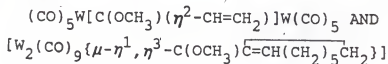


THE SYNTHESIS, STRUCTURE, AND REACTIVITY OF DI-TUNGSTEN  
NONACARBONYL  $\mu$ -CARBENE COMPLEXES: MOLECULAR STRUCTURES OF



by

MONG LIANG

B.S., TUNGHAI UNIVERSITY, 1981

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Approved by:

*David W. Macomber*  
Major Professor

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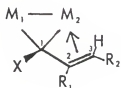
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### Introduction:

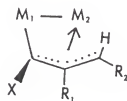
Molecules which contain two transition metal centers bridged by  $\mu$ -carbene ligands have received considerable attention<sup>1</sup> due to their probable involvement in important transition metal-catalyzed processes such as olefin metathesis<sup>2a</sup> and Fischer-Tropsch chemistry.<sup>2b</sup> Within this class of  $\mu$ -carbene complexes is an interesting group of dimetallic complexes containing  $\mu$ - $\eta^1, \eta^3$ -allyl ligands. Over the past 14 years there have been numerous reports on the synthesis, reactivity, and structures of these complexes.<sup>3-43</sup> These investigations include mechanistic and synthetic studies of di-iron,<sup>3-12</sup> di-ruthenium,<sup>13-17</sup> di-rhenium,<sup>18</sup> di-molybdenum,<sup>19-25</sup> di-tungsten,<sup>26-31</sup> di-iridium,<sup>34,35</sup> di-cobalt<sup>36</sup>, and cobalt-tungsten<sup>37,38</sup> carbene complexes. Some analogs with  $\mu$ -phenyl vinylidene ligands bridged to different metals have also been reported.<sup>39-43</sup> It has been found that these di-metal  $\mu$ -allyl carbene complexes are highly reactive towards alkynes,<sup>12,15,25,28,29,37</sup> and have a propensity to undergo alkyne polymerization reactions<sup>15,28</sup> probably due to the easy transformation of the coordinated allyl ligand from an  $\eta^3$ - to an  $\eta^1$ -bonding mode. This provides a vacant site on one metal for alkyne coordination, as a preliminary step for C-C bond formation. Of particular interest is the bonding between the metal and the  $\mu$ - $\eta^1, \eta^3$ -allyl ligand which has been discussed by several research groups for di-iron,<sup>3,5,12</sup> di-cobalt,<sup>36</sup> di-molybdenum,<sup>19,23,24</sup> di-ruthenium,<sup>13,14</sup> di-rhenium,<sup>18</sup> di-tungsten,<sup>26</sup> and

cobalt-tungsten<sup>38</sup> complexes.

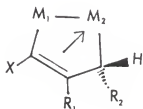
From these above reports, it can be seen that four extreme views of the bonding modes are possible and are depicted below as structures A-D:



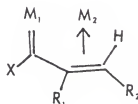
(A)



(B)



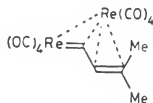
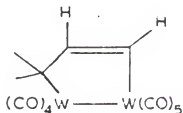
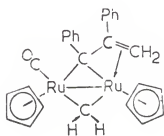
(C)



(D)

Most complexes can be represented as having a large contribution from allylic delocalization (structure B) although some do not conflict with any of the four bonding mode representations<sup>12,13,38</sup> (structures A-D). X-ray crystallography evidence indicates that  $[\text{Ru}_2(\text{CO})(\mu\text{-CH}_2)-(\mu\text{-}$

$C(Ph)C(Ph)CH_2\{\eta-C_5H_5\}_2\}^{14}$  is best described by A,  $W_2(CO)_9[\mu-\eta^1, \eta^3-C(H)CH=C(CH_3)_2]^{26}$  is best described as C, and a "metallabutadiene" E type moiety bound in  $Re_2(CO)_8[\mu-\eta^1, \eta^3-C(H)CH=C(CH_3)_2]^{18}$  has been observed as an analog of D.



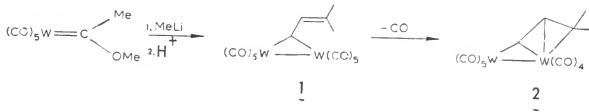
The goal of this study was to develop a convenient synthesis of  $\mu-\eta^1, \eta^3$ -allyl ditungsten carbene complexes from Fischer-type carbene complexes, to investigate their reactivity, and to define the bonding mode of the coordinated ligand.

#### Background:

In 1980, the first dinuclear tungsten complex containing a  $\mu-\eta^1, \eta^3$ -allyl ligand was reported by Levisalles and Rudler.<sup>26</sup> The reaction of MeLi with  $(CO)_5W[C(OCH_3)CH_3]$  provided the stable complex 1, which was found to undergo a fast reaction in solution with loss of one CO ligand and coordination of the free double bond to give complex 2 (Scheme I).



## Scheme I



X-ray crystallography (Fig. 1) of complex 2 shows that a labile CO ligand is contained in the  $\text{W}(\text{CO})_5$  fragment owing to one long tungsten carbonyl length  $\text{W}_1\text{-CO}$  bond (2.11(2) Å) as compared to the average W-CO bond lengths of 1.94(1)-2.07(1) Å. The double bond is only weakly bound to the metal because of a rather long  $\text{W}_2\text{-C}_3$  bond. The very short bond distance between  $\text{C}_1$  and  $\text{C}_2$  (1.24(3) Å) indicates the existence of increased C-C bond order which suggests that structure C may be the best bonding mode representation for this complex 2.

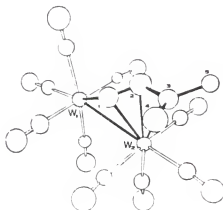
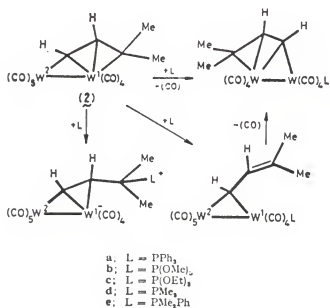


Fig. 1 ORTEP view of complex 2

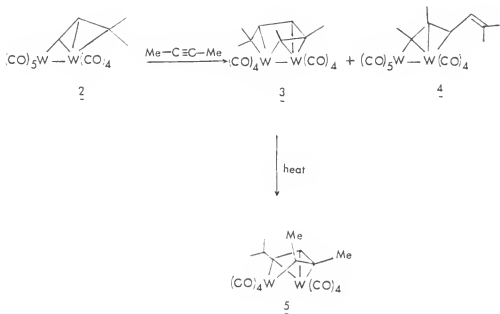
It appears that replacement of the coordinated double bond by CO in 2 occurs easily (Scheme II). However, in the presence of phosphorous-containing nucleophiles, the reactions can take place either at the terminal vinyl carbon (for the stronger nucleophiles, like  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ) or at the metal atom (for the weaker nucleophiles, like  $\text{PPh}_3$  and  $\text{P}(\text{OMe})_3$ ).<sup>27</sup>

Scheme II



The observations described above prompted further studies on the reactivity of these complexes toward alkynes and cycloalkenes (Schemes III, IV, and V). The reaction of complex 2 with but-2-yne at room temperature gave a mixture containing complex 3 (red crystals) in 30% yield and complex 4 (purple crystals) in 12% yield.<sup>29a</sup>

Scheme III

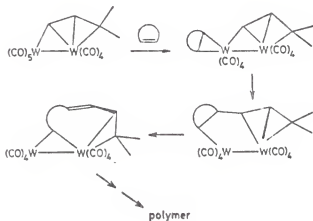


Complex **3**, which contains two sets of  $\mu-\eta^1, \eta^3$ -allyl moieties around the metal centers, undergoes rearrangement to complex **5** upon refluxing in hexane for 1 hr.<sup>29b</sup> The structures of these complexes (**3**, **4** and **5**) were determined by X-ray crystallography.<sup>28,29a,b</sup> The  $^1\text{H}$  NMR and mass spectra of compound **4** show that the terminal double bond is no longer coordinated and there is one additional CO group present as compared to complex **3**.

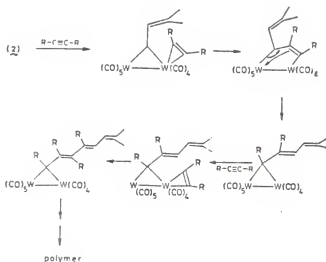
The  $\mu$ -alkylidene bridged complex **2** "catalytically" reacts with but-2-yne and norbornene to give polyalkynes ( $\bar{M}_n$  range from 800 to 16500 under various conditions) and ring-opened polyunsaturated polymers, respectively. The

mechanism may proceed by insertion of the monomer into the tungsten-allyl  $\sigma$ -bond followed by reductive elimination and rearrangement (Schemes IV and V).<sup>28,29a</sup>

Scheme IV

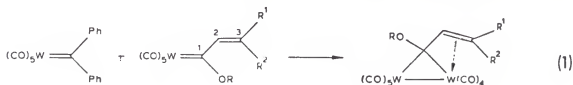


Scheme V



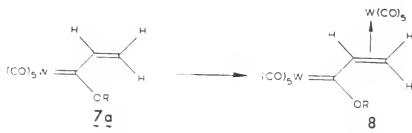
Since we have been successful in our laboratory in obtaining various Fischer-type transition metal carbene

complexes, it was tempting for us to use these to develop a straightforward synthesis of  $\mu$ - $\eta^1$ ,  $\eta^3$ -allyl di-tungsten carbene complexes. A similar approach has been reported by Rudler and co-workers<sup>31</sup> and is depicted in equation 1. It



| $R_1$ | $R_2$ | Yield (%)    |
|-------|-------|--------------|
| H     | H     | not reported |
| Me    | H     | 20           |
| Ph    | H     | not reported |
| Me    | Me    | 0            |

was also reported in this account that a new type of bridged di-tungsten carbene complex,  $(CO)_5W[C(OCH_3)(\eta^2-CH=CH_2)]-W(CO)_5$  (**8**), could be obtained by allowing a solution of **7a** to stand in hexane.<sup>31</sup> No mechanistic explanation for the formation of complex **8** was provided. The single crystal X-ray structure of **8** has recently been determined and details are given below.<sup>46</sup> Likewise, certain aspects of the mechanism of formation of **8** from **7a** have recently been elucidated.<sup>46</sup>



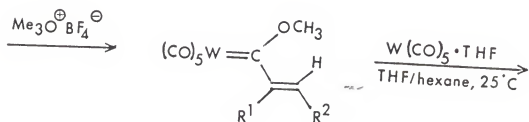
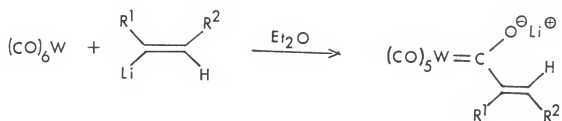
## Results and Discussion

Preparation of  $[W_2(CO)_9\{\mu-\eta^1, \eta^3-C(OCH_3)CR^1=CHR^2\}]$  (7).

