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Synthesis and reactivity of the α,β-unsaturated carbene tungsten complex $(CO)_5W[C(OCH_3)CH{=}CH_2]$

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Abstract

Treatment of $W(CO)_6$ with vinyllithium followed by Me_3OBF_4 in the presence of H_2O produced $(CO)_5W[C(OCH_3)CH{=}CH_2]$ (**1**) (25–30%) and $(CO)_5W[C(OCH_3)$-$(\eta^2$-$CH{=}CH_2)]W(CO)_5$ (**2**) (20–30%). Complex **1** reacted with $(CO)_5W \cdot THF$ to give $W_2(CO)_9[\mu$-η^1,η^3-$C(OCH_3)CH{=}CH_2]$ (**3**) (61%). Heating **2** to 45 °C in toluene produced **3** (65%) which could be converted back to **2** upon treatment with CO. Complex **1** reacted with D_2O in benzene-d_6 to afford **2** and methyl propionate-2,3-d_2 (**4**). A new route to **1** was developed from $W(CO)_6$ in an overall yield of 40% using $(CO)_5W[C(O)CH{=}CH_2]NMe_4$ (**8**) as an intermediate.

Introduction

In 1968 the preparation of the first α,β-unsaturated transition-metal carbene complex, $(CO)_5Cr[C(NHC_6H_{11})C(OCH_3){=}CH_2]$, was described by Aumann and Fischer [1]. Subsequently, the synthesis of the parent α,β-unsaturated chromium carbene complex, $(CO)_5Cr[C(OCH_3)CH{=}CH_2]$, was described in two reports; the first in 1971 [2] and the second, using a slightly different method of preparation than the first, in 1973 [3]. Following these initial reports, many additional reports of mononuclear α,β-unsaturated carbene complexes, which contain various transition metals and ligands, have appeared in the literature [4].

Results and discussion

Our current interests in investigating the preparation and reactivity of transition-metal α,β-unsaturated carbene complexes include: (1) the polymerization of carbene vinyl monomers such as $(CO)_5W[C(OCH_3)CH{=}CH_2]$ (**1**) to novel organometallic polymers [5], (2) the synthesis of ditungsten μ-carbene complexes [6], (3) the formation and reactivity of (μ-bis(carbene))dimetallic complexes [7], and (4) the

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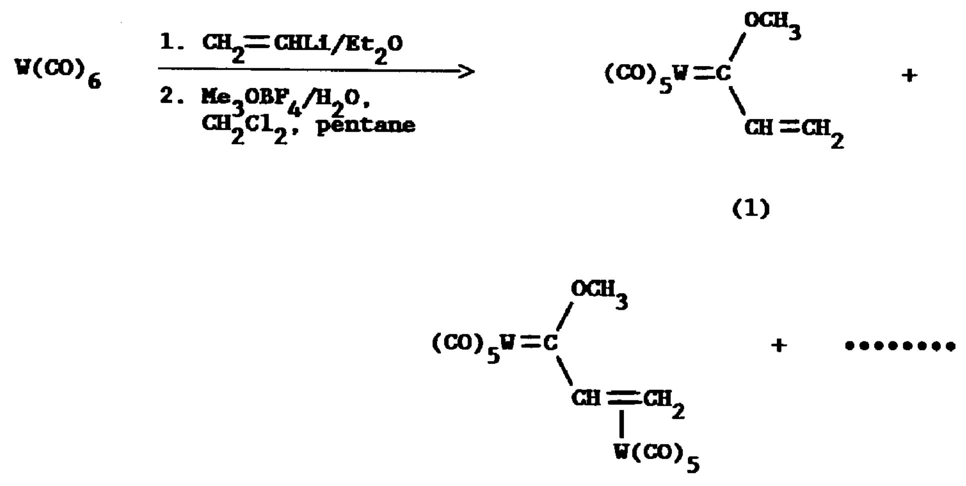


(1)

