

## REACTIONS OF $(\pi\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}$ WITH DIMETHYLACETYLENEDICARBOXYLATE. FORMATION OF DINUCLEAR AND METAL HYDRIDE INSERTION PRODUCTS

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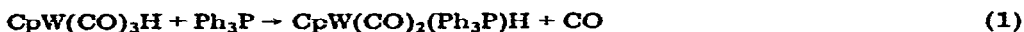
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### Summary

The reaction of  $(\pi\text{-Cp})\text{W}(\text{CO})_3\text{H}$  with dimethylacetylenedicarboxylate in refluxing tetrahydrofuran (THF) produces an acetylene bridged dinuclear tungsten species as the principal product. A minor product is identified as a  $\sigma$ -vinyl complex, presumably formed by metal hydride insertion across the acetylene bond. In contrast, the analogous reaction system at 20°C leads principally to the formation of a  $\sigma$ -vinyl complex isomeric to the minor product formed in refluxing THF. The latter product when heated in THF undergoes loss of CO but is not a precursor of the dinuclear species.

### Introduction

In the course of studying the spectral and photochemical properties of several transition metal hydrides, we have discovered an unusual set of reactions between  $\text{CpW}(\text{CO})_3\text{H}$  (I, Cp =  $\pi\text{-C}_5\text{H}_5$ ) and dimethylacetylenedicarboxylate (DMAD). Previous workers [1] have shown that the reaction of  $\text{CpM}(\text{CO})_3\text{H}$  (M = Mo, W) with a nucleophile such as triphenylphosphine results in a simple bimolecular displacement (eq 1) at room temperature



Similarly CO displacement is also noted for the halogen complexes  $\text{CpM}(\text{CO})_3\text{X}$  (X = halogen, M = Mo, W) [2,3]. Among the ligands which displace CO from  $\text{CpW}(\text{CO})_3\text{Cl}$  is hexafluoro-2-butyne with  $\text{CpW}(\text{CF}_3\text{C}\equiv\text{CCF}_3)_2\text{Cl}$  identified as the product. Reaction of the hydride I with tetrafluoroethylene gives a metal hydride insertion product  $\text{CpW}(\text{CO})_3(-\text{CF}_2\text{CF}_2\text{H})$  [4]; however, to our knowledge other metal hydride insertion reactions of I with olefins or acetylenes have not previous-

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ly been reported. The insertions of alkenes and acetylenes into metal hydride bonds leading to stable  $\sigma$ -alkyl and  $\sigma$ -alkenyl metal complexes are known for a variety of metals [5], and such reactions have been proposed as useful models for metal catalyzed hydrogenation and oligomerization reactions [5,6]. Displacement of CO by acetylene might be an important preliminary step in hydrogenation or oligomerization catalysis pathways [7], thus it is of interest to establish whether the reaction of I with DMAD would proceed by an M-H insertion or a CO displacement pathway.

## Experimental

### Materials

( $\pi$ -Cyclopentadienyl)tungsten(tricarbonyl)hydride [ $\pi$ -CpW(CO)<sub>3</sub>H], was prepared by the literature method [8]. Dimethylacetylenedicarboxylate was purchased from Aldrich and used without further purification. Tetrahydrofuran was purified by distillation from sodium benzophenoneketyl in a nitrogen atmosphere. Hexanes were purified by distillation from P<sub>2</sub>O<sub>5</sub> under nitrogen. NMR solvents and CH<sub>2</sub>Cl<sub>2</sub> were freeze-thaw degassed three times prior to use. All manipulations were performed under an atmosphere of purified nitrogen.

### Instruments

The NMR experiments were carried out on a Varian T-60 instrument for the proton spectra and on a Varian CFT-20 instrument for carbon-13 spectra. Infrared spectra were determined on a Perkin-Elmer 225 model grating infrared spectrophotometer. Mass spectral data were obtained with an AEI MS-902. Inlet temperatures ranged from 100–120°C with the voltage at 70 eV for the high resolution spectra. A Cary 14 UV-visible recording spectrophotometer was used to record the visible spectra.

## Results

### Reaction of CpW(CO)<sub>3</sub>H with DMAD in refluxing THF

When a solution of I (0.70 g) plus an excess of DMAD (2 g) in 30 ml of freshly distilled THF was refluxed overnight under nitrogen, it underwent a color change from light yellow to deep red. Subsequent removal of the solvent and DMAD by high vacuum evaporation afforded a red, gummy material. This was dissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub> and was chromatographed on a 2 × 25 cm silica gel column. Elution with 10% ether/hexane solution allowed the recovery of 0.52 g of an air stable, red material, II. Further elution with ether gave 0.08 g of a second, yellow product, III.