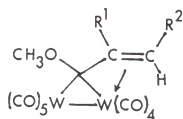
The syntheses of the desired  $\mu$ -carbene ditungsten complexes 7 are outlined in Scheme VI. The required reactants, Fischer-type  $\alpha, \beta$ -unsaturated tungsten carbene complexes 6, were obtained from the reaction of various vinylolithium reagents with  $W(CO)_6$  followed by treatment with  $Me_3O^+BF_4^-$  according to standard literature procedures.<sup>51,54</sup> It was found that the  $\alpha, \beta$ -unsaturated carbene complexes 6 readily reacted with  $W(CO)_5 \cdot THF$  (generated photochemically from  $W(CO)_6$  in THF) to form the complexes 7. This synthetic route provides a more convenient and efficient way to prepare complexes 7 compared to Rudler's original method (eq 1).<sup>31</sup>

The first notable observation was that complex 8, which was determined by single crystal X-ray diffraction methods as having a structure of  $(CO)_5W[C(OCH_3)(\eta^2-CH=CH_2)]W(CO)_5$  (more details about the structure will be discussed below), was obtained in 18% yield along with 6a. Compound 6a melted ca. 15 °C to a viscous liquid which soon solidified into a polymeric glass at room temperature. The mechanism of this polymerization process is not clear, and none of the other carbene complexes (6b-6g) were found to polymerize under these conditions. Second, the low yields of 7c, 7d, and 7e were believed to be due to decomposition of these complexes on silica gel during chromatographic purification. It was subsequently found that the  $\mu$ -carbene di-tungsten complexes

Scheme VI



6



7

Table I. Yields of  $\mu$ -Carbene Di-tungsten Complexes

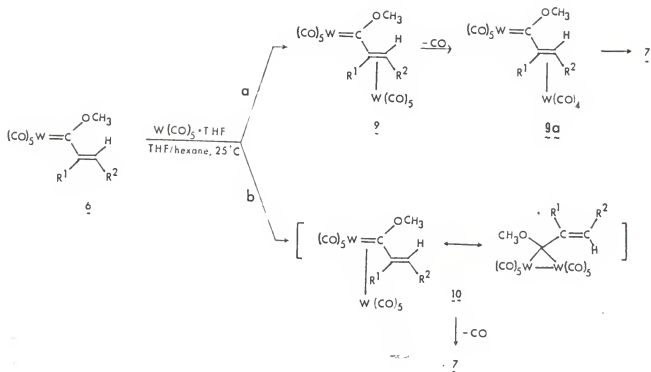
| <u>7</u> | <u>R</u> <sup>1</sup>                | <u>R</u> <sup>2</sup> | <u>Yield (%)</u> |
|----------|--------------------------------------|-----------------------|------------------|
| a        | H                                    | H                     | 60               |
| b        | CH <sub>3</sub>                      | H                     | 68               |
| c        | CH <sub>3</sub>                      | CH <sub>3</sub>       | 21               |
| d        | --(CH <sub>2</sub> ) <sub>3</sub> -- |                       | 34               |
| e        | --(CH <sub>2</sub> ) <sub>4</sub> -- |                       | 21               |
| f        | --(CH <sub>2</sub> ) <sub>6</sub> -- |                       | 90               |
| g        | SiMe <sub>3</sub>                    | H                     | 78               |

complexes could be obtained in much improved yields if the chromatography was conducted at  $-30\text{ }^{\circ}\text{C}$  (see Experimental Section for a diagram of the low temperature chromatography apparatus, Fig. 5). Furthermore, none of the corresponding  $\mu$ -carbene complex was obtained from the reaction of the trans-form of 6c,  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{trans-C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{H}]$ , with  $(\text{CO})_5\text{W} \cdot \text{THF}$ , Rudler and co-workers have also reported a similar finding.<sup>31</sup> This may in part be due to a steric interaction between the trans-methyl group on C(3) of 6c and the  $\text{W}(\text{CO})_4$  fragment.

As  $\text{W}(\text{CO})_5 \cdot \text{THF}$  was added to the Fischer-type tungsten carbene complexes 6 in hexane solution, no reaction appeared to occur until the THF was removed from the reaction mixture. Two possible pathways could account for the formation of the complexes 7 from the reaction between 6 and  $(\text{CO})_5\text{W} \cdot \text{THF}$  (Scheme VII). The coordinatively unsaturated



## Scheme VII



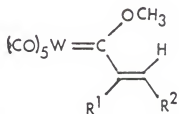
$(CO)_5W$  fragment could complex to the C=C of 6 in an  $\eta^2$ -manner to form complex 9 followed by rearrangement, possibly via 9a, to produce 7. Since it was found that complex 8, which is a structural analog of 9 ( $R^1 = R^2 = H$ ), was converted to 7a slowly at 25 °C,<sup>46</sup> it might be expected that intermediate 9 should be isolable if pathway a was correct. Complexes 9b-g were not observed during the course of these reactions. In pathway b,  $(CO)_5W \cdot THF$  is proposed to insert into the tungsten-carbon carbene bond directly forming 10. In a second step, the C=C of vinyl group coordinates to  $(CO)_5W$  fragment with loss of a CO ligand to form 7. The intermediate 10 proposed in this reaction pathway was not

observed, but structural analogs of 10 have been prepared and characterized crystallographically.<sup>33,44</sup>

Spectral Characterization of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{CR}^1=\text{CHR}^2]$  (6). and  $[\text{W}_2(\text{CO})_9\{\mu-\eta^1, \eta^3-\text{C}(\text{OCH}_3)\text{CR}^1=\text{CHR}^2\}]$  (7). The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral data for complexes 6 and 7 are summarized in Tables II-V. As can be seen in Tables II and

Table II.  $^1\text{H}$  NMR Spectral Data for Complexes 6a-g.

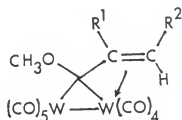
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )



6

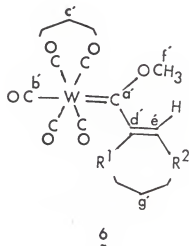
| <u>6</u> | <u>H</u> | <u>OCH<sub>3</sub></u> | <u>R<sup>1</sup></u>            | <u>R<sup>2</sup></u> |
|----------|----------|------------------------|---------------------------------|----------------------|
| a*       | 5.28     | 3.72                   | 7.01                            | 4.63                 |
| b        | 5.49     | 4.62                   | 1.89                            | 5.43                 |
| c        | 6.72     | 4.63                   | 1.79                            | 1.90                 |
| d        | 7.29     | 4.62                   | 2.60-2.50                       | 1.95                 |
| e        | 6.99     | 4.62                   | 2.34-2.31, 2.24-2.22, 1.65-1.60 |                      |
| f        | 7.06     | 4.65                   | 2.45-2.38, 1.70-1.60, 1.55-1.40 |                      |
| g        | 5.71     | 4.50                   | 0.51                            | 5.45                 |

\* in  $\text{C}_6\text{D}_6$

Table III.  $^1\text{H}$  NMR Spectral Data for Complexes  $7\text{a-g}$ . $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )

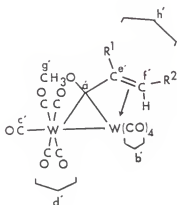
7

| <u>7</u> | <u>OCH<sub>3</sub></u> | <u>H</u> | <u>R<sub>1</sub></u>  | <u>R<sub>2</sub></u> |
|----------|------------------------|----------|---|----------------------|
| a        | 3.10                   | 1.96     | H 4.75  | H 2.98               |
| b        | 3.53                   | 1.90     | CH <sub>3</sub> 1.83  | H 3.06               |
| c        | 3.58                   | 2.93     | CH <sub>3</sub> 1.82  | CH <sub>3</sub> 1.71 |
| d        | 3.67                   | 3.53     | -(CH <sub>2</sub> ) <sub>3</sub> - 2.64, 2.51, 2.36-2.24, 1.44-1.34 |                      |
| e        | 3.64                   | 3.58     | -(CH <sub>2</sub> ) <sub>4</sub> - 3.01, 2.45, 2.35, 1.25-0.85      |                      |
| f        | 3.60                   | 3.03     | -(CH <sub>2</sub> ) <sub>6</sub> - 2.89, 2.46, 1.90-0.90            |                      |
| g        | 3.58                   | 2.16     | SiMe <sub>3</sub> 0.10  | H 3.45               |