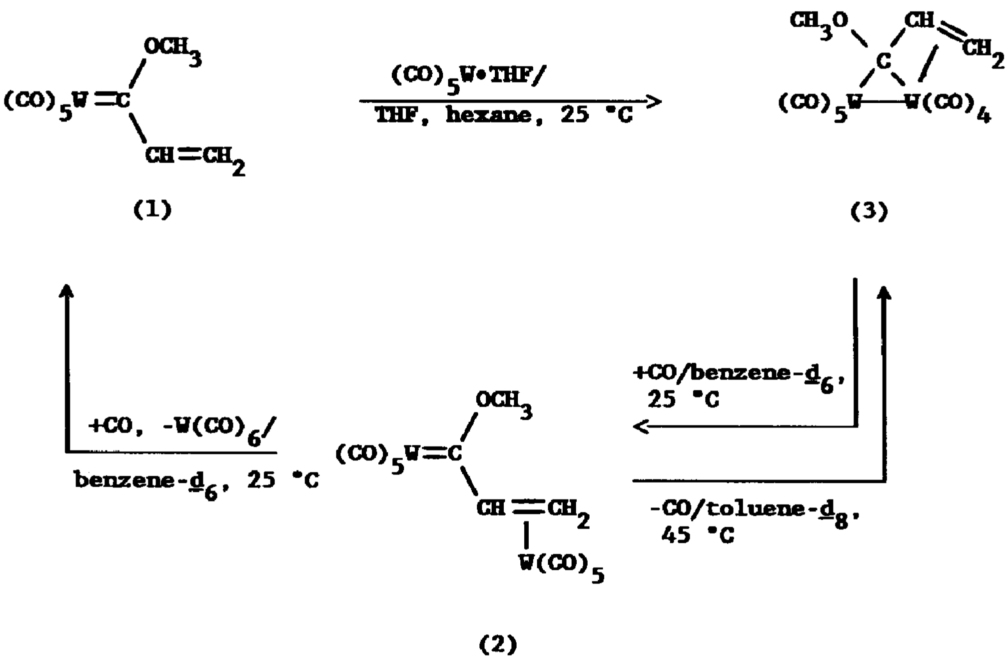
(1)

(2)

conversion of α-(trimethylsilyl)alkyl(aminocarbene) complexes to interesting α,β-unsaturated(aminocarbene) complexes [8].

The preparations of **1** and its relative **2** have been described in two accounts [9,10] using a procedure originally developed for the chromium analog $(CO)_5Cr[C(OCH_3)CH=CH_2]$ [3]. In our hands, treatment of $W(CO)_6$ with vinyllithium followed by alkylation with Me_3OBF_4 produced **1** (25–30%) and **2** (20–30%) (eq. 1). To obtain even these moderate yields of **1** it was necessary to quickly chromatograph the reaction mixture at low temperatures (−20 to −30 °C) on silica gel, collect the pentane eluent at 0 °C, and remove the solvent at 0 °C under high vacuum. Complex **1**, prepared in this manner, was a red-purple crystalline solid. If complex **1** was allowed to melt (m.p. ca. 10 °C) and then stand at 0–25 °C for ca. 1 week, an 80% yield of the orange insoluble homopolymer, $\{-CH_2CH[W]-\}_n$ ($[W] = (CO)_5W[C(OCH_3)]$), was obtained [5]. In contrast to the behavior of **1**, complex **2** remains unchanged at 25 °C in the solid state but does, however, lose a CO ligand at higher temperature in solution to form the ditungsten μ-carbene complex **3** [10] (v. infra).

