## Photochemical Reactions of Transition Metal Organyl Complexes with Olefins, 20[◇]

# Light-Induced Codimerisation of Acetylene and Olefins at a Binuclear Tungsten Complex☆

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$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}C_2H_2)]$ (**1**) and ethylene (**A**) react when irradiated with UV light at 253 K predominantly to $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}\eta^{1:4}\text{-}C_4H_5)(\mu\text{-}H)]$ (**3A**), $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{1:3}\text{-}C_4H_6)]$ (**4A**), and thermolabile $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\eta^4\text{-}C_4H_6)]$ (**5A**). Similarly, propene (**B**), 1-butene (**C**), and (*E*)-2-butene (**D**) yield mixtures of $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}H)(\mu\text{-}\eta^{1:4}\text{-}1,3\text{-dien-1-yl})]$ (**3B**, **3 C**, **3D**), $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{1:3}\text{-}C_4H_5R]$ (**4B**, **4C**), and $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}\eta^{1:2}\text{-}CO)(\eta^4\text{-}1,3\text{-diene})$ (**5B**, **5 C**, **5D**). With **B** and **C** also thermolabile $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-}C_2H_2)(\eta^2\text{-}C_2H_3R)]$ (**2B**, **2C**) are formed. A by-product of the reaction of **1** with **D** is $[W(\eta^5\text{-}C_5H_5)(CO)(H)\{\eta^4\text{-}(E)\text{-}C_5H_7CH_3\}]$, which is generated in two diastereomeric forms (**6**, **6′**). In contrast, **1** yields no complexes with (*Z*)-2-butene (**E**) which contain ligands formed from coordinated acetylene and the olefin. From the reaction mixture only trinuclear $[W_3(\eta^5\text{-}C_5H_5)_3(CO)_5(\mu\text{-}\eta^{1:2}\text{-}C_2H_3)]$ (**7**) was isolated, an alicyclic complex with a W−W single and a W−W triple bond. The crystal and molecular structures of **5D** and **7** were determined by X-ray structure analysis. The constitutions of the other complexes were ascertained by IR and $^1$H-NMR spectroscopy.

## Introduction

Unsaturated hydrocarbons like alkenes or alkynes react in different ways with transition metal complexes. Oligomerisation, cyclooligomerisation and polymerisation are well-known reactions catalysed by transition metal complexes. Pre-requisite for a linkage of unsaturated hydrocarbons by C−C bond formation is the coordination of the substrates at one or two adjacent metal centres. Binuclear complexes offer after a suitable activation the possibility for a simultaneous coordination of two alkenes or alkynes followed by a C−C bond formation between the coordinated hydrocarbons. Examples for these types of reactions are the thermal oligomerisations of alkynes[2][3][4] at $[M_2(\eta^5\text{-}L)_2(CO)_4]$ complexes (M = Cr, Mo; L = $C_5H_5$, $C_9H_7$)[5][6][7][8], which proceed stepwise via $[M_2(\eta^5\text{-}L)_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-alkyne})]$ as intermediates[9]. We have been able to show, that acetylene reacts photochemically with $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}C_2H_2)]$ (M = Mo, W) predominantly to yield $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}\eta^{1:3:3:1}\text{-}C_6H_6)]$[10].

By light-induced CO cleavage $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-}C_2H_2)]$ complexes are generated at low temperatures with potentially free coordination sites, well suited to coordinate unsaturated hydrocarbons. Not only acetylene, but also alkenes are coordinated and linked with the acetylene ligand when $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-}C_2H_2)]$ or $[Mo_2(\eta^5\text{-}C_9H_7)_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-}C_2H_2)]$ is reacted with ethylene or alkenes[11][12]. This system allows a specific generation of hydrocarbons by codimerisation of acetylene and alkenes. In order to study the reaction behaviour of simple alkenes at binuclear complexes also the tungsten homologue $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}C_2H_2)]$ was allowed to react with ethylene and some simple alkenes. The results of these investigations will be discussed in the following.

## Preparative Results

The photoreaction of ($\mu$-$\eta^{2:2}$-acetylene)tetracarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**1**) was carried out at 253 K with the olefins ethylene (**A**), propene (**B**), 1-butene (**C**), (*E*)-2-butene (**D**), or (*Z*)-2-butene (**E**) in petroleum ether/THF or ether/THF. The progress of the reaction is monitored by IR spectroscopy using the $\upsilon$CO stretching bands in the region from 2200 to 1700 cm$^{-1}$. Immediately after the bands of **1** have vanished the irradiation is stopped and the solvent is removed from the reaction mixture. The residue is separated by column chromatography on alumina at 253 K into its components, the isolated compounds are re-crystallised from ether. The complexes were characterised with IR and $^1$H NMR spectroscopy and by C,H elemental analyses.

The photoreaction of **1** with ethylene (**A**) is conducted in petroleum ether/THF (1:1). By column chromatography of the reaction mixture three binuclear complexes can be isolated: ($\mu$-$\eta^{1:4}$-1,3-butadien-1-yl)tricarbonylbis($\eta^5$-cyclopentadienyl)($\mu$-hydrido)ditungsten(*W−W*) (**3A**) ($\mu$-$\eta^{1:3}$-2-butene-1,1-diyl)tetracarbonylbis($\eta^5$-cyclopentadienyl)-

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[◇] Part 19: Ref.[1].

ditungsten(*W*−*W*) (**4A**) and ($\eta^4$-1,3-butadiene)tricarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W*−*W*) (**5A**).

$$1 + C_2H_4 \xrightarrow[243\ K]{h\cdot\nu} [W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}\eta^{1:4}\text{-}C_4H_5)(\mu\text{-}H)]\ \mathbf{(3A)}\ (3\%)$$

$$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{1:3}\text{-}C_4H_6)]\ \mathbf{(4A)}\ (2\%)$$

$$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\eta^4\text{-}C_4H_6)]\ \mathbf{(5A)}\ (2\%)$$

Propene (**B**) and 1-butene (**C**) react with **1** to analogous compounds. In addition to the dienyl bridged hydrido complexes **3B**, **3C** and the related 2-pentene-1,1-diyl and 2-hexene-1,1-diyl complexes **4B**, **4C** the $\eta^4$-diene compounds **5B**, **5C** with bridging $\mu$-$\eta^{1:2}$-CO ligands and the very thermolabile substitution products with olefin acetylene ligands **2B**, **2C** were isolated from the reaction mixtures. The olefin complexes **2B**, **2C** rearrange at room temperature readily into the corresponding dienyl hydrido complexes **3B**, **3C**.

$$1 + C_2H_3R \xrightarrow[243\ K]{h\cdot\nu} [W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-}C_2H_2)(\eta^2\text{-}C_2H_3R)]\ \mathbf{(2B, 2C)}\ (4\%, 5\%)$$

$$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}H)(\mu\text{-}\eta^{1:4}\text{-}C_4H_4R)]\ \mathbf{(3B, 3C)}\ (4\%, 6\%)$$

$$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{1:3}\text{-}C_4H_5R]\ \mathbf{(4B, 4C)}\ (1\%, 1\%)$$

$$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}\eta^{1:2}\text{-}CO)(\eta^4\text{-}C_4H_5R)]\ \mathbf{(5B, 5C)}\ (5\%, 5\%)$$

$$R = CH_3, C_2H_5$$

With (*E*)-2-butene (**D**) one mononuclear and three binuclear complexes are obtained after chromatography. No simple olefin complex has been detected in this case. Again a dienyl-bridged hydrido complex **3D** and a diene complex **5D** are formed. The generation of **4C** must be explained with an isomerisation of the olefin prior to the C−C bond formation. The mononuclear complex **6** contains like **5D** the $\eta^4$-(*E*)-3-methyl-1,3-pentadiene ligand. When **3D** is warmed in solution it rearranges into **5D**.

$$1 + C_4H_8 \xrightarrow[243\ K]{h\cdot\nu} [W_2(\eta^5\text{-}C_5H_5)_2(CO)_3(\mu\text{-}H)(\mu\text{-}\eta^{1:4}\text{-}C_5H_6CH_3)]\ \mathbf{(3D)}\ (5\%)$$

$$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{1:3}\text{-}C_3H_3C_3H_7]\ \mathbf{(4C)}\ (1\%)$$

$$[W_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}\eta^{1:2}\text{-}CO)(\eta^4\text{-}C_5H_7CH_3)]\ \mathbf{(5D)}\ (7\%)$$

$$[W(\eta^5\text{-}C_5H_5)(CO)(H)(\eta^4\text{-}C_5H_7CH_3)]\ \mathbf{(6)}\ (1\%)$$

The photolysis of **1** in presence of (*Z*)-2-butene (**E**) yields no products with ligands, formed from acetylene and the olefin. Possibly, the steric demand of the *Z*-standing methyl groups causes this distinct differences of the reactivity. The starting material **1** is consumed only after 300 min and mainly decomposed into insoluble material. By column chromatography a trinuclear vinyl-bridged complex was isolated in addition to traces of other not yet characterised compounds.

$$2 + C_4H_8 \xrightarrow[243\ K]{h\cdot\nu} [W_3(\eta^5\text{-}C_5H_5)_3(CO)_5(\mu\text{-}\eta^{1:2}\text{-}C_2H_3)]\ \mathbf{(7)}\ (1\%)$$

## $^1$H-NMR Spectra

The $^1$H-NMR spectroscopic data of the isolated complexes **2B**−**7** are given in the Experimental Section. For the binuclear complexes **2B**−**5D**, two singlets of the chemically different $\eta^5$-cyclopentadienyl ligands and additional signals due to ligands formed from acetylene and the olefins **A**−**D** are observed. The chemical shifts and the coupling constants of these signals together with the IR data allow justified suggestions for the constitutions of the complexes.