Table IV.  $^{13}\text{C}$  NMR Spectral Data for Complexes  $\underline{6a}, \underline{b}, \underline{d}, \underline{f}, \underline{g}$ . $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

| $\underline{6}$ | $\underline{a'}$ | $\underline{b'}$ | $\underline{c'}$ | $\underline{d'}$ | $\underline{e'}$ | $\underline{f'}$ | $\underline{g'}$                               |
|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|--|
| $a^*$           | 312.49           | 203.77           | 197.44           | 152.44           | 119.30           | 68.76            |  |
| $b$             | 327.01           | 203.27           | 197.21           | 160.50           | 121.68           | 69.58            | 19.21  |
| $d$             | 311.13           | 203.00           | 197.97           | 161.17           | 157.28           | 69.16            | 34.84, 31.68,<br>23.06                         |
| $f$             | 322.67           | 202.96           | 197.92           | 159.03           | 151.65           | 69.67            | 29.81, 28.91,<br>28.44, 26.78,<br>25.88, 25.62 |
| $g^*$           | 334.45           | 203.88           | 197.86           | 172.13           | 125.17           | 68.24            | -0.91  |

\* in  $\text{C}_6\text{D}_6$

Table V.  $^{13}\text{C}$  NMR Spectral Data for Complexes 7a-g. $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )

7

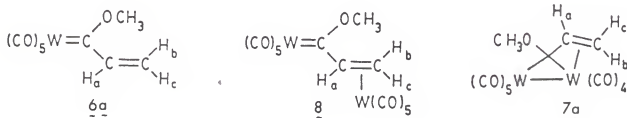
| <u>7</u> | <u>a'</u> | <u>b'</u> | <u>c'</u> | <u>d'</u> | <u>e'</u> | <u>f'</u> | <u>g'</u> | <u>h'</u>                                    | $\text{R}^1$            | $\text{R}^2$  |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|--|-------------------------|---------------|
| 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  | $\text{CH}_3$           | H             |
| c        | 233.88    | 206.37    | 199.59    | 195.87    | 110.77    | 84.93     | 64.03     | 17.10, 15.69                                 | $\text{CH}_3$           | $\text{CH}_3$ |
| d        | 230.63    | 205.98    | 200.16    | 195.94    | 118.52    | 89.12     | 63.54     | 34.42, 32.05<br>21.15                        | -- $(\text{CH}_2)_3$ -- |               |
| e        | 233.73    | 206.53    | 199.33    | 195.76    | 113.30    | 90.74     | 63.87     | 29.65, 27.08<br>21.45, 21.43                 | -- $(\text{CH}_2)_4$ -- |               |
| f        | 233.85    | 206.61    | 199.45    | 195.69    | 111.24    | 89.81     | 64.09     | 32.33, 30.91<br>30.28, 29.65<br>26.76, 26.13 | -- $(\text{CH}_2)_6$ -- |               |
| g        | 235.78    | 206.75    | 199.41    | 195.51    | 102.11    | 63.38     | 63.61     | 26.06  | $\text{SiMe}_3$         | H             |

III, the proton chemical shifts for the vinyl and methoxy protons in 7 all appear at substantially higher field than in 6. The vinylic resonances of the alkene ligand in 7 shift upfield ca. 1-3 ppm relative to 6 upon coordination in an  $\eta^2$ -manner to a tungsten carbonyl fragment. Similar observations have been made in other tungsten carbonyl alkene complexes.<sup>45</sup> This upfield shift may be due to a change in hybridization of the two vinylic carbons away from  $sp^2$  hybridization towards  $sp^3$  upon  $\pi$ -coordination of alkene ligand to tungsten. The chemical shifts of the methoxy resonances in 7a-g are well upfield by ca. 0.5-1.0 ppm of the methoxy resonance in 6. This is probably due to a reduction in partial positive charge on the oxygen bonded to the  $\mu$ -carbene carbon in 7 relative to 6. A charge separated contributing resonance structure for heteroatom stabilized terminal carbene complexes, like 6a-g has a positive charge on oxygen and a negative charge on the metal. Bridging  $\mu$ -carbene complexes like 7a-g containing heteroatoms, have no analogous resonance structures.



Another noteworthy observation from the NMR spectra of these complexes is the decreasing magnitude of the vicinal coupling constants<sup>45a,c,e,46</sup> on going from complexes 6a to 8 to 7a (Table VI). Since vicinal coupling constants usually

Table VI. Vicinal and Geminal Coupling Constants for Complexes 6a, 7a, and 8.



| <sup>1</sup> H NMR (C <sub>6</sub> D <sub>6</sub> ) |                |                |                |                  |                 |                 |                 |
|---|----------------|----------------|----------------|------------------|-----------------|-----------------|-----------------|
| Compound  | ppm            |                |                |                  | Hz              |                 |                 |
|   | H <sub>a</sub> | H <sub>b</sub> | H <sub>c</sub> | OCH <sub>3</sub> | J <sub>ab</sub> | J <sub>ac</sub> | J <sub>bc</sub> |
| <u>6a</u>   | 7.04           | 5.28           | 4.64           | 3.74             | 16.9            | 10.3            | 1.4             |
| <u>8</u>  | 5.16           | 2.82           | 2.47           | 3.67             | 13.6            | 8.2             | 0               |
| <u>7a</u>   | 4.75           | 1.96           | 2.98           | 3.10             | 9.5             | 7.7             | 1.7             |

decrease with increasing C-C bond length or decreasing  $\pi$ -bond order, this finding suggests a further elongation of the C=C in 7a relative to 8 and 6a. The X-ray structure of 8, however, reveals that the C=C bond length is unchanged upon coordination to the  $W(CO)_5$  fragment. Other factors including electronic changes,<sup>47</sup> which could occur upon  $\pi$ -coordination of an alkene ligand to a tungsten carbonyl fragment, may be responsible for changes in vicinal coupling constants.

The  $^{13}C$  NMR spectra of complexes 6a,b,d,f,g and 7a-g are summarized in Tables IV and V which illustrate a predictable chemical shift pattern. The low field portion of the spectra of complexes 6a,b,d,f,g consist of three distinct carbon resonances at ca. 320, 203, and 197 ppm with relative intensities of 1 : 1 : 4. These three resonances are assigned to the carbene carbon, the trans-CO ligand, and four equivalent cis-CO ligands, respectively. The most striking feature in the spectra of complexes 6a,b,d,f,g are the extremely low-field positions of the carbene carbon resonances. The factors giving rise to these low field shifts are not well understood.<sup>48</sup> Moreover, the cis-CO resonances exhibit characteristic  $^{183}W$  satellite peaks with  $J^{13}C-^{183}W$  coupling constants of ca. 125 Hz. The  $\mu$ -carbene carbon resonances for 7a-g (230.63-235.78 ppm) occur at substantially higher field than the corresponding terminal carbene carbon resonances of 6 in their  $^{13}C$  NMR spectra.



The chemical shift values for these  $\mu$ -carbene carbons are somewhat out of the 100-200 ppm range commonly observed for other  $\mu$ -carbene carbons.<sup>49</sup> This downfield shift is probably due to the electronegative methoxy group directly attached to the carbene carbon.

Since it was reported that the  $^{13}\text{C}$ - $^1\text{H}$  coupling constants were proportional to the amount of s-character of the carbon atomic orbitals involved in the bond, these coupling constants may indicate a change in the C-H bond distance.<sup>50</sup> In an attempt to gain further insight into the bonding nature of complexes 6a, 8, and 7a, the  $^{13}\text{C}$ - $^1\text{H}$  coupling constants were determined by obtaining their gated-decoupled  $^{13}\text{C}$  NMR spectra. For compound 8,  $\text{C}_d$ , was found to be a doublet ( $\underline{J}^{13}\text{C}-^1\text{H} = 165 \text{ Hz}$ ),  $\text{C}_e$ , was found to be a triplet ( $\underline{J}^{13}\text{C}-^1\text{H} = 165 \text{ Hz}$ ), and  $\text{C}_f$ , was found to be a quartet ( $\underline{J}^{13}\text{C}-^1\text{H} = 148 \text{ Hz}$ ). These values can be compared to those found for 6a:  $\text{C}_d$ , (d,  $\underline{J}^{13}\text{C}-^1\text{H} = 161 \text{ Hz}$ ),  $\text{C}_e$ , (t,  $\underline{J}^{13}\text{C}-^1\text{H} = 160 \text{ Hz}$ ) and  $\text{C}_f$ , (q,  $\underline{J}^{13}\text{C}-^1\text{H} = 148 \text{ Hz}$ ), and 7a:  $\text{C}_e$ , (d,  $\underline{J}^{13}\text{C}-^1\text{H} = 160 \text{ Hz}$ ),  $\text{C}_f$ , (t,  $\underline{J}^{13}\text{C}-^1\text{H} = 159.7 \text{ Hz}$ ) and  $\text{C}_g$ , (q,  $\underline{J}^{13}\text{C}-^1\text{H} = 144 \text{ Hz}$ ). The smaller magnitude of  $\underline{J}^{13}\text{C}-^1\text{H}$  for  $\text{C}_g$ , in 7a is ascribed to the loss of partial double bond character between the heteroatom (oxygen) and the carbene carbon atom. The  $^{13}\text{C}$ - $^1\text{H}$  coupling constants for the vinylic carbons in 7a and 8 change only slightly upon  $\pi$ -coordination to tungsten carbonyl fragments. Since other factors including changes in electronegativities of the attached atoms or groups could

also influence the magnitude of the  $^{13}\text{C}$ - $^1\text{H}$  coupling constants,<sup>50</sup> the variation of  $J_{^{13}\text{C}-^1\text{H}}$  from  $\underline{6a}$  to  $\underline{8}$  to  $\underline{7a}$  may be too small to be significant as evidence for changes in hybridization of the vinylic carbons.