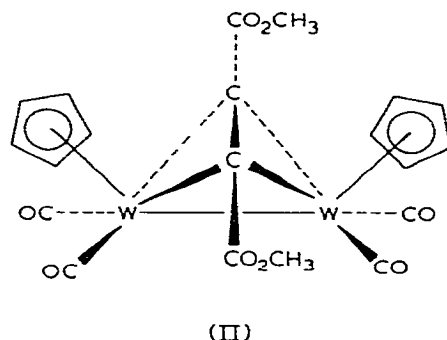
Mass spectral data indicates that II is a binuclear compound with the formulation [CpW(CO)<sub>2</sub>]<sub>2</sub>DMAD. The parent ion *m/e* ratio is 752 and is consistent with that expected for the <sup>186</sup>W—<sup>182</sup>W or <sup>184</sup>W—<sup>184</sup>W isotope combinations for the formula C<sub>24</sub>H<sub>16</sub>O<sub>4</sub>W<sub>2</sub> as are the combustion analysis results (Table 1). IR and NMR spectral data are summarized in Tables 2 and 3. The PMR data for II are consistent with a symmetrical structure.

In addition the <sup>13</sup>C NMR spectrum shows only one type of acetylene carbon at 92.8 ppm. Two other observations support this formulation. First, the infrared

TABLE 1  
COMBUSTION ANALYSIS RESULTS<sup>a</sup> AND MELTING POINT DATA FOR REACTION PRODUCTS

Compound	Proposed formula	Analysis found (calcd) (%)		Melting or decomposition temperature <sup>b</sup> (°C)
		C	H	
II	C <sub>24</sub> H <sub>16</sub> O <sub>4</sub> W <sub>2</sub>	31.83(31.94)	2.22(2.14)	188–190 d (turns dark brown)
III	C <sub>14</sub> H <sub>12</sub> O <sub>7</sub> W	35.41(35.32)	2.56(2.54)	119 d (turns red)
IV	C <sub>14</sub> H <sub>12</sub> O <sub>7</sub> W	35.27(35.32)	2.61(2.54)	112–114 d (turns black)
V	C <sub>13</sub> H <sub>12</sub> O <sub>6</sub> W	35.06(34.86)	2.80(2.70)	117–118 d (turns red)

<sup>a</sup> Analyses performed by Galbraith laboratories Knoxville Tennessee <sup>b</sup> Carried out under a nitrogen atmosphere



spectrum in the metal carbonyl region is very similar to that of an analogously acetylene bridged molybdenum dimer [10]. Second, the electronic spectrum of II (in CH<sub>2</sub>Cl<sub>2</sub>) displays two absorption bands in the near UV-visible region with maxima at 513 nm ( $\epsilon = 720 \text{ m}^{-1} \text{ cm}^{-1}$ ) and 362 nm ( $\epsilon = 4,500$ ). These can be compared with  $\lambda_{\text{max}}$  of 490 and 360 nm of the [CpW(CO)<sub>3</sub>]<sub>2</sub> dimer which have been assigned as transitions involving orbitals of the metal-metal bond [9].

High resolution mass spectral data indicates the product III is a mononuclear metal complex with a parent ion molecular weight of  $478.010 \pm 0.002$ . This corresponds to the addition of one DMAD to the starting material I (calc. mol wt. for C<sub>14</sub>H<sub>12</sub>O<sub>7</sub><sup>186</sup>W) and combustion analysis is consistent with this formulation (Table 1). IR and NMR data are summarized in Tables 2 and 3. A single

TABLE 2  
INFRARED SPECTRA FOR REACTION PRODUCTS IN CH<sub>2</sub>Cl<sub>2</sub>

Complex	$\nu(\text{CO})$ <sup>a</sup> (metal carbonyl and carboxyl groups)
II	2059w, 2013m, 1952s, 1837m, 1690m
III	2035s, 1946(br), 1740(br)
IV	2035s, 1957s, 1934s, 1719m, 1705m
V	2037s, 1960s, 1946s, 1730m, 1710m

<sup>a</sup> In cm<sup>-1</sup>.

TABLE 3  
NMR SPECTRA OF REACTION PRODUCTS AND OTHER SPECIES <sup>a</sup>

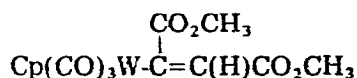
A <sup>1</sup> H NMR Spectra					
Compound	$\pi$ -Cp protons	Methoxy protons		Others	
[CpW(CO) <sub>2</sub> ] <sub>2</sub> DMAD(II)	5 37(10H,s)	3 74(6H,s)			
III	5 50(5H,s)	3 70(3H,s)		6 07(1H,s)	
		3 62(3H,s)			
IV	5 53(5H,s)	3 75(3H,s)		6 47(1H,s)	
		3 71(3H,s)			
V	5 61(5H,s)	3 73(3H,s)		9 48(1H,s)	
		3 70(3H,s)			
dimethyl fumarate		3 78(6H,s)		6 85(2H,s)	
dimethyl maleate		3 75(6H,s)		6 25(2H,s)	
DMAD		3 84(6H,s)			