The photoreactions of **1** with propene (**B**) or 1-butene (**C**) yield the two $\eta^2$-olefin compounds **2B** and **2C**. Both are very temperature sensitive and can not be isolated in a pure state therefore. Two doublets in the $^1$H-NMR spectra at $\delta$ = 2.35, 4.02 (**2B**) and $\delta$ = 2.33, 4.06 (**2C**) with coupling constants of 2 Hz are assigned to the bridging acetylene ligand. Four resonances in the spectrum of **2B** between $\delta$ = 1.03 and 2.30 with the relative intensities of 1:1:3:1 correspond to the $\eta^2$-coordinated propene ligand. Analogously, in the spectrum of **2C** a triplet and two multiplets for an ethyl group and three signals of single intensity between $\delta$ = 0.96 and 2.29 of the vinyl group were found. In solution **2B** and **2C** rearrange already at 273 K quickly into the $\mu$-$\eta^{1:4}$-dienyl-$\mu$-hydrido complexes **4B** and **4C**. Decomposition under formation of the starting material **1** is also observed.

The $^1$H-NMR spectra of the $\mu$-$\eta^{1:4}$-dienyl-$\mu$-hydrido complexes show a strongly high-field shifted signal, typical for bridging hydrido ligands. The signals of the binuclear tungsten compounds **3A**, **3B**, **3C** and **3D** are accompanied by two pairs of $^{183}$W satellites by which the bridging function of the hydrido ligands is further proved.

Five signals of **3A** with single intensity are related to each other by spin-spin couplings have to be assigned to the $\mu$-$\eta^{1:4}$-1,3-butadien-1-yl ligand. The coupling constant $J_{23}$ = 4.5 Hz is indicative for an *s-cis* conformation.

The $^1$H-NMR spectra of **3B** and **3C** show two AB-spin systems each. Two doublets represent H1 and H2 with vicinal coupling constants of 6.0 Hz. Two doublets at higher field are due to H4 (*E*) and H4 (*Z*) with geminal coupling constants of 3.0 and 2.0 Hz. A singlet for **3B**, and two double quadruplets and a triplet for **3C** prove a methyl and an ethyl group at C3.

In the $^1$H-NMR spectra of **3A**−**3D** a second hydrido signal of low intensity is found, which indicates the presence of a second isomer. Spin saturation experiments for **3B** and **3D** prove an exchange process between the two isomers. The increase of temperature causes first broadening of the signals of H1 and H2. At 303 K, they start narrowing again. Simultaneously the conversion to the corresponding $\eta^4$-diene complexes **5B** and **5D** is observed.

The tetracarbonyl complexes with $\mu$-$\eta^{1:3}$-2-alkene-1,1-diyl ligands **4A**−**4C** were isolated only in low yields form the reactions of **1** with **A**−**D**. In the case of **D** as olefin component, an isomerisation to **C** has to be assumed prior CC bond formation. The complexes **4A**−**4C** are stable at room temperature.

The characterisation by $^1$H-NMR spectroscopy is quite simple. Typical for all of these complexes is the resonance of H1 at low field δ = 9.35 (**4A**, **4B**) and δ = 8.97 (**4C**). In the region of the proton resonances of coordinated olefins two signals for H2 and H3 are obtained. The vicinal coupling constants between H1, H2 and H3 reach from 8.5 to 10 Hz. The complexes differ according to the signals of the alkyl substituents (methyl, ethyl, propyl) in 3*E* position.

The $^1$H-NMR spectra of the tricarbonyl-η$^4$-diene complexes **5A**, **5B**, **5C** and **5D** show at 243 K or 253 K the typical signal patterns for η$^4$-coordinated 1,3-butadiene, 2-methyl-1,3-butadiene, 2-ethyl-1,3-butadiene and (*E*)-3-methyl-1,3-pentadiene ligands. According to the stereochemistry of the complexes with the diene ligand in *ortho* orientation to the adjacent cyclopentadienyl ring, proved for **5D** with an X-ray structure analysis, four different stereoisomers (two pairs of enantiomers) are reasonable for such complexes with unsymmetrically substituted diene ligands. There is no evidence for the presence of a second pair of enantiomers in the spectra of **5B**, **5C** and **5D**. Obviously the energy difference between the pairs of enantiomers is too large to a allow a detectable population of the less favoured isomers.

The $^1$H-NMR spectra of the complexes **5A**−**5D** were measured at variable temperatures between 223 and 283 K. Like the corresponding η$^4$-2,3-dimethyl-1,4-butadiene dimolybdenum complex for which an enantiomerisation was proved[13], **5A** shows signal broadening, although the dynamic behaviour could not be studied completely due to its thermal sensitivity. In contrast **5B**−**5D** show no dynamic effects.

The mononuclear complex **6**, **6′** is obtained only in minor amounts as a mixture of stereoisomers. The $^1$H-NMR spectrum of **6**, **6′** contains two sets of eight signals with a proportion of 85:15. Two signals at δ = −9.65 and −6.13 with $^{183}$W satellites of 76 and 74 Hz are assigned to the hydrido ligands. In each case three double doublets, a quadruplet, a singlet, and a doublet, the two latter of threefold intensity correspond with the (*E*)-3-methyl-1,3-pentadiene ligands of the two species. The chemical shifts of the (*E*)-3-methyl-1,3-pentadiene ligands in the two isomers are quite similar, the largest differences are found for H1 *E* and $CH_34$ *E*. As a consequence of the asymmetric tungsten atom, and the asymmetrically substituted diene, two diastereomeric pairs of enantiomers are possible. When *o*-orientation is assumed on the basis of the observed chemical shifts for both isomers, the hydrido ligand is in one diastereomer in the vicinity of C1, in the other in the vicinity of C4. The large difference of the chemical shifts of the hydrido ligands is well understood on the basis of this assumption.

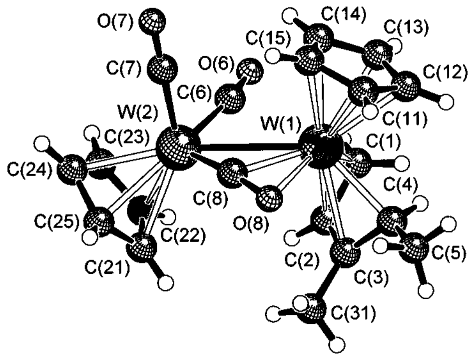
The trinuclear complex **7** is unexpectedly formed when **1** is irradiated in presence of (*Z*)-2-butene and is isolated in form of red-brown crystals in reasonable yield. Only three cyclopentadienyl singlets and three double doublets of single intensity at δ = 7.04, 4.72, 1.79 are observed in the $^1$H-NMR spectrum. The double doublets are indicative for a bridging vinyl ligand. The spectrum is in accord with the molecular structure of **7** determined by X-ray structure analysis.