It was observed that complexes  $\underline{7a-g}$  each exhibited one broad resonance at ca. 205 ppm for the four carbonyl ligands of the tetracarbonyl fragment in their  $^{13}\text{C}$  NMR spectra. A variable temperature  $^{13}\text{C}$  NMR study of  $\underline{7f}$  was undertaken in order to determine at what temperature CO site-exchange occurred on the tungsten tetracarbonyl fragment. Shown in Figure 2 are several  $^{13}\text{C}$  NMR spectra of the carbonyl region of  $\underline{7f}$  at various temperatures. It can be seen in Fig. 2 that fast scrambling of the carbonyl ligands of the  $\text{W}(\text{CO})_5$  fragment occurs, since these CO ligands produced two sharp single resonances down to  $-80^\circ\text{C}$  ( $\delta$  195.97, 200.36 ppm). The  $^{13}\text{C}$  NMR spectrum of a  $\text{CD}_2\text{Cl}_2$  solution of  $\underline{7f}$  shows a broad singlet at 207.16 ppm at  $25^\circ\text{C}$  for the  $\text{W}(\text{CO})_4$  fragment. On cooling, this peak broadens, coalesces at  $-40^\circ\text{C}$ , and reforms into four new sharp resonances of equal intensity at  $-80^\circ\text{C}$ . The steric interaction between the cyclooctene moiety and the carbonyl ligands of the  $\text{W}(\text{CO})_4$  fragment may exert an influence to increase the activation energy of the CO site-exchange process relative to the carbonyl ligands of the  $\text{W}(\text{CO})_5$  fragment.

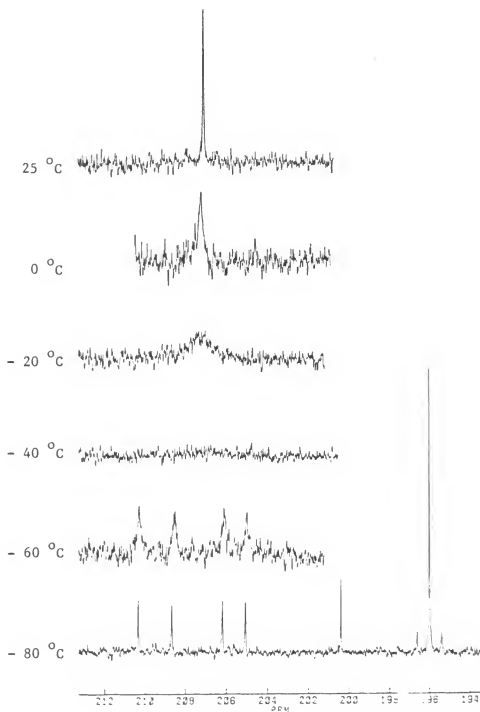


Figure 2. Variable-temperature  $^{13}\text{C}$  NMR spectra of the CO region for  $[\text{W}_2(\text{CO})_9\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{OCH}_3)\overline{\text{C}=\text{CH}(\text{CH}_2)_5\text{CH}_2}\}]$  (7f) in  $\text{CD}_2\text{Cl}_2$  solution.

X-ray Crystal Structures of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)(\eta^2\text{-CH=CH}_2)]\text{W}(\text{CO})_5$  (8) and  $[\text{W}_2(\text{CO})_9\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{OCH}_3)\text{-C}=\text{CH}(\text{CH}_2)_5\text{CH}_2\}]$  (7f). As mentioned previously, there are four possible extreme views of the bonding modes for the coordinated  $\eta^1, \eta^3$ -allyl ligands (A-D). In general, structures having the bonding representation A reveal that C(1) is equidistant from each metal atom. Also, the interaction between olefinic carbons C(2) and C(3) with M(2) suggests that M(2) is approximately equidistant from C(2) and C(3) with a shorter M(2)-C(1) bond distance.<sup>12-14,19,24</sup> Structure B represents the ligand as having a  $\sigma$  M(1)-C(1) bond as well as carbons C(1), C(2), and C(3) bonded symmetrically to M(2) in an  $\eta^3$ -manner. The characteristic feature of this structure B are the similarities of the carbon-carbon bond distances within the bridging moiety, i.e. C(1)-C(2)  $\cong$  C(2)-C(3). Moreover, M(1), C(1), C(2), C(3) are essentially coplanar, with M(1)-C(1) the shortest distance and M(2)-C(3) the longest. In one case, however, M(2) was found to be essentially equidistant to C(1), C(2), and C(3) with iron-carbon bond distances of 2.09, 2.07, and 2.09 Å, respectively.<sup>9b</sup> Structure C exhibits a higher  $\pi$ -bond order between C(1) and C(2), and in some instances, the NMR chemical shift of the proton attached to C(3) can be used as an indication of the extent of contribution from structure C. This is because the proton attached to C(3) in structure C is the most "alkane-like" and therefore appears at highest

field.<sup>12</sup>

Single crystal X-ray crystallographic studies were carried<sup>46</sup> out on complexes 7f and 8 to increase our understanding of the bonding within these systems. The molecular structure of 7f (Fig. 3) reveals two tungsten atoms with a single bond distance of 3.1909(5) Å which are symmetrically bridged by the carbene carbon atom with distances of 2.296(9) Å (W(1)-C(10)) and 2.293(9) Å (W(2)-C(10)). This 3.1909(5) Å W(1)-W(2) bond distance is typical of other tungsten-tungsten single bond distances.<sup>26,58,59</sup> Moreover, the tungsten-carbene bond distances are shorter than the 2.34(1) Å W-C single bond distance in the W(0) compound,  $\text{Et}_4\text{N}^+(\text{CO})_5\text{WCH}(\text{OCH}_3)\text{C}_6\text{H}_5^-$ ,<sup>60</sup> and is longer than the 2.17(2) Å W=C double bond of 8 and the 1.90(5) Å W≡C triple bond of  $\text{I}(\text{CO})_4\text{WCC}_6\text{H}_5$ .<sup>61</sup> In complex 7f, the C(10)-W(1) distance of 2.296(9) Å is 0.043 Å shorter than C(11)-W(1) distance (2.339(9) Å) and 0.087 Å shorter than C(12)-W(1) distance (2.383(9) Å), respectively. This appears to be due to the electronegativity of the methoxy group attached to C(10) which decreases the electron density on C(10) and causes enhanced back-donation of electron density from W(1) to C(10). The nearly equal distances of C(11)-C(10) (1.44(1) Å) and C(11)-C(12) (1.42(1) Å), which are substantially longer than the standard uncoordinated alkene bond length of 1.33 Å<sup>63</sup> and shorter than the C-C single bond length of 1.54 Å, can be regarded as having allylic

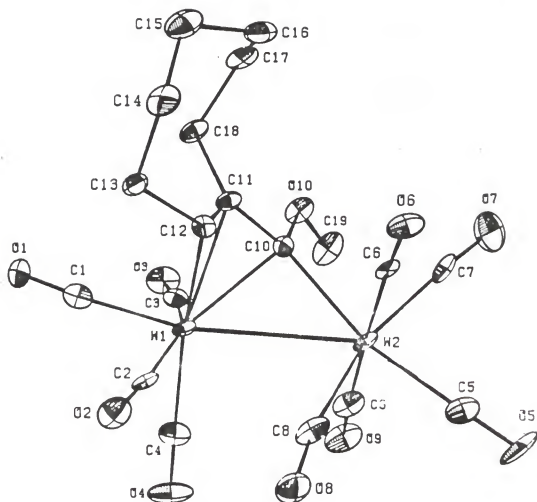


Figure 3. Molecular structure and atom labeling scheme for  $[W_2(CO)_9(\mu-\eta^1, \eta^3-C(OCH_3)\overline{C=CH(CH_2)_5CH_2})]$  (7f)

Table VII. Bond Distances (Å) and Angles (deg) for



| Atoms          |  | Distance  | Atoms          |  | Distance |
|----------------|--|-----------|----------------|--|----------|
| 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)   | W(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)  |

| Atoms                   |  |  | Angle    | Atoms                   |  |  | Angle    |
|-------------------------|--|--|----------|-------------------------|--|--|----------|
| 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) | W(2) -- 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) |
| W(1) -- W(2) -- C(7)    |  |  | 83.2(4)  | C(6) -- W(2) -- C(7)    |  |  | 83.7(4)  |
| C(5) -- W(2) -- C(8)    |  |  | 70.1(3)  | C(5) -- W(2) -- C(8)    |  |  | 80.6(4)  |
| W(1) -- W(2) -- C(8)    |  |  | 90.1(4)  | C(7) -- W(2) -- C(8)    |  |  | 162.6(4) |
| C(6) -- W(2) -- C(9)    |  |  | 81.1(3)  | C(5) -- W(2) -- C(9)    |  |  | 88.7(4)  |
| C(8) -- W(2) -- C(9)    |  |  | 178.5(4) | C(7) -- W(2) -- C(9)    |  |  | 95.1(4)  |
| C(5) -- W(2) -- C(9)    |  |  | 90.8(4)  | C(5) -- W(2) -- C(10)   |  |  | 46.0(2)  |
| C(7) -- W(2) -- C(10)   |  |  | 165.3(4) | C(6) -- W(2) -- C(10)   |  |  | 86.9(3)  |
| C(9) -- 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) -- W(2) -- C(10)  |  |  | 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(17) -- C(18) -- C(17) |  |  | 109.0(8) |

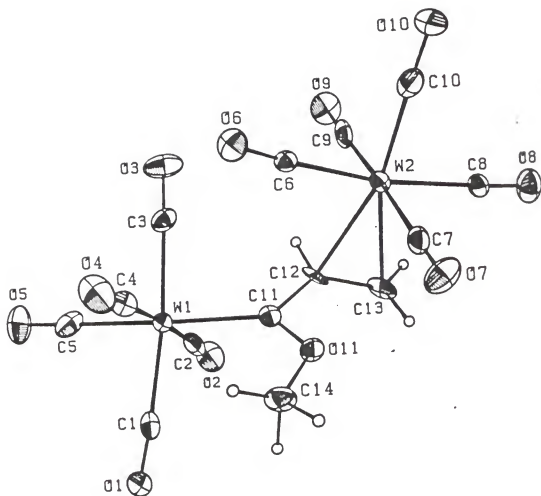


Figure 4. Molecular structure and atom labeling scheme for  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)(\eta^2\text{-CH=CH}_2)]\text{W}(\text{CO})_5$  (**8**).