B <sup>13</sup> C NMR Spectra <sup>b</sup>					
Compound	$\pi$ -Cp	Metal carbonyls	Carboxyl	Methoxyl	Vinyl or Acetylenic
[CpW(CO) <sub>2</sub> ] <sub>2</sub> DMAD	89 7	212 6	175 7	52 4	92 8
W(PhC=CPh) <sub>3</sub> CO <sup>c</sup>		219 2			192 1
					173 8
DMAD			152 4	53 6	74 7
dimethyl maleate			168 0	50 5	128 4
dimethyl fumarate			163 9	50 6	132 8
dimethyl succinate			170 8	50 6	30 0 <sup>d</sup>
PhC=CPh					89 5

<sup>a</sup> All spectra measured in solvent CDCl<sub>3</sub>. Chemical shifts are reported in ppm downfield from the resonance of the appropriate nuclei in internal standard TMS. <sup>b</sup> Proton decoupled. <sup>c</sup> In this complex the acetylenic carbons are inequivalent [10]. <sup>d</sup> Carbons  $\alpha$  to carboxylates.

vinyl proton is seen in the PMR spectrum suggesting that III is a product of metal hydride addition across the acetylenic bond, e.g.,



#### Reaction of $\pi$ -CpW(CO)<sub>3</sub>H with DMAD in THF at room temperature

When the reaction described above was carried out at room temperature and worked up in an identical fashion, a single product (0.75 g) was eluted from the silica gel column with ether. High resolution mass spectral data for this yellow compound (IV) indicates a parent ion mass of 478.014  $\pm$  0.002 indicating that this product is also formed by the addition of one DMAD to the starting complex I. Again, the PMR spectrum displays one vinyl proton (Table 3) suggesting that IV is formed by metal hydride insertion across the DMAD triple bond; however, the NMR and IR data for products III and IV differ, thus, these species must be isomers. IV was also the product when the reaction was carried out in dichloromethane in a similar manner.

It was of interest to determine whether product IV is a precursor to the

formation of the dinuclear species II which formed at higher temperatures. For this reason, a 210 mg sample of IV in 20 ml THF was heated at reflux for 16 h under nitrogen. The result was a slightly orange solution which was worked up by the standard procedure then chromatographed on a 2 × 25 cm silica gel column. Elution with 30% ether/hexane separated out the starting material (~100 mg) while elution with 50% ether/hexane separated a small amount (~20 mg) of a material identified as III from its infrared and NMR spectra. Further elution allowed the separation of a third species (~40 mg), a yellow, air sensitive compound, V. The IR spectrum of V (Table 2) is qualitatively very similar to that of IV, however, the PMR spectrum (Table 3) shows one distinctive difference, the vinyl proton at 6.47 ppm seen in IV is replaced by a markedly lower field singlet at 9.48 ppm. The high resolution mass spectrum shows a parent ion at  $450.0175 \pm 0.0025$ , which compares favorably to the theoretical value of 450.0177 calculated for  $C_{17}H_{12}O_6^{186}W$ , and corresponds to the loss of one CO from IV.

Analysis and melting point data for each of these compounds are listed in Table 1.

## Discussion

The dimeric product II was unexpected for the reaction of the metal hydride with DMAD and at this point we could only speculate regarding the reaction pathways responsible for its formation. Curtis et al. [10] have noted the formation of a similar binuclear complex from the reaction of acetylene and the metal-metal triply bonded dimer  $[CpMo(CO)_2]_2$ . Thus, it is conceivable that loss of hydrogen plus carbon monoxide to form the tungsten analog might precede formation of the acetylene bridged dimer. However, this mechanism appears to be precluded by the observation that I is relatively stable under conditions where II was formed in high yield. A solution of I alone in refluxing THF underwent partial decomposition after 16 h to unidentified products but more than 80% was recovered unchanged. Similar heating with small quantities of added DMAD led only to the formation of small quantities of II and not to catalytic decomposition of I. Attempts to effect the insertion reaction or to form a binuclear complex by reaction of diphenylacetylene with I were unsuccessful. Conditions identical to those under which II or IV are produced gave no reaction as evidenced by the infrared spectra of the solutions which were identical from start to finish. In all cases I could be trapped from the reaction solutions by the low temperature reaction with DMAD to give yields of IV essentially identical to those found in the absence of diphenylacetylene. Additionally, reaction of I with diphenylacetylene and a small amount of DMAD produced a small quantity of II, but no reaction between I and diphenylacetylene could be observed. Thus it appears that the electron-withdrawing methyl carboxylate groups are activating the acetylene toward reaction with I.