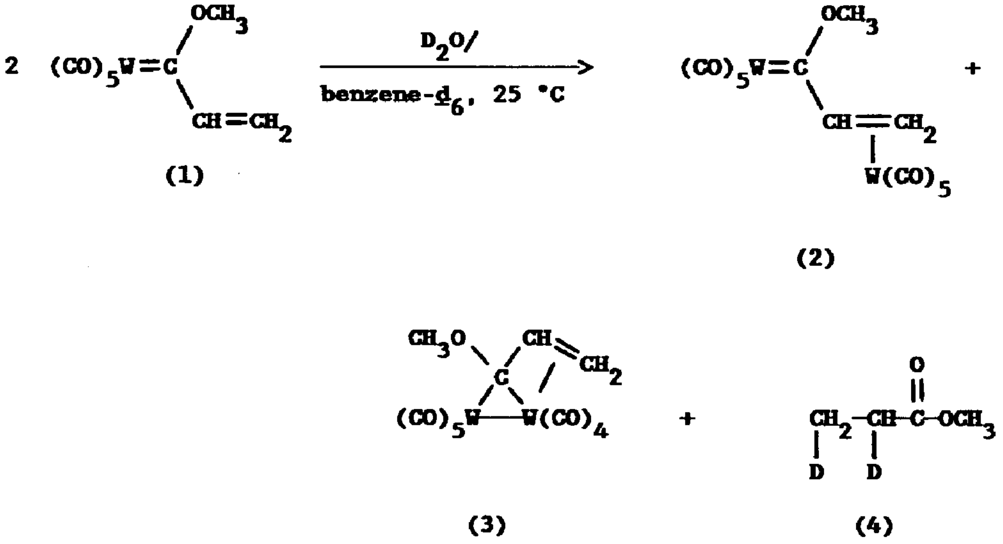
Compound **3**, which contains a μ-η^1,η^3-allylidene ligand, was obtained in 65% yield upon heating a toluene solution of **2** at 45 °C (Scheme 1). The conversion of **2** to **3** could also be conveniently followed by ^1H NMR spectroscopy in toluene-d_8 solution. The progress of the reaction was monitored by observing a decrease in the intensity of the methoxy resonance of **2** (δ 3.67 ppm) with concomitant increase in the methoxy resonance of **3** (δ 3.10 ppm) as well as changes in the vinylic resonances. It was subsequently discovered that **3** could easily be converted back to **2** merely by passing a stream of CO through a solution of **3**. The conversion of **3** to **2**, in benzene-d_6 solution using CO, was followed by ^1H NMR spectroscopy. It was also observed, using ^1H NMR spectroscopy, that upon prolonged passage of CO through this solution of **2** and **3**, that **2** was slowly converted to **1** and $W(CO)_6$ (see Experimental section for details). As previously reported [6], complex **3** could be obtained directly from **1** in 61% yield by treating a hexane solution of **1** with $(CO)_5W \cdot THF$ (generated photochemically from $W(CO)_6$ in THF). Interestingly,



Scheme 1

complex **2** was never observed during the conversion of **1** to **3**. The reactions described in Scheme 1 are noteworthy, in that, there are very few examples of facile interconversions of terminal carbene complexes (e.g. **2**) and μ-carbene complexes (e.g. **3**) [11]

We next turned our attention to understanding how complex **2** was formed under the conditions described in eq. 1. Upon further investigation we found, using ^1H NMR spectroscopy, that a toluene-d_8 solution of complex **1** was slowly converted in the presence of H_2O to **2** and methyl propionate. Over the course of this conversion



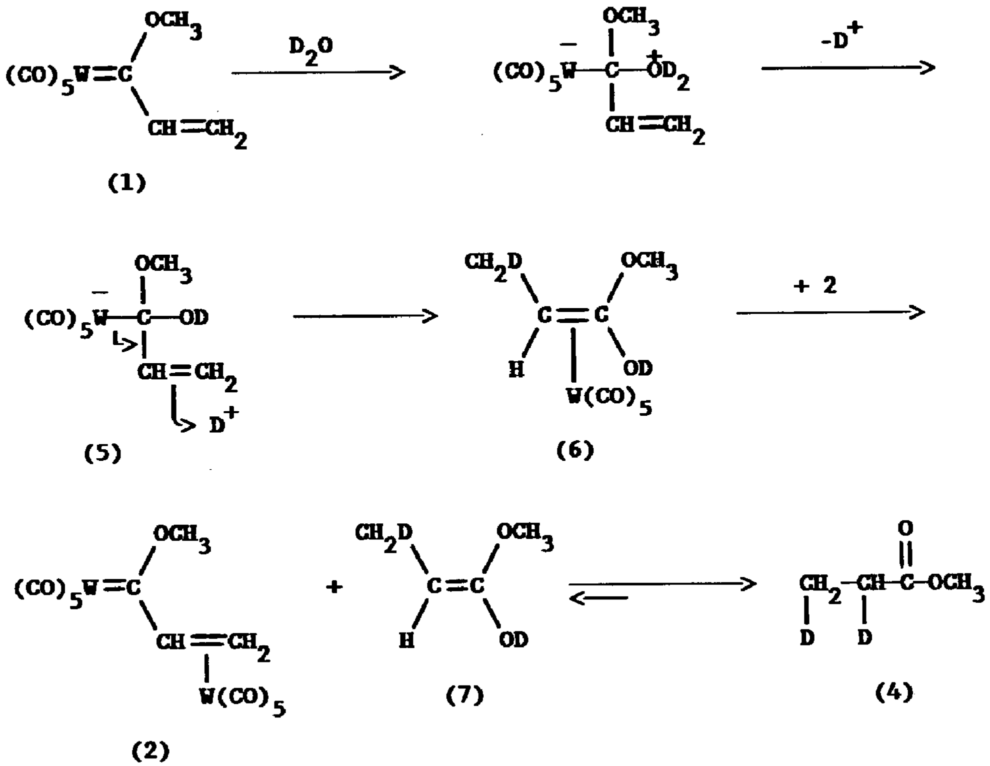
(2)