Table VIII. Bond Distances (Å) and Angles (deg) for  
 $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)(\eta^2\text{-CH=CH}_2)]\text{W}(\text{CO})_5$  (8)

| Atoms          | Distance | Atoms          | Distance |
|----------------|----------|----------------|----------|
| W(2) -- C(1)   | 2.03(3)  | W(2) -- C(2)   | 2.06(2)  |
| W(2) -- C(1)   | 2.06(2)  | W(1) -- C(4)   | 2.03(2)  |
| W(2) -- C(5)   | 2.03(2)  | W(1) -- C(11)  | 2.17(2)  |
| W(2) -- C(6)   | 2.03(2)  | W(2) -- C(7)   | 2.06(2)  |
| W(2) -- C(8)   | 2.05(2)  | W(2) -- C(9)   | 2.05(2)  |
| W(2) -- C(10)  | 1.98(2)  | W(2) -- C(13)  | 2.40(2)  |
| W(2) -- C(12)  | 2.37(2)  | O(3) -- C(1)   | 1.25(2)  |
| O(2) -- C(2)   | 1.34(2)  | O(3) -- C(1)   | 1.11(2)  |
| O(4) -- C(4)   | 1.24(3)  | O(5) -- C(5)   | 1.33(2)  |
| O(8) -- C(4)   | 1.35(2)  | O(7) -- C(7)   | 1.32(2)  |
| O(8) -- C(8)   | 1.33(2)  | O(9) -- C(9)   | 1.35(3)  |
| O(10) -- C(10) | 1.35(3)  | O(11) -- C(11) | 1.33(2)  |
| O(11) -- C(14) | 1.47(2)  | C(11) -- C(12) | 1.81(2)  |
| C(12) -- C(13) | 1.36(3)  |                |          |

| Atoms                   | Angle    | Atoms                  | Angle    |
|-------------------------|----------|------------------------|----------|
| C(1) -- W(1) -- C(2)    | 90.4(8)  | C(1) -- W(1) -- C(3)   | 174.0(8) |
| C(2) -- W(1) -- C(3)    | 92.0(8)  | C(1) -- W(1) -- C(4)   | 86.0(8)  |
| C(2) -- W(1) -- C(6)    | 174.5(8) | C(3) -- W(1) -- C(4)   | 91.2(8)  |
| C(3) -- W(1) -- C(5)    | 84.8(8)  | C(2) -- W(1) -- C(8)   | 89.6(8)  |
| C(3) -- W(1) -- C(9)    | 87.8(6)  | C(4) -- W(1) -- C(8)   | 89.3(8)  |
| C(1) -- W(1) -- C(11)   | 96.3(7)  | C(2) -- W(1) -- C(11)  | 84.0(7)  |
| C(3) -- W(1) -- C(11)   | 89.2(7)  | C(4) -- W(1) -- C(11)  | 90.4(8)  |
| C(9) -- W(2) -- C(11)   | 174.5(8) | C(4) -- W(2) -- C(7)   | 89.3(7)  |
| C(4) -- W(2) -- C(8)    | 147.9(7) | C(7) -- W(2) -- C(8)   | 87.4(7)  |
| C(4) -- W(2) -- C(9)    | 90.7(7)  | C(7) -- W(2) -- C(9)   | 177.4(7) |
| C(8) -- W(2) -- C(9)    | 91.2(7)  | C(4) -- W(2) -- C(10)  | 82.8(8)  |
| C(7) -- W(2) -- C(10)   | 92.9(8)  | C(8) -- W(2) -- C(10)  | 85.8(8)  |
| C(9) -- W(2) -- C(10)   | 89.7(8)  | C(4) -- W(2) -- C(12)  | 83.7(7)  |
| C(7) -- W(2) -- C(12)   | 95.2(7)  | C(8) -- W(2) -- C(12)  | 100.2(7) |
| C(9) -- W(2) -- C(12)   | 82.2(7)  | C(10) -- W(2) -- C(12) | 106.3(7) |
| C(4) -- W(2) -- C(13)   | 115.2(7) | C(7) -- W(2) -- C(13)  | 85.4(7)  |
| C(8) -- W(2) -- C(13)   | 74.1(7)  | C(9) -- W(2) -- C(13)  | 92.0(7)  |
| C(10) -- W(2) -- C(13)  | 141.9(7) | C(12) -- W(2) -- C(13) | 33.2(7)  |
| C(11) -- O(11) -- C(14) | 120(1)   | W(1) -- C(1) -- O(3)   | 178(2)   |
| W(1) -- C(1) -- O(2)    | 174(2)   | W(1) -- C(1) -- O(5)   | 178(2)   |
| W(2) -- C(4) -- O(4)    | 177(2)   | W(1) -- C(1) -- O(8)   | 178(2)   |
| W(2) -- C(4) -- O(8)    | 178(2)   | W(2) -- C(7) -- O(7)   | 179(2)   |
| W(1) -- C(1) -- O(11)   | 174(2)   | W(2) -- C(9) -- O(9)   | 179(2)   |
| W(1) -- C(1) -- C(12)   | 120(1)   | W(1) -- C(1) -- O(11)  | 133(1)   |
| W(2) -- C(12) -- C(11)  | 131(1)   | O(11) -- C(1) -- C(12) | 107(2)   |
| C(11) -- C(12) -- C(11) | 131(1)   | W(2) -- C(12) -- C(13) | 73(2)    |
| C(11) -- C(12) -- C(11) | 131(1)   | W(1) -- C(12) -- C(12) | 75(1)    |

delocalization within the C(10)-C(11)-C(12) group. This structural data is consistent with that found in compound 8 which contains a 1.51(2) Å C-C single bond (C(11)-C(12)) and a 1.36(3) Å C-C double bond (C(12)-C(13)). Furthermore, the C(11)-O(11) bond distance of 1.32(2) Å in 8 (Figure 4) is shorter than the C(sp<sup>2</sup>)-O theoretical bond distance of 1.41 Å<sup>64</sup> and indicates that the oxygen substituent is engaged in π-bonding to the carbene carbon. Likewise, the longer C(10)-O(10) bond distance of 1.38(1) Å found in complex 7f may be ascribed to the loss of any multiple bonding between these two atoms. These results suggest that the μ-η<sup>1</sup>, η<sup>3</sup>-allyl ligand in 7f can be viewed as having either structure A or B.

Another interesting feature of structure 8 is the finding that no trans-influence is observed for the carbonyl group trans to the carbene ligand (C(5)). This influence has, however, been observed in other carbene complexes.<sup>60,65</sup> On the other hand, the carbonyl ligand trans to the alkene group in this complex (C(10)) is 0.06 Å shorter than the average of cis tungsten-carbonyl distances. This is consistent with a greater degree of back-bonding to the trans CO.<sup>60</sup>

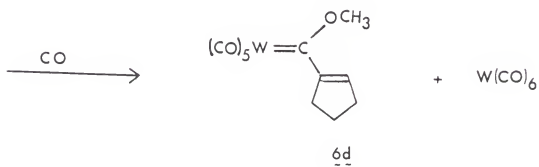
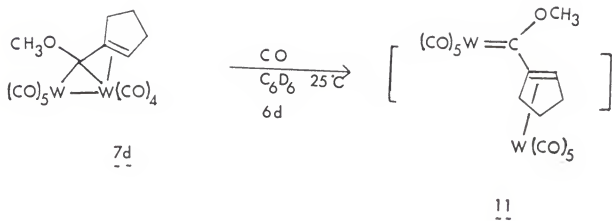
Reactions of 7a, 7d, and 8 with carbon monoxide. The reactions of 7a, 7d, and 8 with carbon monoxide were carried out in Wilmad 5 mm 507-TR screw cap NMR tubes which were sealed with teflon-faced silicon rubber septums. A 12-in



however, affords complex 7a in 65% yield with loss of one carbon monoxide ligand. As was mentioned before, complex 7a can be obtained directly from 6a in 61% yield by treating a hexane/THF solution of 6a with  $(\text{CO})_5\text{W}\cdot\text{THF}$ . Complex 8 was not observed during this latter reaction.

In an attempt to prepare analogs of 8, complex 7d was treated with carbon monoxide (Scheme IX) in a similar manner as described above. The reaction was followed by  $^1\text{H}$  NMR spectroscopy and only resonances for complexes 7d and 6d were observed. At no time were any resonances corresponding to complex 11 observed. At the end of the reaction, which required ca. 6 days,  $^1\text{H}$  NMR spectroscopy revealed only complex 6d while the  $(^1\text{H})^{13}\text{C}$  NMR spectrum showed 6d along with  $\text{W}(\text{CO})_6$  ( $\delta$  191.09 ppm).