## Crystal and Molecular Structures of 5D and 7

Reddish brown crystals of tricarbonylbis(η$^5$-cyclopentadienyl)[η$^4$-(*E*)-3-methyl-1,3-pentadiene]ditungsten-(*W*−*W*) (**5D**) are obtained in reasonable yields when **1** is allowed to react with (*E*)-2-butene. The complex crystallises in the monoclinic space group $P2_1/n$ with constants of the unit cell of $a$ = 1089.3(2), $b$ = 1240.5(3), $c$ = 1303.7(2) pm, and ß = 95.914(14)°. The molecular structure of **5D** resembles to that of tricarbonylbis(η$^5$-methylcyclopentadienyl)(η$^4$-2,3-dimethyl-1,3-butadiene)dimolybdenum-(*Mo*−*Mo*)[12]. The W1−W2 bond length in the binuclear complex is found with 311.69(8) pm, typical for a W−W single bond[14]. The distances of the cyclopentadienyl ligands from the tungsten centres differ slightly from each other, W1 being somewhat closer with 196.9 pm than W2 with 202.1 pm. The (*E*)-3-methyl-1,3-pentadiene is η$^4$-coordinated to W1 and adopts *ortho* orientation[15]. The diene is originated by C−C bond formation between the acetylene ligand and the olefin **D**. Remarkably, the methyl groups being in *E* position in **D** are now in *Z* position to each other in **5D**. While W1−C1 = 221.3(10) pm and W1−C4 = 222.8(9) pm are of similar length, W1−C2 = 233.0(9) pm is found distinctly shorter than W1−C3 = 239.4(9) pm. Like in other η$^4$-diene complexes the C−C bond lengths of the diene entity are equal within experimental error. From the three CO ligands coordinated to W2, one is found in a normal terminal bond situation. The second CO ligand is semibridging to W1 with W1−C6 = 290.8( 9) pm and W2−C6−O6 = 166.2(9)°. The third one forms a bridge between the two tungsten centres by a side-on coordination to W1 and shows only a slight bending with W2−C8−O8 = 169.1(11)°. By this type of coordination the CO ligand donates four electrons to the two tungsten centres. Examples for bridging, 4e-donor CO ligands are known for homo binuclear complexes[13][16][17][18] but especially for heteronuclear complexes[19][20][21][22][23][24].

The brown, trinuclear tungsten complex **7** crystallises in the monoclinic space group $P2_1/n$ with constants of the unit cell of $a$ = 780.61(7) pm, $b$ = 2197.1(3) pm, $c$ = 1403.80(11) pm, and ß = 100.753(6)°. It shows noticeably different W−W bond lengths with W1−W2 = 304.65(11) pm and W2−W3 = 254.07(10) pm. They are in accord with W−W single[14] and triple bonds[25][26][27]. The three cyclopentadienyl ligands have similar distances to the pertinent metal centres with 201.0, 204.2, and 202.6 pm. Three of the five CO ligands are normal terminal ones. In contrast the CO ligands 5 and 6 are found in a special stereochemical situation. This kind of bond situation for CO ligands was observed for the first time in tetracarbonylbis(η$^5$-pentamethylcyclopentadienyl)dichromium[28], a binuclear complex with Cr−Cr triple bond and with four only slightly bent CO ligands, although heavily inclined toward the adjacent metal centres. Similar molecular geometries were also found for tetracarbonylbis(η$^5$-cyclopentadienyl)dimolybdenum[5], tetracarbonylbis(η$^5$-cyclopentadienyl)dichromium[29] and tetracarbonylbis(η$^5$-indenyl)dimolybdenum[8].

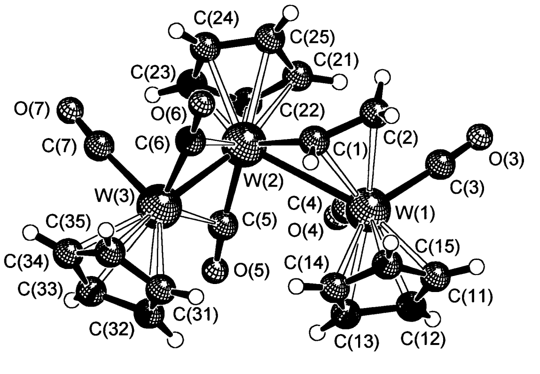
Figure 1. SCHAKAL projection of the molecular structure of **5D**; selected bond lengths [pm] and bond angles [°][a]; M(1) centre of C(11)−C(15), M(2) centre of C(21)−C(25)



[a]W(1)−W(2) 311.69(8), W(1)−M(1) 196.9, W(2)−M(2) 202.1, W(1)−C(1) 221.3(10), W(1)−C(2) 233.0(9), W(1)−C(3) 239.4(9), W(1)−C(4) 222.8(9), W(1)−C(6) 290.8(9), W(1)−C(8) 212.2(9), W(1)−O(8) 220.3(6), W(2)−C(6) 196.7(11), W(2)−C(7) 193.9(11), W(2)−C(8) 190.3(10), C(6)−O(6) 115.7(12), C(7)−O(7) 115.7(12), C(8)−O(8) 124.5(11); M(1)−W(1)−W(2) 116.1, M(2)−W(2)−W(1) 141.6, W(1)−W(2)−C(6) 65.3( 4), W(1)−W(2)−C(7) 94.0( 5), W(1)−W(2)−C(8) 41.9(4), W(2)−C(6)−O(6) 166.2(9), W(2)−C(7)−O(7) 178.2(9), W(2)−C(8)−O(8) 169.1(71).

Complex **7** can be considered to contain two subunits. The first one is related to ($\eta^{3}$-allyl)dicarbonyl($\eta^{5}$-cyclopentadienyl)metal complexes of group 6[30], the second to tetracarbonylbis($\eta^{5}$-cyclopentadienyl)dichromium[28].

Figure 2. SCHAKAL projection of the molecular structure of **7**; selected bond lengths [pm] and bond angles [°]; M(1) centre of C(11)−C(15), M(2) centre of C(21)−C(25), M(3) centre of C(31)−C(35)[a]



[a]W(1)−W(2) 304.65(11), W(2)−W(3) 254.07(10), W(1)−M(1) 201.0, W(2)−M(2) 204.2, W(3)−M(3) 202.6, W(1)−C(1) 221(2), W(1)−C(2) 230(2), W(2)−C(1) 210(2), W(2)−C(5) 194(2), W(2)−C(6) 253(2), W(3)−C(5) 236(2), W(3)−C(6) 192(2), W(3)−C(7) 202(2); W(1)−W(2)−W(3) 110.47(3), M(1)−W(1)−W(2) 125.5, M(2)−W(2)−W(1) 116.0, M(2)−W(2)−W(3) 132.8, M(3)−W(3)−W(2) 159.2, W(2)−C(5)−O(5) 168(2), W(3)−C(6)−O(6) 168.3(14), W(3)−C(7)−O(7) 175(2).

The bonding situation of the first subunit can be compared with those in the well-known ($\eta^{3}$-allyl)dicarbonyl($\eta^{5}$-cyclopentadienyl)metal complexes. Formally W2, which is bonded to C1 and W1, replaces a sp$^{2}$-methylene group. In the second entity, vice versa, W1 and C1 replace in a formal sense a terminal CO ligand. In contrast to tetracarbonylbis($\eta^{5}$-cyclopentadienyl)dichromium and the related compounds with all four CO ligands inclined to the adjacent metal centres, in complex **7** only two of them show this special type of coordination. This result is a good evidence for the assumption, that the inclination of only slightly bent CO ligands to a second metal centre and long metal−oxygen bonds is primarily due to steric and not due to electronic reasons. While for the two independent units of tetracarbonylbis($\eta^{5}$-cyclopentadienyl)dichromium the angle Cr−Cr−M (M centre of the cyclopentadienyl ligand) is found with 158.7 and 165.0°, respectively, and in tetracarbonylbis($\eta^{5}$-cyclopentadienyl)dimolybdenum close to 180°, the corresponding angles in **7** are W3−W2−M2 = 132.8(9)° and W2−W3−M3 = 159.2(9)°.

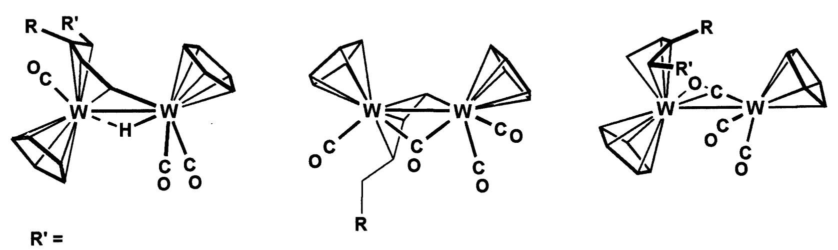
In complex **7** the three W atoms show an angular arrangement with W1−W2−W3 = 110.4(1)°. The plane defined by the three tungsten atoms is more or less perpendicular to the planes of the three cyclopentadienyl ligands with dihedral angles of 88.6, 82.2, and 82.9°. Remarkably, the two CO ligands 4 and 7 deviate only slightly from this plane and the C−W bonds penetrate the plane with 4.1 and 6.9°. W2, W3, C5 and C6 form an idealised parallelogram which is folded along the line W2, W3 with 162.4°. The distances W2−C5 and W3−C6 are short and amount 194(2) pm and 192(2) pm. The distances W2−C6 and W3−C5 are distinctly longer with 253(2) pm and 236(2) pm. The angles at C5 and C6 are found with 71.7(9) and 68.1(8)°, at W2 and W3 with 104.9(10) and 112.0(10)°. The sum of this angles is 356.7° as a consequence of the folding.