the intensities of the resonances for **1** decreased with concomitant increases in the intensities for **2** and methyl propionate in approximately equimolar amounts. The methyl propionate observed during this conversion exhibited the following ^1H NMR resonances: δ 3.33 (s, 3 H), 2.00 (q, 2 H), and 0.94 ppm (t, 3 H). The $^{13}C\{^1H\}$ NMR spectrum exhibited resonances at δ 173.94, 50.89, 27.22, and 9.06 ppm. To gain additional insight into this interesting conversion, complex **1** was allowed to react with D_2O in benzene-d_6 over a several day period (eq. 2). The progress of the reaction was monitored periodically by ^1H NMR spectroscopy. After 8 d at 25 °C, compounds **1**, **2**, **3**, and **4** were present in the following percentages: **1** (20%), **2** (29%), **3** (11%), **4** (40%). The percentages of these compounds were determined by integrating the corresponding three-proton methoxy resonances of **1** (δ 3.74 ppm), **2** (δ 3.67 ppm), **3** (δ 3.10 ppm), and **4** (δ 3.32 ppm). The formation of **3** (eq. 2) probably arises by loss of a CO ligand from **2** as previously described (Scheme 1).

The reaction described in eq. 2 was also conducted in a preparative manner so that compound **4** could be isolated and its spectroscopic values measured. The volatile products from this reaction were analyzed by GC/MS analysis and ^{13}C NMR spectroscopy. The mass spectral analysis indicated a mixture consisting of 90% of **4** ($m/e = 90$, M^+) and 10% of undeuterated methyl propionate ($m/e = 88$, M^+). The $^{13}C\{^1H\}$ NMR spectrum of this mixture exhibited the following resonances: δ 173.99 (C=O), 50.89 (OCH$_3$), 27.17 ($CH_3\mathit{C}H_2CO_2CH_3$), 26.89 ($CH_2D\mathit{C}HDCO_2CH_3$), 9.05 ($\mathit{C}H_3CH_2CO_2CH_3$), and 8.79 ppm ($\mathit{C}H_2DCHDCO_2CH_3$). Furthermore, the resonances at δ 26.89 and 8.79 ppm appeared as triplets with $J(^{13}C-^2H) = 19.5$ and 19.3 Hz, respectively. The upfield shifts of ^2H-substituted carbons as compared to ^1H-substituted carbons (ca. 0.3 ppm for **4** vs. methyl propionate) have previously been observed in many organic systems [12]. Likewise, the magnitudes of the $^{13}C-^2H$ coupling constants observed for **4** are within the range commonly seen for ^2H directly bonded to an sp^3-hybridized carbon [12a]. The source of the ^1H in the formation of the 10% undeuterated methyl propionate (eq. 2) was not determined, however, small amounts of water could have been present in the starting material **1**.