Scheme IX



## Experimental Section

All reactions involving organometallic reagents were carried out under a nitrogen atmosphere. Hexane, pentane, methylene chloride, and toluene were freshly distilled from calcium hydride under nitrogen. Diethyl ether (anhydrous) was pre-dried over sodium wire and freshly distilled from sodium/benzophenone under nitrogen. Tetrahydrofuran was stored over potassium hydroxide pellets, pre-dried from sodium wire, and freshly distilled from sodium/benzophenone under nitrogen. Solutions were transferred by syringe or by cannula under positive nitrogen pressure.  $W(CO)_6$  was obtained from Columbia Organic Chemicals Co., Inc. Aldrich reagent grade vinyl magnesium bromide, tin tetrachloride, 2-bromopropene, 2,3-dibromobutane, bromine, quinoline, trichlorovinylsilane, and t-butyllithium were used without further purification. Trimethyloxonium tetrafluoroborate was obtained from Lancaster Synthesis Ltd. The low temperature chromatography was carried out on a 3.0 cm x 22 cm column packed with 230-400 mesh (60 Å) silica gel (Fig. 5). The silica gel was purchased from Aldrich Chemical Co., Inc. Proton NMR (400.14 MHz) and C-13 NMR (100.61 MHz) spectra were recorded on a Bruker WM-400 spectrometer. The multiplicities of the NMR spectra absorptions are indicated by : s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; dd, doublet of doublets; and tt, triplet of triplets. Mass spectra were obtained on a

Finnigan 4000 series mass spectrometer. Elemental analyses were performed by Microlytics, South Deerfield, MA 01373. The X-ray structures were determined by Professor Robin D. Rogers, Northern Illinois University, DeKalb, Illinois 60115.

Preparation of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{CH}=\text{CH}_2]^{51}$  (6a). To a stirred solution of 2.00 g (5.68 mmol) of tungsten hexacarbonyl in 100 mL of dry ether under nitrogen was added dropwise 0.174 g (5.10 mmol) of vinylolithium<sup>52</sup> in 25 mL of dry ether via cannula. After the reaction mixture was stirred 1 h at room temperature the solvent was removed under high vacuum. To the resulting orange-brown residue was then added 100 mL of dry methylene chloride and the residue scraped off the sides of the flask. Trimethyloxonium tetrafluoroborate (0.75 g, 5.06 mmol) was added and dispersed in the mixture by rapid stirring. Deoxygenated water (2 mL) was added and the mixture stirred for 1 min. The solution was quickly dried by filtering through a layer of anhydrous  $\text{Na}_2\text{SO}_4$  mixed with celite. After the solvent was removed under high vacuum, the dark red residue was chromatographed on silica gel at 0 °C. Eluting the column with hexane produced a red band which was collected under nitrogen. Removal of the solvent afforded 0.50 g (25%) of complex 6a as a dark red liquid. Further elution of the column with 10%  $\text{CH}_2\text{Cl}_2$ /hexane produced another red band which was collected and the solvent concentrated under vacuum. Cooling this solvent at

$-12^{\circ}\text{C}$  gave 0.65 g (18%) of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)(\eta^2\text{-CH=CH}_2)]\text{W}(\text{CO})_5$  (8).

$(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{CH=CH}_2]$  (6a)

$^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  7.01 (dd, 1 H,  $\underline{J} = 16.9, 10.3$  Hz, =CH); 5.28 (dd, 1 H,  $\underline{J} = 16.9, 1.4$  Hz, =CH<sub>2</sub>); 4.63 (dd, 1 H,  $\underline{J} = 10.3, 1.4$  Hz, =CH<sub>2</sub>); 3.72 (s, 3 H, OCH<sub>3</sub>).

$^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  312.49 (s, C (carbene)); 203.77 (s, trans-CO); 197.44 (s, 4 cis-CO), 152.44 (d,  $\underline{J}^{13}\text{C-}^1\text{H} = 161$  Hz, =CH); 119.30 (t,  $\underline{J}^{13}\text{C-}^1\text{H} = 160$  Hz, =CH<sub>2</sub>); 68.76 (q,  $\underline{J}^{13}\text{C-}^1\text{H} = 148$  Hz OCH<sub>3</sub>).

$(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)(\eta^2\text{-CH=CH}_2)]\text{W}(\text{CO})_5$  (8)

$^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  5.16 (dd, 1 H,  $\underline{J} = 13.6, 8.2$  Hz, =CH); 3.67 (s, 3H, OCH<sub>3</sub>); 2.82 (d, 1 H,  $\underline{J} = 13.6$  Hz, =CH<sub>2</sub>); 2.47 (d, 1 H,  $\underline{J} = 8.2$  Hz, =CH<sub>2</sub>).

$^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  310.71 (s, C (carbene) ); 202.78, 201.56 (s, 2 trans-CO); 197.52, 194.81 (s, 8 cis-CO); 91.60 (d,  $\underline{J}^{13}\text{C-}^1\text{H} = 165$  Hz, =CH); 67.32 (q,  $\underline{J}^{13}\text{C-}^1\text{H} = 148$  Hz, OCH<sub>3</sub>); 48.22 (t,  $\underline{J}^{13}\text{C-}^1\text{H} = 165$  Hz, =CH<sub>2</sub>).

Preparation of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{C}(\text{CH}_3)=\text{CH}_2]$  (6b). To a stirred solution of 0.168 g (0.024 mol) of finely cut lithium in 40 mL of dry ether under nitrogen at room temperature was added dropwise 1.06 mL (0.012 mol) of 2-bromopropene in 10 mL dry ether to maintain a gentle reflux. After refluxing for 4 h, the mixture was transferred via cannula to a stirred suspension of tungsten hexacarbonyl (3.52 g, 0.01 mol) in 150 mL dry ether over a 30-min period



at room temperature. After the reaction mixture was stirred for 1 h at room temperature the ether was removed under aspirator vacuum. To the resulting red-brown residue was then added 50 mL of degassed water and the residue scraped off the sides of the flask. Trimethyloxonium tetrafluoroborate (1.48 g, 0.01 mol) was added and dispersed in the mixture by rapid stirring. The mixture was extracted with three 100 mL portions of pentane in the air. After the solution was dried over anhydrous magnesium sulfate and filtered, the pentane was removed by aspirator vacuum and chromatographed on silica gel. (3 cm x 12 cm, hexane as eluant) to give 1.74 g (43%) of 6b.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.49 (broad s, 1 H, =CH<sub>2</sub>); 5.43 (broad s, 1 H, =CH<sub>2</sub>); 4.62 (s, 3 H, OCH<sub>3</sub>); 1.89 (s, 3 H, CH<sub>3</sub>).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  327.01 (C (carbene)); 203.27 (trans-CO); 197.21 (4 cis-CO); 160.50 (=CH); 121.68 (=CH<sub>2</sub>); 69.58 (OCH<sub>3</sub>); 19.21 (CH<sub>3</sub>).

Preparation of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{cis}-\text{C}(\text{CH}_3)=\text{CHCH}_3]$  (6c). To a stirred solution of 0.168 g (0.024 mol) of finely cut lithium in 40 mL ether under nitrogen at room temperature was added dropwise 1.22 mL (0.012 mol) of 2-bromo-2-butene<sup>53</sup> in 10 mL ether to maintain a gentle reflux. After refluxing for 4 h, the mixture was transferred via cannula to a stirred suspension of tungsten hexacarbonyl (3.52 g, 0.01 mol) in 150 mL of ether over a 30-min period at room temperature. After the reaction mixture was stirred 1 h at

room temperature the ether was removed under aspirator vacuum. To the resulting red-brown residue was then added 50 mL of degased water and the residue scraped off the sides of the flask. Trimethyloxonium tetrafluoroborate (1.48 g, 0.01 mol) was added and dispersed in the mixture by rapid stirring. The mixture was extracted with three 100 mL portions of pentane in the air. After the solution was dried over anhydrous magnesium sulfate and filtered, the pentane was removed by aspirator vacuum. The residue was chromatographed on silica gel (3.0 cm x 12 cm, hexane as eluant) to give a cis & trans isomeric mixture of 6c. The cis and trans isomers was separated by medium pressure liquid chromatography using hexane as solvent on silica gel. Concentration of the less polar fraction and cooling to -12 °C produced 0.47 g ( 11% ) of cis-6c.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.72 (q, 1 H,  $\underline{J} = 6.8$  Hz, =CH); 4.63 (s, 3 H,  $\text{OCH}_3$ ); 1.90 (d, 3 H,  $\underline{J} = 6.8$  Hz,  $\text{CH}_3$ ); 1.79 (s, 3 H,  $\text{CH}_3$ ).

$\text{MS}$  (EI, 16.6 eV, 28 °C): 422  $\text{M}^+$ (33), 394 (100), 366 (40), 338 (47), 310 (46), 282 (74).

Preparation of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\overline{\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}_2}]^{54}$  (6d). To a stirred solution of 0.357 g (0.051 mol) of finely cut lithium in 10 mL of THF under nitrogen at room temperature was added dropwise 1.20 g (0.0081 mol) of 1-bromocyclopentene<sup>55</sup> in 3 ml of THF to maintain a gentle reflux. After refluxing for 1 h, the mixture was transferred via cannula to a stirred suspension of tungsten hexacarbonyl

(2.37 g, 0.0067 mol) in 50 mL THF over a 30-min period at room temperature. After the reaction mixture was stirred 1 h at room temperature the THF was removed under high vacuum. To the resulting red-brown residue was then added 50 mL of degassed water and the residue scraped off the sides of the flask. Trimethyloxonium tetrafluoroborate (1.00 g, 0.0067 mol) was added and dispersed in the mixture by rapid stirring. The mixture was extracted with three 100 mL portions pentane in the air. After the solution was dried over anhydrous magnesium sulfate and filtered, the pentane was removed under aspirator vacuum and chromatographed on silica gel (3.0 cm x 12 cm, hexane as eluant). Concentration of the dark red fraction and cooling to  $-12^{\circ}\text{C}$  produced 1.19 g (41%) of 6d.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.29 (broad s, 1 H, =CH); 4.62 (s, 3 H,  $\text{OCH}_3$ ); 2.60-2.50 (m, 4 H,  $\text{CH}_2$ ); 1.95 (p, 2 H,  $J = 7.4$  Hz,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  311.13 (C (carbene) ); 203.00 ( trans-CO ); 197.97 (4 cis-CO); 161.17 ( =C ); 157.28 ( =CH ); 69.16 ( $\text{OCH}_3$ ); 34.84, 31.68, 23.06 ( $\text{CH}_2$ ).