Complex **7** is also related to dinuclear complexes with $\mu$-$\eta^{2:1}$-vinyl-bridging ligands[31][32]. It is an interesting example for a trinuclear complex with formal electron numbers of 17, 14, and 15 at the three tungsten centres. W−W single and triple bonds have to be considered for this trinuclear, angular 46 electron complex taking into account the 18 electron rule.

## Discussion

The photoreaction of ($\mu$-$\eta^{2:2}$-acetylene)tetracarbonylbis($\eta^{5}$-cyclopentadienyl)ditungsten(*W*−*W*) (**1**) with ethylene yields at 253 K three complexes, [$W_2$($\eta^{5}$-$C_5H_5$)$_2$(CO)$_3$(H)($\mu$-$\eta^{1:4}$-1,3-butadien-1-yl)] (**3A**), [$W_2$($\eta^{5}$-$C_5H_5$)$_2$(CO)$_4$($\mu$-$\eta^{1:3}$-2-butene-1,1-diyl)] (**4A**), and [$W_2$($\eta^{5}$-$C_5H_5$)$_2$(CO)$_3$($\eta^{4}$-1,3-butadiene)] (**5A**) which are closely related to each other and allow conclusions about the reaction behaviour of unsaturated hydrocarbons in the coordination spheres of two tungsten centres. All products contain $C_4$ ligands, which result from a C−C bond formation between acetylene and ethylene and successive H shifts.

Binuclear complexes become accessible by photochemically induced formation of $C_4$ ligands from acetylene and ethylene which are only partially formed when 1,3-butadiene is reacted directly with [$M_2$($\eta^{5}$-$C_5H_4CH_3$)$_2$(CO)$_6$] complexes (M = Mo, W)[33]. With [$Mo_2$($\eta^{5}$-$C_5H_4CH_3$)$_2$(CO)$_6$] 1,3-butadiene yields [Mo($\eta^{5}$-$C_5H_4CH_3$)(CO)$_2${$\eta^{3}$-(*E*)-2-butenyl}], [Mo($\eta^{5}$-$C_5H_4CH_3$)(CO)$_2${$\eta^{3}$-(*Z*)-2-butenyl}], [$Mo_2$($\eta^{5}$-$C_5H_4CH_3$)$_2$(CO)$_3$($\eta^{4}$-butadiene)], and [$Mo_2$($\eta^{5}$-$C_5H_4CH_3$)$_2$(CO)$_2$($\mu$-$\eta^{4}$-butadiene)][13]. In the case of the photoreaction of [$W_2$($\eta^{5}$-$C_5H_4CH_3$)$_2$(CO)$_6$] with 1,3-butadiene the only isolable product is [$W_2$($\eta^{5}$-



| R = | R' = | | | |
|---|---|---|---|---|
| H | H | **3A** | **4A** | **5A** |
| $CH_3$ | H | **3B** | **4B** | **5B** |
| $C_2H_5$ | H | **3C** | **4C** | **5C** |
| $CH_3$ | $CH_3$ | **3D** | | **5D** |

$C_5H_4CH_3)_2(CO)_4\{\mu$-$\eta^{1:3}$-(*E*)-2-butene-1,1-diyl}],[18] the analogue to **4A**.

Examples of C−C bond formations between small molecules in the coordination sphere of metals have been observed already in the past. $[Ru_2(\eta^5$-$C_5H_5)_2(CO)_2$-$(CH_3CN)(\mu$-vinyl)]$^+$ reacts with ethylene to $[Ru_2(\eta^5$-$C_5H_5)_2$-$(CO)_2(\mu$-H)($\mu$-$\eta^{2:2}$-1,3-butadiene)]$^+$ and by deprotonation to $[Ru_2(\eta^5$-$C_5H_5)_2(CO)_2(\mu$-$\eta^{2:2}$-1,3-butadiene)][34]. Similarly, binuclear complexes with alkylidene bridges like $[M_2(\eta^5$-$C_5H_5)_2(CO)_3(\mu$-ethylidene)] (M = Fe, Ru) react with alkynes to the correspondingly substituted $\mu$-$\eta^{1:3}$-alkenediyl complexes[35][36].

Closely related to ($\mu$-$\eta^{1:4}$-1,3-butadiene-1-yl)tricarbonylbis($\eta^5$-cyclopentadienyl)($\mu$-hydrido)ditungsten(*W−W*) (**3A**), one of the products of the photoreaction of **1** with **A** is $[Mo_2(\eta^5$-$C_5H_4CH_3)_2(CO)_3(H)(\eta^{1:4}$-1,3-cycloheptadien-1-yl)], which is obtained when $[Mo_2(\eta^5$-$C_5H_4CH_3)_2(CO)_4]$ is irradiated in presence of 1,3-cycloheptadiene. The cyclic, $\eta^{1:4}$-coordinated dienyl and the hydrido ligand form bridges between the two metal centres[37]. Comparable bonding situations are also found in $[Rh_2\{(i$-$C_3H_7)_2PCH_2CH_2P(i$-$C_3H_7)_2\}_2(\mu$-H)($\eta^{1:4}$-1,3-butadiene-1-yl)], a product of the reaction of $[Rh_2\{(i$-$C_3H_7)_2PCH_2CH_2P(i$-$C_3H_7)_2\}_2(\mu$-$H)_2]$ with 1,3-butadiene[38]. In both cases the diene is transformed into a dienyl ligand by hydrogen shift to the metal centre.

($\eta^4$-1,3-Butadiene)tricarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**5A**) belongs to a group of complexes with side-on-coordinated, bridging CO ligands, donating 4 electrons to the metal centres. $[M_2(\eta^5$-$C_5H_4CH_3)_2(CO)_3(\eta^4$-diene)] complexes (M = Mo, W) are generated photochemically from $[M_2(\eta^5$-$C_5H_4CH_3)_2(CO)_4]$ with certain dienes[13][18]. They may be considered as derivatives of $[Mo_2(\eta^5$-$C_5H_5)_2(CO)_5]$ which is stabile only in matrix[39]. Of special interest is the 4-electron carbonyl bridge with a υCO band around 1600 cm$^{-1}$[13][18].

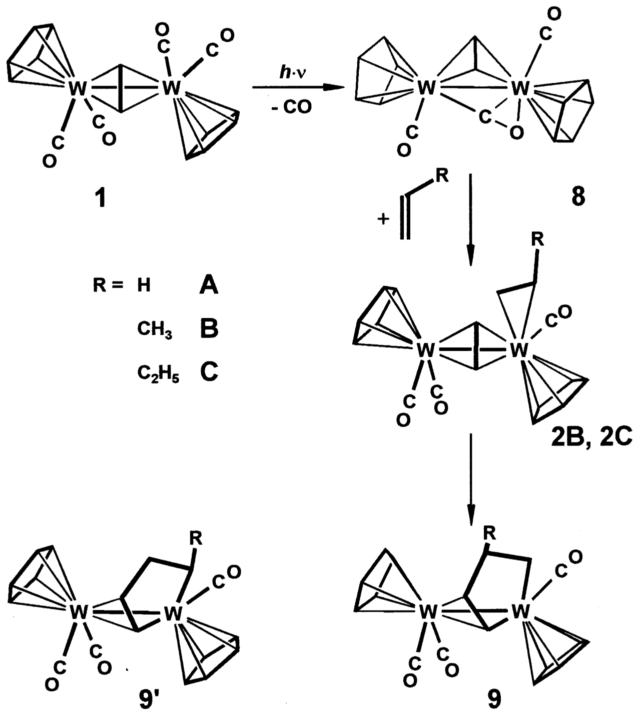
($\mu$-$\eta^{1:3}$-2-Butene-1,1-diyl)tetracarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**4A**) contains a 1,3-metalladiene core. Complexes of this type are generated under quite different conditions. $[Mo_2(\eta^5$-$C_5H_5)_2(CO)_4]$ reacts thermally with 3,3-dimethylcyclopropene by ring opening to $[Mo_2(\eta^5$-$C_5H_5)_2(CO)_4(\mu$-$\eta^{1:3}$-3-methyl-2-butene-1,1-diyl)][40][41]. The photoreaction of $[W_2(\eta^5$-$C_5H_4CH_3)_2(CO)_4]$ with 1,3-butadiene yields the analogous 2-butene-1,1-diyl complex[18]. 1,3-Metalladiene complexes may adopt *s-cis*[30][41] or *s-trans* configurations[42][43]. The $^1$H-NMR-spectroscopic data of **4A** are in accord with the *s-cis* configuration.