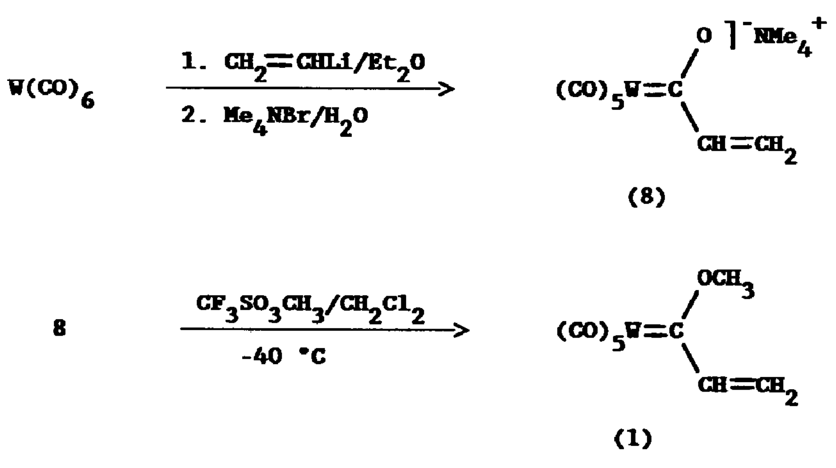
A proposed mechanism for the formation of **2** and **4**, according to eq. 2, is outlined in Scheme 2. The first proposed step involves nucleophilic attack of D_2O at the carbene carbon of **1** followed by loss of D^+ to yield **5**. Electrophilic addition of D^+ to the carbon–carbon double bond of intermediate **5** along with bond reorganization could produce the $(CO)_5W$-alkene adduct **6**. A similar process, as suggested for the conversion of **5** to **6**, has been proposed by Casey and co-workers for an α,β-unsaturated chromium carbene complex [13]. Complex **6** could then exchange its alkene ligand for **1**, to produce **2**, and the dideuterated enol form of methyl propionate (**7**). Tautomerization of **7** in the presence of D_2O would then afford the observed methyl propionate-2,3-d_2 (**4**). Traces of acids or bases may accelerate the conversion of **1** and D_2O to **2** and **4**; moreover, this may explain the ready formation of **2** under the reaction conditions described in eq. 1. It is also possible that unsaturated tungsten carbonyl fragments present during the preparation of **1** (eq. 1), could accelerate the formation of **2**.

At this stage of the investigation, and after having realized that the presence of water lowers the yield of **1** (eq. 1), we set out to develop a high-yield route to **1** that avoided aqueous conditions during the final alkylation step. Thus, the tetramethylammonium pentacarbonylacyltungstate complex **8** was discovered to be a key



Scheme 2

intermediate in our new route to **1** (Scheme 3). Treatment of $W(CO)_6$ with vinyllithium followed by exchange of Li^+ with Me_4N^+ Br^-, according to literature methods [14], produced **8** in 50% yield as an air-stable red-orange solid. Large amounts (15 g) of **8** have been prepared and can be conveniently stored unchanged for several months at 0 °C under a nitrogen atmosphere. Alkylation of **8** with



Scheme 3

$CF_3SO_3CH_3$ at −40 °C in anhydrous methylene chloride cleanly produced pure **1** in 80% yield without the need for chromatographic purification. Interestingly, in contrast to the preparation of **1** described in eq. 1, complex **1**, prepared according to Scheme 3, did not undergo bulk polymerization upon prolonged standing. Furthermore, if **1**, prepared according to Scheme 3, was subjected to silica gel chromatography and then allowed to stand at 0 °C for several days, an 85% yield of the corresponding homopolymer was produced [15].

Experimental

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-400 instrument at 400.1 and 100.6 MHz, respectively. ^1H NMR data are reported as follows: chemical shift in parts per million referenced to residual solvent proton resonance (multiplicity, coupling constant(s) in hertz, number of protons). ^{13}C NMR data are reported as follows: chemical shift in parts per millions referenced to residual solvent carbon resonances (multiplicity). Low-resolution mass spectra were acquired on a Finnigan 4000 instrument. Gas chromatographic/mass spectral analyses were carried out on a 6 ft column of 30% SE30 on Chromosorb W at 60 °C and 35 eV. Elemental analyses were performed by Microlytics, South Deerfield, MA.

Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Pentane, hexane, methylene chloride, and toluene were distilled from CaH_2 under nitrogen. Vinyllithium was prepared from tetravinyltin [16] according to the method of Marks et al. [17]. All reagents and starting materials obtained from commercial sources were used without further purification. Deuterium oxide (99.8 atom% D) was purchased from Aldrich Chemical Company. Deuterated benzene and toluene were dried over CaH_2 followed by vacuum transfer from sodium metal. These dried degassed solvents were stored in sealed flasks in an inert atmosphere dry box. Column chromatography was conducted under nitrogen on E. Merck silica gel 60 (40–63 μm) using a modified [18] low-temperature air-sensitive flash chromatography apparatus [19].

$(CO)_5W[C(OCH_3)CH{=}CH_2]$ (1) and $(CO)_5W[C(OCH_3)(\eta^2\text{-}CH{=}CH_2)]W(CO)_5$ (2)

This procedure was patterned after the preparation of the chromium analog of **1** [3]. In a 250 ml three-neck flask were placed $W(CO)_6$ (1.75 g, 5.0 mmol) and 80 ml of diethyl ether. To this was added dropwise a diethyl ether solution (20 ml) of vinyllithium (0.17 g, 5.0 mmol). After the addition was complete the reaction mixture was stirred for one hour and then the solvent was removed under high vacuum. The resulting residue was taken up in 100 ml of 1/1 methylene chloride/pentane and trimethyloxonium tetrafluoroborate (0.71 g, 5.0 mmol) was added with vigorous stirring. To this mixture was added 1.0 ml of degassed water. After stirring for 4 min the dark red reaction mixture was quickly filtered through a small column of anhydrous Na_2SO_4/celite/silica gel under nitrogen. The resulting dark red filtrate was collected at 0 °C and the solvent was removed under high vacuum at this temperature. The crude products were chromatographed at −25 °C; eluting the column with pentane produced a red band which was collected at 0 °C under nitrogen. Removal of the solvent under high vacuum at 0 °C gave 0.49 g (25%) of **1** as red-purple crystals. ^1H NMR (benzene-d_6) δ 7.04 (dd, J 16.9, 10.3 Hz, 1H, $CH{=}$), 5.28 (dd, J 16.8, 1.4 Hz, 1H, $=CH_2$), 4.64 (dd, J 10.4, 1.4 Hz, 1H, $=CH_2$), 3.74 (s, 3H, OCH_3); ^{13}C NMR (benzene-d_6) δ 312.49 (s, W=*C*), 203.77 (s, W–*C*O, *trans*), 197.44 (s, W–*C*O, *cis*), 152.44 (d, *C*H=), 119.30 (t, =*C*H_2), 68.76 (q, O*C*H_3).

Further elution of the column with 15% methylene chloride/pentane produced another red band which was collected under nitrogen. Removal of the solvent under vacuum and recrystallization from 10% methylene chloride/hexane produced red crystals of **2** (0.72 g, 20%). ^{1}H NMR (benzene-d_6) δ 5.16 (dd, *J* 13.6, 8.2 Hz, 1H, C*H*=), 3.67 (s, 3H, OCH_3), 2.82 (d, *J* 13.5 Hz, 1H, =CH_2), 2.47 (d, *J* 8.2 Hz, 1H, =CH_2); ^{13}C NMR (benzene-d_6) δ 310.71 (s, W=*C*), 202.78(s), 201.56(s), 197.52(s), 194.81(s), 91.60(d, *C*H=), 67.32 (q, O*C*H_3), 48.22 (t, =*C*H_2); MS, *m/e* for ^{184}W (assignment, relative intensity) 718 (M^+, 65), 690 ($M^+ -$ CO, 3), 662 ($M^+ -$ 2CO, 10), 634 ($M^+ -$ 3CO, 6), 606 ($M^+ -$ 4CO, 21), 578 ($M^+ -$ 5CO, 40), 550 ($M^+ -$ 6CO, 100), 522 ($M^+ -$ 7CO, 62), 494 ($M^+ -$ 8CO, 50), 466 ($M^+ -$ 9CO, 36), 438 ($M -$ 10CO, 28), 394 ($M^+ -$ W(CO)$_5$, 51), 366 ($M^+ -$(CO)$_5$W $-$ CO, 51), 338 (M^+ $-$(CO)$_5$W $-$ 2CO, 99), 310 ($M^+ -$(CO)$_5$W $-$ 3CO, 67), 295 ($M^+ -$(CO)$_5$W $-$ 3CO $-$ CH$_3$, 41), 282 ($M^+ -$(CO)$_5$W $-$ 4CO, 49), 267 ($M^+ -$(CO)$_5$W $-$ 4CO $-$ CH$_3$, 50), 254 ($M^+ -$(CO)$_5$W $-$ 5CO, 58), 239 ($M^+ -$(CO)$_5$W $-$ 5CO $-$ CH$_3$, 31).