Preparation of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\overline{\text{C}=\text{CH}(\text{CH}_2)_3\text{CH}_2}]$  (6e). To a stirred solution of 1.88 g (4.9 mmol) of cyclohexanone 2,4,6-triisopropylbenzenesulfonylhydrazone<sup>56</sup> in 10 mL of THF under nitrogen at  $-78^{\circ}\text{C}$  was added dropwise 4.9 mL (9.8 mmol) of 2 M n-butyllithium in hexane. After stirring for 30 min at  $-78^{\circ}\text{C}$ , the mixture was transferred via cannula to

a stirred suspension of tungsten hexacarbonyl (1.72 g, 4.9 mmol) in 75 mL dry ether over 30-min period at room temperature. After the reaction mixture was stirred for 1 h at room temperature the ether was removed under aspirator vacuum. To the resulting red-brown residue was then added 40 mL of dry pentane and the residued scraped off the sides of the flask. The pentane was decantated and to the residue was added 45 mL of degased water. Trimethyloxonium tetrafluoroborate ( 0.72 g, 4.9 mmol) was added and dispersed in the mixture by rapid stirring. The mixture was extracted with three 100 mL portions of pentane in the air. After the solution was dried over anhydrous sodium sulfate and filtered the pentane was removed by aspirator vacuum and chromatographed on silica gel ( 3.0 cm x 12 cm, hexane as eluant) to give 1.09 g ( 49% ) of 6e.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.99 (broad s, 1 H, =CH); 4.62 (s, 3 H, OCH<sub>3</sub>); 2.34-2.31 (m, 2 H, CH<sub>2</sub>); 2.24-2.22 (m, 2 H, CH<sub>2</sub>); 1.65-1.60 (m, 4 H, CH<sub>2</sub>).

Preparation of (CO)<sub>5</sub>W[C(OCH<sub>3</sub>)C=CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>] (6f). To a stirred solution of 1.60 g (0.0084 mol) of 1-bromocyclooctene<sup>55</sup> in 25 mL THF under nitrogen at -78 °C was added dropwise 10 mL of 1.7 M (0.017 mol) t-butyllithium solution in pentane. After stirring for 4 h, the mixture was transferred via cannula to a stirred suspension of tungsten hexacarbonyl (2.50 g, 0.0071 mol) in 30 mL THF over a 30-min period at room temperature. After the reaction mixture was stirred for 1 h at room temperature the solvent

was removed under high vacuum. To the resulting red-brown residue was then added 50 mL of degased water and the residue scraped off the sides of the flask. Trimethyloxonium tetrafluoroborate (1.05 g, 0.0079 mol) was then added and dispersed in the mixture by rapid stirring. The mixture was extracted with three 100 mL portions of pentane in the air. After the solution was dried over anhydrous magnesium sulfate and filtered, the pentane was removed under aspirator vacuum and chromatographed on silica gel (3.0 cm x 12 cm, hexane as eluant). Concentration of the dark red fraction and cooling to  $-12^{\circ}\text{C}$  produced 2.21 g (65%) of 6f.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.06 (t, 1 H,  $J = 8.6$  Hz, =CH); 4.65 (s, 3 H,  $\text{OCH}_3$ ); 2.45-2.38 (m, 4 H,  $\text{CH}_2$ ); 1.70-1.60 (m, 2 H,  $\text{CH}_2$ ); 1.55-1.40 (m, 4 H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  322.67 (C (carbene)); 202.96 (trans-CO), 197.92 (4 cis-CO); 159.03 ( =C ); 151.65 ( =CH ), 69.67 ( $\text{OCH}_3$ ); 29.81, 28.91, 28.44, 26.78, 25.88, 25.62 ( $\text{CH}_2$ ).

Preparation of  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{C}(\text{Si}(\text{CH}_3)_3)=\text{CH}_2]$  (6g). The procedure described for the preparation of 6f was followed except that 1-bromo-1-(trimethylsilyl)ethylene<sup>57</sup> was used.

The product was obtained as dark red crystals in 33% yield.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.71 (s, 1 H, =CH); 5.45 (s, 1 H, = $\text{CH}_2$ ); 4.5 (s, 3 H,  $\text{OCH}_3$ ); 0.15 (s, 9 H,  $\text{SiMe}_3$ ).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  334.45 (C(carbene)); 203.88 (trans-CO); 197.86(4 cis-CO); 172.13 ( =C ); 125.17 ( = $\text{CH}_2$  ); 68.24 ( $\text{OCH}_3$ ); -0.91 ( $\text{SiMe}_3$ ).

Preparation of  $[W_2(CO)_9\{\mu-\eta^1, \eta^3-C(OCH_3)CH=CH_2\}]$  (7a). Freshly dried and degassed THF (50 mL) was transferred in vacuo into a 60 mL water-jacketed Schlenk tube charged with  $W(CO)_6$  (0.36 g, 1.02 mmol). This solution was irradiated under  $N_2$  pressure at 25 °C for 4 h by using an Hanovia medium pressure mercury-vapor lamp, during which time the solution change color to light yellow. The THF solution was transferred into a suspension of  $(CO)_5W[C(OCH_3)CH=CH_2]$  (6a) (0.25 g, 0.64 mmol) in 10 mL hexane at room temperature via cannula. After the reaction mixture was stirred for 15 min at room temperature the solvent was removed under high vacuum. The resulting dark red residue was then chromatographed on silica gel (3.0 cm x 12 cm,  $CH_2Cl_2$ /hexane 1 : 10) at -30 °C. Eluting first was a mixture of  $W(CO)_6$  and the starting tungsten carbene complex 6a followed by 7a. Recrystallization from hexane gave 0.26 g (60%) of 7a as dark red crystals.

$^1H$  NMR ( $C_6D_6$ )  $\delta$  4.75 (dd, 1 H,  $J = 9.5, 7.7$  Hz, =CH); 3.10 (s, 3 H,  $OCH_3$ ); 2.98 (dd, 1 H,  $J = 7.7, 1.7$  Hz, =CH<sub>2</sub>); 1.96 (dd, 1 H,  $J = 9.5, 1.7$  Hz, =CH<sub>2</sub>).

$^{13}C$  NMR ( $C_6D_6$ )  $\delta$  232.56 (s, C(carbene) ); 205.10 (s, 4 CO); 201.24 (s, trans-CO); 196.14 (s, 4 cis-CO); 80.92 (d,  $J_{13C-1H} = 160.0$  Hz, =CH); 59.00 (q,  $J_{13C-1H} = 144.3$  Hz,  $OCH_3$ ); 56.15 (t,  $J_{13C-1H} = 159.7$  Hz, =CH<sub>2</sub>).

Preparation of  $[W_2(CO)_9\{\mu-\eta^1, \eta^3-C(OCH_3)C(CH_3)=CH_2\}]$  (7b). The procedure described for the preparation of  $[W_2(CO)_9\{\mu-$

$\eta^1, \eta^3\text{-C}(\text{OCH}_3)\text{CH}=\text{CH}_2$ ] (7a) was follow except that 6d was used. The product was obtained as dark red crystals : yield 68%, mp 84 °C (dec.). An analytical sample was obtained after three further recrystallizations.

$^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  3.53 (s, 3 H,  $\text{OCH}_3$ ); 3.06 (d, 1 H,  $\underline{J}$  = 1.9 Hz, = $\text{CH}_2$ ); 1.90 (d, 1 H,  $\underline{J}$  = 1.9 Hz, = $\text{CH}_2$ ); 1.83 (s, 3 H,  $\text{CH}_3$ ).

$^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  231.13 (s, C(carbene) ); 206.12 (s, 4 CO); 199.64 (s, trans-CO); 195.77 (s, 4 cis-CO); 107.61 (s, =C ); 63.92 (q,  $\underline{J}^{13}\text{C-}^1\text{H}$  = 144.0 Hz,  $\text{OCH}_3$ ); 63.45 (t,  $\underline{J}^{13}\text{C-}^1\text{H}$  = 159.0 Hz, = $\text{CH}_2$ ); 22.67 (q,  $\underline{J}^{13}\text{C-}^1\text{H}$  = 128.9 Hz,  $\text{CH}_3$ ).

Anal. Calcd. for  $\text{C}_{14}\text{H}_8\text{O}_{10}\text{W}_2$  : C, 23.89; H, 1.14. Found : C, 24.07; H, 1.23.

Preparation of [ $\text{W}_2(\text{CO})_9\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{OCH}_3)\text{cis-}(\text{CH}_3)\text{CH}=\text{CH}_2\}$ ] (7c). The procedure described for the preparation of 7a was follow except that 6c was used and the chromatography was conducted at room temperature. The product was obtained as dark red crystals: yield 21%, mp: 86-88 °C (dec.). An analytical sample was obtained after three further recrystallization from 30%  $\text{CH}_2\text{Cl}_2$ /hexane.