Also with propene (**B**), 1-butene (**C**), or (*E*)-2-butene (**D**) hydrido-dienyl, 2-alkene-1,1-diyl and 1,3-diene complexes are formed. With **B** and **C** in addition the thermolabile, simple substitution products ($\mu$-$\eta^{2:2}$-acetylene)tricarbonylbis($\eta^5$-cyclopentadienyl)($\eta^2$-propene)ditungsten(*W−W*) (**2B**) and the corresponding 1-butene complex (**2C**) can be isolated and characterised by IR and $^1$H-NMR spectroscopy. At room temperature **2B**, **2C** rearrange readily into the hydrido-dienyl complexes **3B**, **3C**.

The isolated products give good evidence for the route of the photochemical reaction when ($\mu$-$\eta^{2:2}$-acetylene)tetracarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**1**) is irradiated in the presence of olefins. In a primary step one CO ligand is cleaved from **1**. In contrast to mononuclear, electronically and coordinativly unsaturated carbonylmetal complex fragments with 16 electrons, the 32 electron intermediate, ($\mu$-$\eta^{2:2}$-acetylene)tricarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**8**), is probably stabilised by formation of a 4-electron carbonyl bridge like in the diene complexes **5A**−**5D**. This stabilisation would prolong the life time of **8**, but it might also delay the coordination of the olefin.

Addition of an olefin to **8** yields ($\eta^2$-acetylene)tricarbonylbis($\eta^5$-cyclopentadienyl)($\eta^2$-olefin)ditungsten(*W−W*) (**2**) which is moderately stable with propene or 1-butene as olefin component. In **2** two unsaturated hydrocarbon ligands are coordinated to a metal centre, a pre-requisite for a C−C bond formation. Insertion of the olefin into a W−C bond of the $W_2C_2H_2$ core yields the intermediate ($\mu$-$\eta^{1:2:1}$-1-butene-1,4-diyl)tricarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**9**).

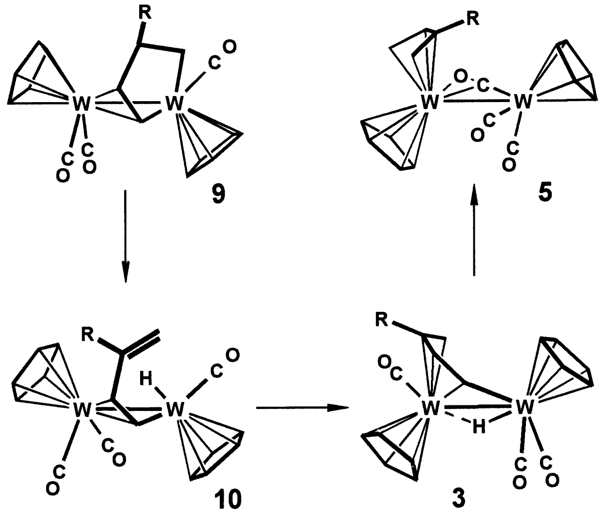
In a formal approach the $W_2C_2H_2$ fragment can be classified as a ditungstatetrahedrane and the $WC_2H_4$ entity as a tungstacyclopropane. By using this approach, the C−C bond formation is a kind of reductive elimination or reductive rearrangement, because it is accompanied by the cleavage of two W−C bonds. Also the electron deficit in **9** is possibly compensated by a 4-electron carbonyl bridge.



Unsymmetrically substituted olefins like **B** or **C** may form up to four different stereoisomers of **9**.

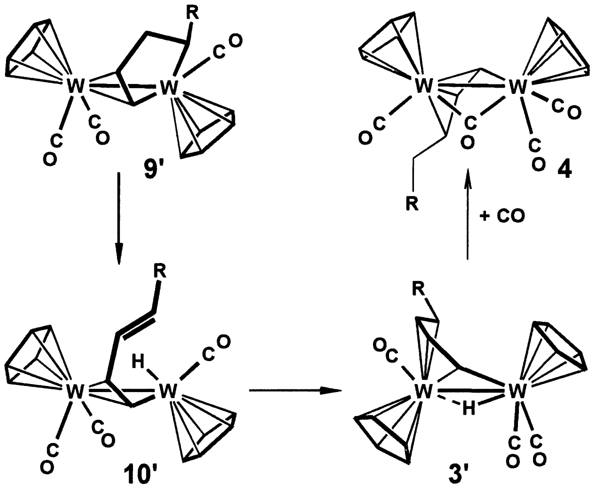
The 1-alkene-1,4-diyl ligands in **9** contain in β-position methylene or methine groups, which are susceptible to a β-elimination. This elimination leads immediately to the (μ-η$^{1:4}$-diene-1-yl)tricarbonylbis(η$^5$-cyclopentadienyl)hydridoditungsten(*W*−*W*) complexes **3A**−**3D**.

In general, the complexes **3** rearrange at room temperature by H shift to C1 of the diene-1-yl ligand quickly into the (diene)tricarbonylbis(η$^5$-cyclopentadienyl)ditungsten complexes **5**. This reaction can also be interpreted as a reductive rearrangement, leading to 32-electron complexes.



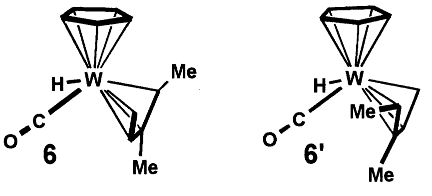
In addition to the hydrogen transfer to C1 also a transfer to C4 of the 1,3-butadiene-1-yl ligand and the coordination of carbon monoxide is possible which generates the (μ-η$^{1:3}$-2-alkene-1,1-diyl)tetracarbonylbis(η$^5$-cyclopentadienyl)ditungsten(*W*− *W*) complexes **4A**, **4B** and **4C**.

Interestingly, the complexes **3B**−**3D** and **5B**−**5D** contain branched hydrocarbon ligands which are formed from acetylene and the olefins by C−C bond formation between acetylene and C2 of the olefins. Although the methyl groups in **D** are in *E* position, in the products **3D** and **5D** they are found in *Z* position, therefore a rotation around the C3−C4 bond has to be considered while intermediate **9** rearranges into **3**.



No branched hydrocarbon ligands are found in **4B** and **4C**, so the C−C bond formation involves C1 of the olefins. Furthermore, no corresponding dienyl-hydrido or diene complexes are observed. Obviously, the dienyl-hydrido precursor complexes **9** rearrange faster and are not detectable therefore. Small amounts of **4C** are also isolated from the reaction mixture of **1** and **D**. There are two explanations for this result. Either the olefin **D** contains impurities of **C** or the olefin is isomerised under the reaction conditions prior the C−C bond formation.

The by-product of the reaction of **1** with **D**, carbonyl(η$^5$-cyclopentadienyl)hydrido{η$^4$-(*E*)-3-methyl-1,3-pentadiene}tungsten is generated in the two diastereomeric forms **6**, and **6′**. In addition to the centre of chirality at the tungsten atoms, the unsymmetrically substituted 1,3-diene ligand is planar chiral. Therefor diastereomers have to be expected and are obtained in a ratio of 0.85:0.15.



Finally, it should be mentioned, that (*Z*)-2-butene (**E**) does not form hydrocarbon ligands with acetylene at all. The only product obtained is the trinuclear tungsten complex **7** with a W−W single and a W−W triple bond and a vinyl bridge.

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## Experimental Section

All treatments and reactions were performed under dry, oxygen-free nitrogen. Solvents were dried with sodium/benzophenone or phosphorus pentoxide and saturated with nitrogen. − For column chromatography neutral alumina (Macherey, Nagel & Co KG, Düren) was heated in vacuum at 423 K and deactivated with 5% of water, saturated with nitrogen. − Photolysis reactions were conducted using a high-pressure mercury lamp (TQ 718, Heraeus Noblelight GmbH, Kleinostheim) operating at 700 W, which was immersed into a 750-ml vessel of Duran® with a cooling jacket. − C,H elemental analyses: Perkin-Elmer microanalyser 240. − IR (2200−1500 cm$^{-1}$): Perkin-Elmer Model 881. − $^1$H NMR: Puls-FT-NMR-Spektrometer AMX 400 (Bruker) at 400.13 MHz. Chemical shifts are given relatively to TMS calculated from the solvent as internal standard. − ($\mu$-$\eta^{2:2}$-Acetylene)tetracarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**1**) was prepared according to literature procedures[6][9]. All other reagents were commercial products.