$W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)CH{=}CH_2]$ *(3)*

In a water-jacketed Pyrex Schlenk tube were placed W(CO)$_6$ (0.335 g, 0.95 mmol) and 50 ml of tetrahydrofuran. The solution was then irradiated from the outside with a medium-pressure mercury-vapor lamp for 4 h. This light yellow solution was transferred via cannula to a solution of **1** (0.25 g, 0.63 mmol) in 10 ml of hexane. The reaction mixture was stirred for 15 min and then the solvent was removed under vacuum. The resulting residue was chromatographed on silica gel at $-35\,^\circ$C using hexane. A red band was collected under nitrogen and the solvent was removed under vacuum. Recrystallization from hexane produced 0.26 g (61%) of **3** as dark red crystals. ^{1}H NMR (benzene-d_6) δ 4.75 (dd, *J* 9.5, 7.7 Hz, 1H, C*H*=), 3.10 (s, 3H, OCH_3), 2.98 (dd, *J* 7.8, 1.7 Hz, 1H, =CH_2), 1.96 (dd, *J* 9.4, 1.7 Hz, 1H, =CH_2); ^{13}C NMR (benzene-d_6) δ 232.56 (s, W–*C*–W), 205.10 (broad s), 201.24 (s), 196.14 (s), 80.92(d, *C*H=), 59.00(q, O*C*H_3), 56.15(t, =*C*H_2).

Complex **3** was also prepared from **2** as described below: In a 50 ml two-neck round bottom flask fitted with a nitrogen inlet value and a mercury overpressure valve were placed **2** (0.287 g, 0.40 mmol) and 8 ml of toluene. The reaction mixture was then heated at 45 °C with stirring for 22 h. The solvent was then removed under high vacuum and the resulting residue was chromatographed on silica gel at $-25\,^\circ$C using 10% methylene chloride/hexane. A small amount of brown residue did not dissolve in the chromatography solvent. This residue was soluble in acetone-d_6, however, no ^{1}H NMR resonances could be observed. A dark red band eluted off the column and was collected under nitrogen. Removal of the solvent under high vacuum gave 0.179 g (65%) of **3**.

This same reaction was also conducted in an NMR tube as follows: Complex **2** (21.8 mg, 0.030 mmol) and 0.50 ml of toluene-d_8 were placed in a 5 mm NMR tube. The tube was placed in an oil bath at 45 °C and the progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. After 8 h the resonances for complex **2** had completely disappeared. Present in the ^{1}H NMR spectrum were resonances for **3**, **1** (trace), and a singlet at δ 2.78 of very low intensity (unidentified).

Reaction of 3 with carbon monoxide

In a Wilmad 5 mm 507-TR screw cap NMR tube were placed complex **3** (25.2 mg, 0.037 mmol) and 0.5 ml of benzene-d_6. The NMR tube was sealed with a teflon-faced silicone rubber septum and open-top screw cap. A 12-in 22 gauge needle was then inserted through the septum along with a 2-in 23 gauge needle connected to a mercury over pressure valve. A very slow stream of carbon monoxide was then bubbled through the solution. The needles were periodically removed and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 4.5 h, complexes **1**, **2**, and **3** were present in the following approximate percentages: **1** (trace), **2** (50%), **3** (50%). After 12 h, the following approximate percentages were observed: **1** (50%), **2** (50%), **3** (trace). After 36 h only complex **1** was observed by ^{1}H NMR spectroscopy. The ^{13}C{^{1}H} NMR spectrum of this last sample exhibited resonances for complex **1** and $W(CO)_6$ (δ 191.12 ppm).

