C using methylene chloride/hexane (1:10). A red band was collected under nitrogen and the solvent removed under vacuum. Recrystallization from hexane at 0 °C afforded 0.26 g (60%) of **3a** as dark red crystals: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.75 (dd, J = 9.5, 7.7 Hz, 1 H), 3.10 (s, 3 H), 2.98 (dd, J = 7.8, 1.7 Hz, 1 H), 1.96 (dd, J = 9.4, 1.7 Hz, 1 H).

$\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)C(CH_3){=}CH_2]}$ (3b). The procedure described for the preparation of **3a** was followed except that complex **1b** was used in place of **1a**. Crystallization from hexane at 0 °C gave **3b** (68%): dark red crystals; mp 84 °C dec; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.53 (s, 3 H), 3.06 (d, J = 1.9 Hz, 1 H), 1.90 (d, J = 1.9 Hz, 1 H), 1.83 (s, 3 H). Anal. Calcd for $\mathrm{C_{14}H_8O_{10}W_2}$: C, 23.89; H, 1.14. Found: C, 24.07; H, 1.23.

$\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)C(CH_3){=}CHCH_3]}$ (3c). The procedure described for the preparation of **3a** was followed except that complex **1c** was used in place of **1a** and the chromatography conducted at 25 °C. Crystallization from 30% methylene chloride/hexane at 0 °C gave **3c** (21%): dark red crystals; mp 86–88 °C dec; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.58 (s, 3 H), 2.93 (q, J = 6.2 Hz, 1 H), 1.82 (s, 3 H), 1.71 (d, J = 6.1 Hz, 3 H). Anal. Calcd for $\mathrm{C_{15}H_{10}O_{10}W_2}$: C, 25.09; H, 1.40. Found: C, 25.29; H, 1.45.

$\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)\overline{C{=}CH(CH_2)_2C}H_2]}$ (3d). The procedure described for the preparation of **3a** was followed except that complex **1d** was used in place of **1a** and the chromatography conducted at 25 °C. Crystallization from hexane at 0 °C gave **3d** (34%): dark red crystals; mp 78–84 °C dec; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.67 (s, 3 H), 3.53 (d, J = 3.3 Hz, 1 H), 2.64–2.51 (m, 2 H), 2.36–2.24 (m, 2 H), 1.44–1.34 (m, 2 H). Anal. Calcd for $\mathrm{C_{16}H_{10}O_{10}W_2}$: C, 26.33; H, 1.38. Found: C, 26.42; H, 1.40.

$\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)\overline{C{=}CH(CH_2)_3C}H_2]}$ (3e). The procedure described for the preparation of **3a** was followed except that complex **1e** was used in place of **1a** and the chromatography conducted at 25 °C. Crystallization from hexane at 0 °C gave **3e** (21%): dark red crystals; mp 100–102 °C dec; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.64 (s, 3 H), 3.58 (m, 1 H), 3.01 (tt, J = 5.7, 4.9 Hz, 1 H), 2.45 (m, 1 H), 2.35 (m, 2 H), 1.25–0.85 (m, 4 H). Anal. Calcd for $\mathrm{C_{17}H_{12}O_{10}W_2}$: C, 27.44; H, 1.63. Found: C, 27.56; H, 1.67.

$\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)\overline{C{=}CH(CH_2)_5C}H_2]}$ (3f). The procedure described for the preparation of **3a** was followed except that complex **1f** was used in place of **1a**. Crystallization from hexane at 0 °C gave **3f** (90%): dark red crystals; mp 83–84 °C dec; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.60 (s, 3 H), 3.03 (dd, J = 4.6, 4.5 Hz, 1 H), 2.89 (tt, J = 3.3, 3.0 Hz, 1 H), 2.46 (m, 1 H), 1.90–0.90 (m, 10 H). Anal. Calcd for $\mathrm{C_{19}H_{16}O_{10}W_2}$: C, 29.56; H, 2.09. Found: C, 29.68; H, 2.06.

$\mathrm{W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)C(SiMe_3){=}CH_2]}$ (3g). The procedure described for the preparation of **3a** was followed except that complex **1g** was used in place of **1a**. Chromatography on silica gel at −30 °C using methylene chloride/hexane (1:10) gave **3g** (78%): dark red liquid; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.58 (s, 3 H), 3.45 (s, 1 H), 2.16 (s, 1 H), 0.10 (s, 9 H). Anal. Calcd for $\mathrm{C_{16}H_{14}O_{10}SiW_2}$: C, 25.22; H, 1.85. Found: C, 25.36; H, 1.85.

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Registry No. **1a**, 83801-34-7; **1b**, 108104-17-2; **1c**, 111772-17-9; **1d**, 111772-18-0; **1e**, 111772-19-1; **1f**, 111772-20-4; **1g**, 111772-21-5; **3a**, 83801-30-3; **3b**, 111772-22-6; **3c**, 111772-23-7; **3d**, 111772-24-8; **3e**, 111772-25-9; **3f**, 111772-26-0; **3g**, 111772-27-1; $\mathrm{W(CO)_5\cdot THF}$, 36477-75-5; $\mathrm{W(CO)_6}$, 14040-11-0; W, 7440-33-7.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, and least-squares plane results (3 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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[38] $\mathrm{(CO)_5W\cdot THF}$ was prepared according to literature procedures[39] as follows: $\mathrm{W(CO)_6}$ (0.25 g, 0.71 mmol) was dissolved in 50 mL of THF and irradiated for 4–7 h. This reaction was followed by IR spectroscopy, and after 4 h, the spectrum exhibited bands at 1970 (m) ($\mathrm{W(CO)_6}$), 1925 (s), and 1890 (m) cm^{-1}. The intensities of these bands remained the same even after irradiation for a total of 7 h. To a solution which had been irradiated for 4 h was added excess triphenylphosphine to determine the amount of $\mathrm{(CO)_5W\cdot THF}$ formed in this reaction. This solution was stirred at 25 °C for 1 h and then chromatographed on silica gel. $\mathrm{(CO)_5WPPh_3}$ (0.32 g, 73%) was isolated from this chromatography and exhibited bands in its IR spectrum at 2080 (w) and 1940 (s) cm^{-1} in hexane. The ^{1}H NMR spectrum of this $\mathrm{(CO)_5WPPh_3}$ sample showed no triphenylphosphine present.

[39] Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F. *J. Organomet. Chem.* **1973**, *47*, 391.