1. *Photoreaction of ($\mu$-$\eta^{2:2}$-Acetylene)tetracarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(W−W)* (**1**) *with Ethylene* (**A**): 1.6 g (2.5 mmol) of ($\mu$-$\eta^{2:2}$-acetylene)tetracarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**1**) was dissolved in 750 ml of petroleum ether/THF (1:1). The solution was cooled to 243 K, and for 10 min ethylene (**A**) was condensed into it. During the photolysis nitrogen was bubbled through the solution and the progress of the reaction was controlled by IR spectroscopy in regular intervals. Irradiation was continued until the υCO bands of **1** had vanished. The solvent was removed in vacuo at 253 K and the residue was separated by column chromatography on alumina into two main fractions. The residue of the first main fraction was dissolved in 10 ml of ether and was subject of a further chromatography.

*1st Fraction* (pentane/ether 2:1): Starting material **1**.

*2nd Fraction* (pentane/ether 2:1): Pink solution; after removal of the solvent and crystallisation from ether, thermolabile ($\eta^4$-1,3-butadiene)tricarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**5A**) was obtained as red powder. Due to the thermal sensitivity of **5A** only a spectroscopic characterisation was possible (2%). − IR: $\tilde{\nu}$ = 1905 (s), 1825 (s), 1555 (m) cm$^{-1}$. − $^1$H NMR ($CD_2Cl_2$, 213 K): $\delta$ = 5.41 (ddd, *J* = 7.5, 7.0, 7,0, 1 H, H2), 3.23 (ddd, *J* = 7.5, 7.0, 7.0 Hz, 1 H, H3), 2.92 (dd, *J* = 7.0, 4.0 Hz, 1 H, H4 *E*), 2.15 (d, *J* = 7.0, 2.0 Hz, 1 H, H1 *E*), 1.47 (dd, *J* = 7.0, 2.0 Hz, 1 H, H1 *Z*), 1.43 (dd, *J* = 7.0, 4.0 Hz, 1 H, H4 *Z*); 5.43 (s, 5 H, $C_5H_5$), 5.07 (s, 5 H, $C_5H_5$).

*3rd Fraction* (pentane/ether, 2:1): Orange solution. During the removal of the solvent, orange crystals of ($\mu$-$\eta^{1:4}$-1,3-butadien-1-yl)tricarbonylbis($\eta^5$-cyclopentadienyl)($\mu$-hydrido)ditungsten(*W−W*) (**3A**) started to precipitate. The solid residue was crystallised from ether (3%). − IR: $\tilde{\nu}$ = 1925 (sh), 1910 (s), 1835 (s) cm$^{-1}$. − $^1$H NMR ($CD_2Cl_2$, 243 K): $\delta$ = 4.52 (dd, *J* = 6.5, 1.0 Hz, 1 H, H1), 4.19 (dd, *J* = 6.5, 4.5 Hz, 1 H, H2), 4.00 (dddd, *J* = 9.0, 7.5, 4.5, 1.0 Hz, 1 H, H3), 2.00 (dd, *J* = 7.5, 3.0 Hz, 1 H, H4 *E*), 1.42 (dd, *J* = 9.0, 3.0 Hz, 1 H, H4 *Z*), 5.46 (s, 5 H, $C_5H_5$), 5.20 (s, 5 H, $C_5H_5$), 17.62 [s, $^1J(^{183}W-^1H)$ = 46, 54 Hz, 1 H, W−H]. − $C_{17}H_{16}O_3W_2$ (636.01): calcd. C 32.1, H 2.5; found C 31.9, H 2.5.

*4th Fraction* (ether): Bright green solution, which turned red during removal of the solvent. By crystallisation of the residue from ether ($\mu$-$\eta^{1:3}$-2-butene-1,1-diyl)tetracarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W−W*) (**4A**) was isolated as red crystalline powder (2%). − IR: $\tilde{\nu}$ = 1945 (vs), 1900 (s), 1840 (s), 1775 (m) cm$^{-1}$. − $^1$H NMR ($CD_3COCD_3$, 253 K): $\delta$ = 9.35 (dd, *J* = 9.0, 1.0 Hz, 1 H, H1), 6.24 (dd, *J* = 9.0, 9.0 Hz, 1 H, H2), 1.47 (dqd, *J* = 9.0, 6.0, 1.0 Hz, 1 H, H3), 1.80 (d, *J* = 6.0 Hz, 3 H, H4), 5.53 (s, 5 H, $C_5H_5$), 5.46 (s, 5 H, $C_5H_5$).

2. *Photochemical Reactions of* **1** *with Propene* (**B**): According to Procedure 1, 2.0 g (3.15 mmol) of **1** and propene (**B**) in 750 ml of ether/THF (6:1) were irradiated at 253 K for 85 min. After removal of the solvent, the residue was separated by column chromatography.

*1st Fraction* (pentane/ether 3:1): Starting material **1**.

*2nd Fraction* (pentane/ether 3:1): Orange solution, which contains a mixture of **1** and ($\mu$-$\eta^{2:2}$-acetylene)tricarbonylbis($\eta^5$-cyclopentadienyl)($\eta^2$-propene)ditungsten(*W−W*) (**2B**) (4%). Even after repeated chromatography complex **2B** could not be obtained in a pure state. − IR: $\tilde{\nu}$ = 1957 (m), 1914 (s), 1826 (s) cm$^{-1}$. − $^1$H NMR ($C_7D_8$, 233 K): $\delta$ = $C_3H_6$ 1.03 (dd, *J* = 9.5, 2.0 Hz, 1 H, H1 *E*), 1.82 (dd, *J* = 11.0, 2.0 Hz, 1 H, H1 *Z*), 2.30 (ddq, *J* = 11.0, 9.5, 6.0 Hz, 1 H, H2), 1.85 (d, *J* = 6.0 Hz, 3 H, H3); $C_2H_2$ 2.35 (d, *J* = 2.0 Hz, 1 H, H1), 4.02 (d, *J* = 2.0 Hz, 1 H, H2); 4.98 (s, 5 H, $C_5H_5$), 4.95 (s, 5 H, $C_5H_5$).

*3rd Fraction* (pentane/ether 2:1): Red solution, which already yielded tricarbonylbis($\eta^5$-cyclopentadienyl)($\eta^4$-2-methyl-1,3-butadiene)ditungsten(*W−W*) (**5B**) as red, microcrystalline powder (5%). − IR: $\tilde{\nu}$ = 1899 (s), 1806 ( m), 1551 (m) cm$^{-1}$. − $^1$H NMR ($C_7D_8$, 243 K): $\delta$ = 2.71 (dd, *J* = 4.0, 1.5 Hz, 1 H, H1 *E*), 1.36 (dd, *J* = 4.0, 2.0 Hz, 1 H, H1 *Z*), 1.34 (s, 3 H, 2-$CH_3$), 4.96 (dddd, *J* = 7.0, 7.0, 2.0, 1.5 Hz, 1 H, H3), 2.90 (dd, *J* = 7.0, 2.5 Hz, 1 H, H4 *E*), 1.57 (dd, *J* = 7.0, 2.5 Hz, 1 H, H4 *Z*), 5.07 (s, 5 H, $C_5H_5$), 4.91 (s, 5 H, $C_5H_5$). − $C_{18}H_{18}O_3W_2$ (650.04): calcd. C 33.26, H 2.79; found C 33.4, H 2.8.

*4th Fraction* (pentane/ether 1:1): Yellow-orange zone; after removal of the solvent and crystallisation from ether, tricarbonylbis($\eta^5$-cyclopentadienyl)($\mu$-hydrido)($\mu$-$\eta^{1:4}$-3-methyl-1,3-butadien-1-yl)ditungsten(*W−W*) (**3B**) was isolated as orange powder (4%). − IR: $\tilde{\nu}$ = 1924 (sh), 1909 (s), 1831 (s) (υCO); 1961 (w) (υMH) cm$^{-1}$. − $^1$H NMR ($CDCl_3$, 243 K): $\delta$ = 4.39 (dd, *J* = 6.0, 2.0 Hz, 1 H, H1), 4.03 (d, *J* = 6.0 Hz, 1 H, H2), 2.11 (s, 3 H, 3-$CH_3$), 1.89 (d, *J* = 3.0 Hz, 1 H, H4 *E*), 1.59 (d, *J* = 3.0 Hz, 1 H, H4 *Z*), 5.45 (s, 5 H, $C_5H_5$), 5.11 (s, 5 H, $C_5H_5$), −17.38 (d, *J* = 2.0 Hz, $^1J^{183}W-^1H$ 46, 56 Hz, 1 H, W−H). − $C_{18}H_{18}O_3W_2$ (650.04): calcd. C 33.26, H 2.79; found C 32,2, H 2,6.