Reaction of 1 with D_2O

In a 25 ml single-neck round bottom flask were placed complex **1** (0.51 g, 1.30 mmol), 1.0 ml of benzene-d_6, and D_2O (0.10 ml, 5.5 mol). The flask was then sealed under nitrogen with a high vacuum valve and stirred for 5 d. To the reaction mixture was then added a small amount of anhydrous Na_2SO_4. The volatile components of the flask were then vacuum transferred to a 5 mm NMR tube and sealed under vacuum. The volatile products from this reaction were identified as methyl propionate and methyl propionate-2,3-d_2 (**4**). ^{1}H NMR (benzene-d_6) δ 3.32 (s, 3H), 1.96 (m, 1H) 0.90 (m, 2H); ^{13}C{^{1}H} NMR (benzene-d_6) δ 173.99, 50.89. 27.17, 26.89 (t, $J(^{13}C-^2H)$ 19.5 Hz), 9.05, 8.79 (t, J ($^{13}C-^2H$) 19.3 Hz). The NMR tube was opened and the contents subjected to GS/MS analysis.

In another experiment complex **1** (14.5 mg, 0.037 mmol), 0.50 ml of benzene-d_6, and D_2O (10.0 μl, 0.55 mmol) were sealed under vacuum in a 5 mm NMR tube. The progress of the reaction was monitored periodically by ^{1}H NMR spectroscopy. After standing for 6 d, compounds **1**, **2**, **3**, and **4** were present in the following approximate percentages: **1** (54%), **2** (22%), **3** (6%), **4** (18%). After 8 d, the following approximate percentages were observed: **1** (20%), **2** (29%), **3** (11%), **4** (40%). After 12 d mainly compound **4** was present with minor amounts of **1**, **2**, **3** observed. There was also present a small amount of an insoluble brown solid.

$(CO)_5W[C(O)CH=CH_2]NMe_4$ (8)

To a stirred solution of $W(CO)_6$ (7.2 g, 0.02 mol) in 350 ml of anhydrous ether was added dropwise a solution of vinyllithium (0.58 g, 0.017 mmol) in 50 ml of ether over the course of 1 h. After the addition was complete, the solution was stirred for an additional 2 h and the solvent removed under vacuum. The resulting orange-brown residue was dissolved in 30 ml of nitrogen-saturated water and the solution was rapidly filtered. A saturated solution of Me_4NBr (7.9 g, 0.051 mol) in 10 ml of nitrogen-saturated water was added to the filtrate and the resulting precipitate was collected. This precipitate was dried under vacuum, dissolved in a minimum amount of methylene chloride, reprecipitated with hexane, and dried under high vacuum to give **8** (3.8 g, 50%) as an orange powder. ^{1}H NMR (acetone-d_6) δ 6.06 (dd, J 17.9, 10.6 Hz, 1H, $CH=$), 5.40 (dd, J 17.7, 2.4 Hz, 1H, $=CH_2$), 5.11 (dd, J 10.5, 2.4 Hz, 1H, $=CH_2$), 3.45 (s, 12H, NMe_4). IR (methylene chloride): 2055(w), 1985(vs) cm^{-1}. Anal. Found: C, 31.97; H, 3.30; N, 3.06. $C_{12}H_{15}NO_6W$ calcd.: C, 31.79; H, 3.31; N, 3.09%.

$(CO)_5W[C(OCH_3)CH=CH_2]$ (1) from 8 and $CF_3SO_3CH_3$

To a stirred solution of 2.00 g (4.6 mmol) of **8** in 30 ml of anhydrous methylene chloride at −40 °C was added 0.52 ml (4.6 mmol) of $CF_3SO_3CH_3$. The solution was stirred for 1 h at −40 °C and the solvent was removed under vacuum. The resulting dark red residue was taken up in 25 ml of pentane, filtered through celite, and the solvent was removed under vacuum to afford **1** (1.44 g, 80%).

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