$^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  3.58 (s, 3 H,  $\text{OCH}_3$ ); 2.93 (q, 1 H,  $\underline{J}$  = 6.2 Hz, =CH); 1.82 (s, 3 H,  $\text{CH}_3$ ), 1.71 (d, 3 H,  $\underline{J}$  = 6.1 Hz,  $\text{CH}_3$ ).

$^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  233.88 ( C(carbene) ); 206.37 (4 CO); 199.59 (trans-CO); 195.87 (4 cis-CO); 110.77( =C ); 84.93( =CH ); 64.03 ( $\text{OCH}_3$ ); 17.10, 15.69 ( $\text{CH}_3$ ).

Anal. Calcd. for  $C_{15}H_{10}O_{10}W_2$  : C, 25.09; H, 1.40. Found : C, 25.29; H, 1.45.

Preparation of  $[W_2(CO)_9\{\mu-\eta^1, \eta^3-C(OCH_3)\overline{C=CH(CH_2)_2CH_2}\}]$  (7d). The procedure described for the preparation of 7a was followed, except that 6d was used and the chromatography was conducted at room temperature. The product was obtained as dark red crystals : yield 34%, mp: 78-84 °C (dec.).

$^1H$  NMR ( $C_6D_6$ )  $\delta$  3.67 (s, 3 H, OCH<sub>3</sub>); 3.53 (d, 1 H,  $\underline{J}$  = 3.3 Hz, =CH); 2.64-2.51 (m, 2 H, CH<sub>2</sub>); 2.36-2.24 (m, 2 H, CH<sub>2</sub>); 1.44-1.34 (m, 2 H, CH<sub>2</sub>).

$^{13}C$  NMR ( $C_6D_6$ )  $\delta$  230.63 ( C(carbene) ); 205.98 (4 CO); 200.16 (trans-CO); 195.94 (4 cis-CO); 118.52 ( =C ); 89.12 ( =CH ); 63.54 (OCH<sub>3</sub>); 34.42, 32.05, 21.15 (CH<sub>2</sub>).

Anal. Calcd. for  $C_{16}H_{10}O_{10}W_2$ : C, 26.33; H, 1.38. Found: C, 26.42; H, 1.40.

Preparation of  $[W_2(CO)_9\{\mu-\eta^1, \eta^3-C(OCH_3)\overline{C=CH(CH_2)_3CH_2}\}]$  (7e). The procedure described for the preparation of 7a was followed, except that 6e was used and the chromatography was conducted at room temperature. The product was obtained as dark red crystals: yield 21%, mp: 100-102 °C (dec.).

$^1H$  NMR ( $C_6D_6$ )  $\delta$  3.64 (s, 3 H, OCH<sub>3</sub>); 3.58 (m, 1 H, =CH); 3.01 (tt, 1 H,  $\underline{J}$  = 5.7, 4.9 Hz, CH<sub>2</sub>); 2.45 (m, 1 H, CH<sub>2</sub>); 2.35 (m, 2 H, CH<sub>2</sub>); 1.25-0.85 (m, 4 H, CH<sub>2</sub>).

$^{13}C$  NMR ( $C_6D_6$ )  $\delta$  233.73 ( C(carbene) ); 206.53 (4 CO); 199.33 (trans-CO); 195.76 (4 cis-CO); 113.30 ( =C ); 90.74 ( =CH ); 63.87 (OCH<sub>3</sub>); 29.65, 27.08, 21.45, 21.43 (CH<sub>2</sub>).



Anal. Calcd. for  $C_{17}H_{12}O_{10}W_2$ : C, 27.44; H, 1.63. Found: C, 27.56; H, 1.67.

Preparation of  $[W_2(CO)_9\{\mu-\eta^1, \eta^3-C(OCH_3)\overline{C=CH(CH_2)_5CH_2}\}]$  (7f). The procedure described for the preparation of 7a was followed except that 6f was used. The product was obtained as dark red crystals: yield 90%, mp: 83-84 °C (dec.).

$^1H$  NMR ( $C_6D_6$ )  $\delta$  3.60 (s, 3 H,  $OCH_3$ ), 3.03 (dd, 1 H,  $\underline{J} = 4.5, 4.6$  Hz, =CH); 2.89 (tt, 1 H,  $\underline{J} = 3.3, 3.0$  Hz,  $CH_2$ ); 2.46 (m, 1 H,  $CH_2$ ); 1.90-0.90 (m, 10 H,  $CH_2$ ).

$^{13}C$  NMR ( $C_6D_6$ )  $\delta$  233.85 (s, C(carbene)); 206.61 (s, 4 CO); 199.45 (trans-CO); 195.69 (4 cis-CO); 111.24 (=C); 89.81(=CH); 64.09 ( $OCH_3$ ), 32.33, 30.91, 30.28, 29.65, 26.76, 26.13 ( $CH_2$ ).

Anal. Calcd. for  $C_{19}H_{16}O_{10}W_2$ : C, 29.56; H, 2.09. Found: C, 29.68; H, 2.06.

Preparation of  $[W_2(CO)_9\{\mu-\eta^1, \eta^3-C(OCH_3)C(SiMe_3)=CH_2\}]$  (7g). The procedure described for the preparation of 7a was followed except that 6g was used. The product was obtained as dark red viscous liquid: yield 78%.

$^1H$  NMR ( $C_6D_6$ )  $\delta$  3.58 (s, 3 H,  $OCH_3$ ); 3.45 (s, 1 H, = $CH_2$ ); 2.16 (s, 1 H, = $CH_2$ ); 0.10 (s, 9 H,  $SiMe_3$ ).

$^{13}C$  NMR ( $C_6D_6$ )  $\delta$  235.78 (s, C(carbene)); 206.75 (s, 4 CO); 199.41 (s, trans-CO); 195.51 (s, 4 cis-CO), 102.11 (s, =C); 63.61 (t,  $\underline{J}^{13}C-^1H = 161.8$  Hz, = $CH_2$ ); 63.38 (q,  $\underline{J}^{13}C-^1H = 144.5$ ,  $OCH_3$ ); 26.06 (m,  $SiMe_3$ ).

Anal. Calcd. for  $C_{16}H_{14}O_{10}SiW_2$ : C, 25.22; H, 1.85. Found: C, 25.36; H, 1.85.

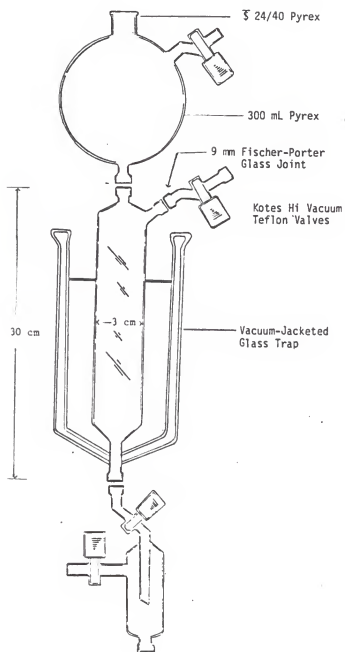


Fig. 5 Diagram of low temperature chromatography apparatus

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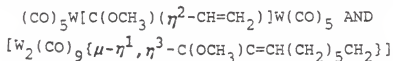
## VITA

The author was born in Taichung, Taiwan on August 4, 1959. A Bachelor of Science degree in chemistry was received from Tunghai University, Taichung, Taiwan in June of 1981.

Upon graduation, the author went into the military service as a second lieutenant for two years. Then he worked as a teaching assistant in Department of Chemistry, Tunghai University for one year.

In August, 1984, he enrolled in the Department of Chemistry, Kansas State University in pursuit of a M.S. degree.

THE SYNTHESIS, STRUCTURE, AND REACTIVITY OF DI-TUNGSTEN  
NONACARBONYL  $\mu$ -CARBENE COMPLEXES: MOLECULAR STRUCTURES OF



by

MONG LIANG

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AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

Reactions of Fischer-type  $\alpha, \beta$ -unsaturated tungsten carbene complexes with  $(\text{CO})_5\text{W}\cdot\text{THF}$  (generated photochemically from  $\text{W}(\text{CO})_6$  and THF) in hexane solution provided dinuclear tungsten carbene complexes (7) which contained  $\mu\text{-}\eta^1, \eta^3$ -allyl carbene ligands. The structure of  $[\text{W}_2(\text{CO})_9\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{OCH}_3)\overline{\text{C}=\text{CH}(\text{CH}_2)_5\text{CH}_2}\}]$  (7f) was established by X-ray crystallography, and was found to contain two tungsten atoms at an interatomic distance consistent with the presence of a single bond ( $\text{W}(1)\text{-W}(2)$  3.1909(5) Å). The C-C bond lengths in the  $\mu\text{-}\eta^1, \eta^3$ -allyl system are 1.44(1) Å (C(10)-C(11)) and 1.42(1) Å (C(11)-C(12)). Two possible reaction pathways for formation of 7 are also discussed.

Heating  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)(\eta^2\text{-CH}=\text{CH}_2)]\text{W}(\text{CO})_5$  (8) to 45 °C in toluene produced  $[\text{W}_2(\text{CO})_9\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{OCH}_3)\text{CH}=\text{CH}_2\}]$  (7a) which could be converted back to 8 upon treatment with carbon monoxide. On prolonged passage of carbon monoxide through a  $\text{C}_6\text{D}_6$  solution of 8,  $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{CH}=\text{CH}_2]$  (6a) and  $\text{W}(\text{CO})_6$  were produced. A single crystal X-ray diffraction study of 8 revealed the overall structure to contain two  $(\text{CO})_5\text{W}$  fragments connected by an  $\alpha, \beta$ -unsaturated carbene moiety.