*5th Fraction* (pentane/THF 1:1): The residue of the red-brown solution was crystallised from ether. Tetracarbonylbis($\eta^5$-cyclopentadienyl)($\mu$-$\eta^{1:3}$-2-penten-1,1-diyl)ditungsten(*W−W*) (**4B**) was obtained as red-brown crystals (1%). − IR: $\tilde{\nu}$ = 1948 (vs), 1905 (s), 1848 (s), 1775 (m) cm$^{-1}$. − $^1$H NMR ($CD_3COCD_3$, 283 K): $\delta$ = 9.35 (dd, *J* = 8.5, 1.0 Hz, 1 H, H1), 6.20 (dd, *J* = 10.0, 8.5 Hz, 1 H, H2), 1.50 (dddd, *J* = 10.0, 10.0, 3.5, 1.0 Hz, 1 H, H3), 1.65 (ddq, *J* = 14.0, 10.0, 7.5 Hz, 1 H, H4), 2.10 (dqd, *J* = 14.0, 7.5, 3.5, Hz, 1 H, H4′), 1.01 (t, *J* = 7.5 Hz, 3 H, H5), 5.52 (s, 5 H, $C_5H_5$), 5.46 (s, 5 H, $C_5H_5$). − $C_{19}H_{18}O_4W_2$ (678.05): calcd. C 33.66, H 2.68; found C 33.4, H 2.8.

3. *Photochemical Reactions of* **1** *with 1-Butene* (**C**): According to Procedure 1, 1.6 g (2.5 mmol) of **1** and 1-butene (**C**) were irradiated in 750 ml of ether/THF (6:1) for 90 min with UV light. Column chromatography on $Al_2O_3$ yielded four characterised products.

*1st Fraction* (pentane/ether 3:1): Yellow zone, very small amount of substance, discarded.

*2nd Fraction* (pentane/ether 3:1): Starting material **1**.

*3rd Fraction* (pentane/ether 3:1): Orange solution; after removal of the solvent, a mixture of **1** and ($\mu$-$\eta^{2:2}$-acetylene)($\eta^2$-1-butene)tricarbonylbis($\eta^5$-cyclopentadienyl)ditungsten(*W*−*W*) (**2C**) was isolated as orange powder (5%). Even by repeated chromatography, **2C** could not be isolated in pure form. − IR: $\tilde{\nu}$ = 1965 (m), 1921 (s), 1834 (m) cm$^{-1}$. − $^1$H NMR ($C_7D_8$, 233 K): $C_4H_8$: $\delta$ = 0.96 (dd, *J* = 9.5, 2.5 Hz, 1 H, H1 *E*), 1.75 (dd, *J* = 11.0, 2.5 Hz, 1 H, H1 *Z*), 2.29 (m, *J* = 11.0, 9.5, 4.0 Hz, 1 H, H2), 1.20 (m, *J* = 14.0, 7.0 Hz, 1 H, H3), 2.02 (m, *J* = 14.0, 7.0, 4.0 Hz, 1 H, H3′), 1.41 (t, *J* = 7.0 Hz, 3 H, H4); $C_2H_2$: $\delta$ = 2.33 (d, *J* = 2.0 Hz, 1 H, H1), 4.06 (d, *J* = 2.0 Hz,1 H, H2); 4.96 (s, 5 H, $C_5H_5$), 4.90 (s, 5 H, $C_5H_5$).

*4th Fraction* (pentane/ether 2:1): Red solution, after removal of the solvent tricarbonylbis($\eta^5$-cyclopentadienyl)($\eta^4$-3-methylene-1-pentene)ditungsten(*W*−*W*) (**5C**) was obtained as red, crystalline powder (5%). − IR: $\tilde{\nu}$ = 1900 (s), 1806 (m), 1551 (m) cm$^{-1}$. − $^1$H NMR ($CDCl_3$, 253 K): $\delta$ = 2.60 (d, *J* = 4.0 Hz, 1 H, H1 *E*), 1.39 (d, *J* = 4.0 Hz, 1 H, H1 *Z*); 2-$C_2H_5$: $\delta$ = 0.89 (m, *J* = 7.0 Hz, 2 H), 0.99 (t, *J* = 7.0 Hz, 3 H); $\delta$ = 4.85 (dd, *J* = 7.0, 7.0 Hz, 1 H, H3), 2.42 (dd, *J* = 7.0, 2.5 Hz, 1 H, H4 *E*), 1.58 (dd, *J* = 7.0, 2.5 Hz, 1 H, H4 *Z*), 5.39 (s, 5 H, $C_5H_5$), 5.08 (s, 5 H, $C_5H_5$). − $C_{19}H_{20}O_3W_2$ (664.07): calcd. C 34.37, H 3.04; found C 34.5, H 3.2.

*5th Fraction* (ether): Yellow-orange solution, from which after removal of the solvent tricarbonylbis($\eta^5$-cyclopentadienyl)($\mu$-hydrido)($\mu$-$\eta^{1:4}$-3-methylene-1-penten-1-yl)ditungsten(*W*−*W*) (**3C**) results as an orange powder (6%). − IR: $\tilde{\nu}$ = 1924 (sh), 1909 (s), 1830 (s) ($\upsilon$CO); 1961 (w) ($\upsilon$MH) cm$^{-1}$. − $^1$H NMR ($CDCl_3$, 243 K): $\delta$ = 4.43 (d, *J* = 6.0 Hz, 1 H, H1), 4.06 (d, *J* = 6.0 Hz, 1 H, H2); 3-$C_2H_5$: $\delta$ = 1.84 (dq, *J* = 16.0, 7.0 Hz, 1 H), 1.72 (dq, *J* = 16.0, 7.0 Hz, 1 H), 1.24 (t, *J* = 7.0 Hz, 3 H); $\delta$ = 1.87 (d, *J* = 2.0 Hz, 1 H, H4 *E*), 1.53 (d, *J* = 2.0 Hz, 1 H, H4 *Z*), 5.44 (s, 5 H, $C_5H_5$), 5.09 (s, 5 H, $C_5H_5$), −17.37 [s, $^1J(^{183}W-^1H)$ = 47, 53 Hz, 1 H, W−H]. − $C_{19}H_{20}O_3W_2$ (664.07): calcd. C 34.37, H 3.04; found C 34.7, H 3.0.

*6th Fraction* (pentane/THF 1:1): From the red solution tetracarbonylbis($\eta^5$-cyclopentadienyl)($\mu$-$\eta^{1:3}$-2-hexene-1,1-diyl)ditungsten(*W*−*W*) (**4C**) was obtained after recrystallisation in form of red crystals (1%). − IR: $\tilde{\nu}$ = 1945 (vs), 1901 (s), 1842 (s), 1771 (m) cm$^{-1}$. − $^1$H NMR ($CDCl_3$, 253 K): $\delta$ = 8.97 (d, *J* = 9.0 Hz, 1 H, H1), 5.90 (dd, *J* = 9.0, 9.0 Hz, 1 H, H2), 1.72 (m, *J* = 9.0, 3.5 Hz, 1 H, H3), 2.12 (m, *J* = 3.5 Hz, 1 H, H4), 1.45 (m, *J* = 7.0 Hz, 3 H, H5), 0.89 (t, *J* = 7.0 Hz, 3 H, H6), 5.35 (s, 5 H, $C_5H_5$), 5.23 (s, 5 H, $C_5H_5$).

4. *Photochemical Reactions of* **1** *with (E)-2-Butene* (**D**): According to Procedure 1, 1.6 g (2.5 mmol) of **1** and (*E*)-2-butene (**D**) were irradiated with UV light in 750 ml of ether/THF (6:1) for 85 min. The reaction mixture was separated into its components by column chromatography.

*1st Fraction* (pentane/ether, 3:1): Yellow zone of small intensity; after crystallisation of the residue from pentane, few yellow crystals of carbonyl($\eta^5$-cyclopentadienyl)hydrido[$\eta^4$-(*E*)-3-methyl-1,3-pentadiene]tungsten (**6**, **6′**) were isolated (1%). − IR: $\tilde{\nu}$ = 1927 cm$^{-1}$. − $^1$H NMR ($CD_2Cl_2$, 253 K): Major isomer (0.85): $\delta$ = −0.12 (dd, *J* = 9.0, 4.0 Hz, 1 H, H1 *Z*), 1.49 (ddd, *J* = 8.0, 4.0, 3.0 Hz, 1 H, H1 *E*), 4.07 (dd, *J* = 9.0, 8.0 Hz, 1 H, H2), 2.37 (s, 1 H, 3-$CH_3$), 0.42 (q, *J* = 6.0 Hz, 1 H, H4 *Z*), 1.91 (dd, *J* = 6.0, 1.0 Hz, 3 H, H5), 4.87 (s, 5 H, $C_5H_5$), −6.13 [dd, *J* = 3.0, 1.0, Hz, $^1J(^{183}W-^1H)$ = 74 Hz, 1 H, W−H); minor isomer (0.15): $\delta$ = −0.04 (dd, *J* = 7.0, 3.5 Hz, 1 H, H1 *Z*), 1.49 (ddd, *J* = 7.0, 3.5, 1.0 Hz, 1 H, H1 *E*), 4.44 (dd, *J* = 7.0, 7.0 Hz, 1 H, H2), 2.46 (s, 1 H, 3-$CH_3$), 0.70 (q, *J* = 6.0 Hz, 1 H, H4 *Z*), 1.41 (d, *J* = 6.0 Hz, 3 H, H5), 4.87 (s, 5 H, $C_5H_5$), −9.65 [d, *J* = 1.0, Hz, $^1J(^{183}W-^1H)$ = 76 Hz, 1 H, W−H).