The proton and  $^{13}C$  NMR spectra clearly indicate a symmetrically bridged structure for II. The "tetrahedrane" type framework, previously suggested for the similar molybdenum complex [10] satisfies the effective atomic number rule and is consistent with the spectral data. This type of metal-acetylene bonding has been demonstrated with other binuclear metal complexes [11] and is one

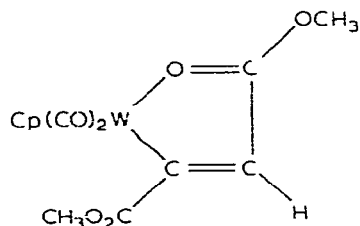
of the structures suggested by low-energy-electron-diffraction studies for acetylene chemisorbed on a platinum surface [12]

The NMR spectra are assigned in analogy to known compounds. Since the methyl group proton and carbon chemical shifts for II are not markedly different from those of other methylcarboxylate groups (Table 2), a similar conclusion can be made for the carboxylate carbon, i.e., the resonance at 175.7 ppm can be assigned to the carboxylate carbon of II. This leaves the resonance at 92.8 ppm to be assigned to the acetylenic carbons. Notably, this resonance appears only 18 ppm downfield from that of the acetylenic carbons of free DMAD. In comparison, chemical shift differences of 80–100 ppm are noted for the acetylenic carbons of diphenyl acetylene when complexed to tungsten in  $W(PhC\equiv CPh)_3CO$ , a species which shows considerable tungsten–acetylene bonding [13]. Thus, one might interpret the small difference for the acetylenic carbons of II as indicating relatively weak metal acetylenic bonding with the hybridization of these carbons lying between  $sp$  and  $sp^2$ . This explanation seems unlikely given the robust nature of II, which is stable in refluxing THF and is essentially inert to visible light photolysis in chlorocarbon solvents. (In contrast the dimeric species  $[CpW(CO)_3]_2$  is readily cleaved by photolysis to monomeric radicals which are trapped by reaction with chlorocarbons [9,14].) Thus an alternative explanation of the  $^{13}C$  NMR data is attractive, namely that the metal–acetylene interaction is very strong with the electronic environment of the acetylenic carbons lying between  $sp^2$  and  $sp^3$  hybridization. The carboxylate carbon resonances, more like those of dimethyl succinate than those of DMAD or dimethylmaleate, are consistent with this interpretation.

The relative configurations of the isomeric products III and IV can be inferred from comparisons of the vinyl proton chemical shift. The vinyl proton of IV appears downfield from that of III by 0.4 ppm. The PMR spectra of a similar pair of isomers (resulting from the *cis*-addition of  $Cp_2ReH$  to DMAD and subsequent isomerization to give the *trans* adduct) showed the *trans* isomer vinyl proton ( $\delta$  6.94 ppm) at 0.46 ppm downfield from the *cis* isomer vinyl proton ( $\delta$  6.48 ppm) [5b]. Similarly, the vinyl protons of dimethylfumarate appear about 0.6 ppm downfield from those of dimethylmaleate. Thus, these data strongly suggest that III is the product of *cis* insertion of the metal hydride across the acetylenic bond and IV is the product of *trans* insertion. Attempts were made to confirm these assignments by low temperature protonolysis of III and IV with dry HCl [15] or with trifluoroacetic acid in chloroform solution, however, the decomposition of the complexes was accompanied by the formation of polymeric organic products. Notably, the low temperature reaction of  $HMn(CO)_5$  with DMAD in ether has been reported to occur with stereospecific *trans* addition of metal hydride across the carbon–carbon triple bond [16].

The detailed mechanism of the formation of IV has not been established; however, it is unlikely to be radical in nature since polymerization of the acetylene was not noted. Also, formation of metal radicals in dichloromethane would have led to the formation of  $CpW(CO)_3Cl$  (which was not found) since the radical  $[CpW(CO)_3]$  is highly reactive towards chlorine abstraction in chlorocarbon solvents [9,14]. In addition, IV does not appear to be an intermediate in the formation of II. This is demonstrated by the fact that II is not formed on refluxing IV (1) alone in THF, (2) with  $CpW(CO)_3H$  in THF, or (3) with additional

DMAD in THF. For each of these conditions, only one major product, V, plus some III were isolated. It is tempting to propose the structure shown below for V as it satisfies the 18 electron rule and accounts for the loss of CO. A similar product is formed when the manganese pentacarbonyl analog of IV is heated in



carbon tetrachloride [16]. However, for both the manganese compound [16] and a similar rhenium complex [5b] the NMR chemical shift of the vinyl protons occur within the normal range while the "vinyl" proton of V is dramatically shifted to lower field.

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