*2nd Fraction* (pentane/ether 3:1): Starting material **1**.

*3rd Fraction* (pentane/ether, 2:1): Red-brown solution, already during removal of the solvent red-brown crystals of tricarbonylbis($\eta^5$-cyclopentadienyl)[$\eta^4$-(*E*)-3-methyl-1,3-pentadiene]ditungsten(*W*−*W*) (**5D**) precipitated (7%). − IR: $\tilde{\nu}$ = 1901 (s), 1810 (m), 1548 (m) cm$^{-1}$. − $^1$H NMR ($C_7D_8$, 253 K): $\delta$ = 2.88 (dd, *J* = 7.0, 3.0 Hz, 1 H, H1 *E*), 1.55 (dd, *J* = 7.0, 3.0 Hz, 1 H, H1 *Z*), 4.81 (t, *J* = 7.0, 7.0 Hz, 1 H, H2), 1.23 (s, 3 H, 3-$CH_3$), 1.66 (q, *J* = 6.0 Hz, 1 H, H4 *Z*), 2.03 (d, *J* = 6.0 Hz, 3 H, H5), 5.08 (s, 5 H, $C_5H_5$), 4.79 (s, 5 H, $C_5H_5$). − $C_{19}H_{20}O_3W_2$ (664.07): calcd. C 34.37, H 3.04; found C 34.3, H 2.9.

*4th Fraction* (pentane/ether 2:1): Orange fraction, which yielded after removal of the solvent an orange mixture of **5D** and tricarbonylbis($\eta^5$-cyclopentadienyl)($\mu$-hydrido)[$\mu$-$\eta^{1:4}$-(*E*)-3-methyl-1,3-pentadien-1-yl]ditungsten(*W*−*W*) (**3D**) (5%). Even by repeated chromatography **3D** was not obtained in a pure state. − IR: $\tilde{\nu}$ = 1923 (s), 1902 (s), 1834 (s) cm$^{-1}$. − $^1$H NMR ($CDCl_3$, 243 K): $\delta$ = 4.54 (dd, *J* = 6.5, 1.5 Hz, 1 H, H1), 3.93 (d, *J* = 6.5 Hz, 1 H, H2), 2.05 (s, 3 H, 3-$CH_3$), 2.26 (q, *J* = 6.5 Hz, 1 H, H4 *Z*), 1.37 (d, *J* = 6.5 Hz, 3 H, H5), 5.47 (s, 5 H, $C_5H_5$), 5.12 (s, 5 H, $C_5H_5$), −18.14 [d, *J* = 1.5 Hz, $^1J(^{183}W-^1H)$ = 47, 56 Hz, 1 H, W−H). − $C_{19}H_{20}O_3W_2$ (664.07): calcd. C 34.4, H 3.0; found C 34,6, H 2,8.

*5th Fraction* (pentane/THF 4:1): Bright-red zone, after recrystallisation red crystals of **4C** (1%).

5. *Photochemical Reactions of* **1** *with (Z)-2-Butene* (**E**): According to Procedure 1, 1.8 g (2.8 mmol) of **1** and (*Z*)-2-butene (**E**) were irradiated with UV light in 750 ml of ether/THF (6:1) for 300 min. The reaction mixture contained large amounts of insoluble decomposition products. It was filtered through compressed filter flakes and brought to dryness at 253 K.

*1st Fraction* (pentane/ether 3:1): Starting material **1**.

*2nd Fraction* (pentane/ether 3:1): Yellow-orange solution, discarded.

*3rd Fraction* (ether): Red-brown solution; after partial removal of the solvent and cooling to 198 K, red-brown crystals of pentacarbonyltris($\eta^5$-cyclopentadienyl)($\mu$-$\eta^{1:2}$-vinyl)tritungsten(*W*−*W*−*W*) (**7**) were formed (1%). − IR: $\tilde{\nu}$ = 1925 (sh), 1910 (vs), 1849 (s), 1840 (sh) cm$^{-1}$. − $^1$H NMR ($CDCl_3$, 253 K): $\delta$ = 7.04 (dd, *J* = 11.0, 11.0 Hz, 1 H, H1), 4.72 (dd, *J* = 11.0, 1.0 Hz, 1 H, H2 *E*), 1.79 (dd, *J* = 11.0, 1.0 Hz, 1 H, H2 *Z*), 5.43 (s, 5 H, $C_5H_5$), 5.37 (s, 5 H, $C_5H_5$), 4.88 (s, 5 H, $C_5H_5$). − $C_{22}H_{18}O_5W_3$ (913.93): calcd. C 28.91, H 1.99; found C 30.3, H 2.4.

6. *X-ray Structural Analysis of* **5D**[44]: $C_{19}H_{20}O_3W_2$, *M* = 664.05 g·mol$^{-1}$, monoclinic space group $P2_1/n$, *a* = 1089.3(2), *b* = 1240.5(3), *c* = 1303.7(2) pm, $\beta$ = 95.914(14)°, *V* = 1.7522(6) nm$^3$, *Z* = 4, $\rho$(calcd.) = 2.517 g·cm$^{-3}$. Crystal size 0.40 × 0.25 × 0.05 mm, *T* = 293 K. Using a CAD4 diffractometer (Enraf Nonius), radiation Mo-$K_\alpha$, wavelength $\lambda$ = 71.073 pm, scan type $\omega$-$^1/_3$q, 4487 reflections were collected in the $\theta$ range 2.27−22.45°. After data reduction, 2267 symmetry-independent reflections ($R_{int}$ = 0.0512) were obtained. The structure was solved by direct methods using SHELXS-86[45] and refined by full-matrix least-squares against $F^2$ with SHELXL-93[46]. 232 parameters were refined to $R[I > 2\sigma(I)]$ = 0.0281, $wR2$(all data) = 0.0750. The hydrogen atoms of the cyclopentadienyl ligands and the methyl groups were located geometrically. All the other hydrogen atoms were detected. For the refinement the C−H distance was set to 97 pm, and the tempera-

ture factors of the hydrogen atoms were fixed at 1.2 times $U_{\mathrm{eq}}$ of the corresponding carbon atoms.

7. *X-ray Structural Analysis of 7*[44]: $C_{22}H_{18}O_5W_3$, $M$ = 913.91 g·mol$^{-1}$, monoclinic space group $P2_1/n$, $a$ = 780.61(7), $b$ = 2197.1(3), $c$ = 1403.80(11) pm, $\beta$ = 100.753(6)°, $V$ = 2.3654(4) nm$^3$, $Z$ = 4, $\rho$(calcd.) = 2.566 g·cm$^{-3}$. Crystal size 0.62 × 0.30 × 0.03 mm, $T$ = 293 K. Using a CAD4 diffractometer (Enraf Nonius), radiation Mo-$K_\alpha$, wavelength $\lambda$ = 71.073 pm, scan type $\omega$-$\theta$, 4426 reflections were collected in the $\theta$ range 1.74−24.99°. After data reduction, 3880 symmetry-independent reflections ($R_{\mathrm{int}}$ = 0.099) were obtained. The structure was solved by direct methods using SHELXS-86[45] and refined by full-matrix least squares against $F^2$ with SHELXL-93[46]. 280 parameters were refined to $R[I > 2\sigma(I)]$ = 0.0491, $wR2$(all data) = 0.1245. The hydrogen atoms of the cyclopentadienyl ligands were located geometrically. All the other hydrogen atoms were found. For the refinement the temperature factor of the hydrogen atoms was set to the 1.2-fold value of that of the related carbon atom. The data set was modified using PLATON-92[47] to account for a multiply disordered ether molecule on a centre of inversion.

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☆ Dedicated to Professor Dr. *Gottfried Huttner* on the occasion of his 60th birthday.

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