

Anionic initiated coupling of tungsten carbene complexes: synthesis of the first (μ -tris(carbene))trimetallic complex

David W. Macomber * and Mu-Huang Hung

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506 (U.S.A.)

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Abstract

Treatment of $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{C}(\text{CH}_3)=\text{CH}_2]$ (**1**) with $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CONa}$ in THF at -78°C followed by HCl produced: $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{CH}(\text{CH}_3)\text{CH}_2\text{OC}(\text{CH}_3)_2\text{C}_2\text{H}_5]$ (**3**) (1%), $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CO}\{(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{C}(\text{CH}_3)\text{CH}_2]\}-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}(\text{OCH}_3)$ (**5**) (< 1%), $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CO}\{(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{C}(\text{CH}_3)\text{CH}_2]\}_2\text{H}$ (**6**) (< 1%), and the (μ -tris(carbene))trimetallic complex $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CO}\{(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{C}(\text{CH}_3)\text{CH}_2]\}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}(\text{OCH}_3)$ (**9**) (15%) as well as several, as yet, unidentified compounds. Complex **9** was characterized by analytical and spectroscopic methods; moreover, it was converted to the corresponding triester (**10**) upon PDC/DMSO oxidation. Upon standing at 0°C for long periods complex **1** was converted into a new (μ -bis(carbene))ditungsten complex $(\text{CO})_5\text{W}\{\text{C}(\text{OCH}_3)-[\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{C}(=\text{CH}_2)]\text{C}(\text{OCH}_3)\}\text{W}(\text{CO})_5$ (**11**) in low yield.

Introduction

Transition-metal carbene or alkylidene complexes comprised of one carbene fragment have been extensively studied [1] since Fischer's original report in 1964 [2]. In contrast, there are only a limited number of complexes comprised of two carbene fragments bonded to two metals [3*]; moreover, to our knowledge, there are no reported (μ -tris(carbene))trimetallic complexes in which three carbene fragments are bonded to three transition metals. We now report on the synthesis of the first (μ -tris(carbene))trimetallic complex by an anionic initiated coupling of α,β -unsaturated tungsten carbene complexes.

Results and discussion

As part of our continuing interest in the polymerization of carbenevinyl monomers [4], we attempted to polymerize the α,β -unsaturated tungsten carbene complex

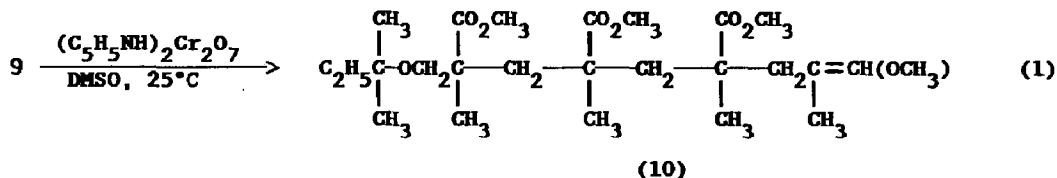
* Reference numbers with asterisks indicate notes in the list of references.

$(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{C}(\text{CH}_3)=\text{CH}_2]$ (**1**) using various anionic initiators. We found, however, that polymer formation never took place; instead, oligomeric products were produced. Thus, treatment of **1** with 1 equiv. of $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CONa}$ at -78°C in THF followed by HCl produced several organometallic compounds (Scheme 1). Some of these new compounds **3**, **5**, **6**, and **9** were isolated from the reaction mixture, in varying degrees of purity, through chromatography. On the other hand, because of separation difficulties, there were many compounds that remain, as yet, unidentified (see Experimental section). Compound **3** was obtained in 1% yield as an analytically pure orange liquid by a combination of chromatography (hexane) and vacuum distillation. ^1H NMR, ^{13}C NMR, and MS spectroscopic methods confirmed the structure of **3**; moreover, as expected, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** exhibited eleven resonances. Increasing the polarity of the chromatography solvent from hexane to 10% methylene chloride/hexane eluted several compounds which, after repeated preparative TLC, afforded compounds **5** (< 1%, ca. 70% pure) and **6** (< 1%, ca. 90% pure). Because **5** and **6** could not be completely separated from each other, analytical samples were not obtained. Furthermore, because only small amounts of impure **5** and **6** were available, the structural assignments were based entirely on ^1H NMR spectroscopy and, are therefore, tentative. Nevertheless, the ^1H NMR spectra of **5** and **6** are consistent with the assigned structures; moreover, the chemical shift values are similar to those observed for the analogous compounds **3** and **9**.

Increasing the polarity of the chromatography solvent still further to 3% ethyl acetate/hexane afforded several fractions consisting mostly of compound **9**. Following recrystallization, compound **9** was obtained analytically pure as orange crystals in 15% yield. The structure of **9** was confirmed by NMR spectroscopy. Both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **9** clearly showed the presence of three different tungsten carbene fragments. For example, three downfield resonances at δ 350.05, 348.57, and 347.25 ppm were observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) spectrum of **9** which are characteristic of Fischer-type tungsten carbene-carbon resonances [5]. Furthermore, the three tungstenpentacarbonyl fragments, which are associated with these carbene carbons, exhibited resonances at δ 201.81, 201.36, and 201.21 ppm for the *trans*-CO ligands and δ 197.81, 197.75, and 197.61 ppm for the *cis*-CO ligands. The remaining carbon resonances of **9** were assigned by obtaining a DEPT [6] spectrum (Fig. 1). Figure 1a is a partial $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) of **9** showing all the CH_3 , CH_2 , and quaternary carbon resonances. Figure 1b, on the other hand, is a DEPT $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) of the same region showing the CH_3 carbon resonances with positive amplitudes, the CH_2 carbon resonances with negative amplitudes, and the quaternary carbon resonances as absent. Clearly, the four quaternary carbon resonances are observed at δ 75.78 ($\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CO}$), 68.04, 65.95, and 64.00 ppm. The eleven CH_3 carbon resonances are observed at δ 70.43 ($\text{W}=\text{C}(\text{OCH}_3)$), 70.10 ($\text{W}=\text{C}(\text{OCH}_3)$), 69.95 ($\text{W}=\text{C}(\text{OCH}_3)$), 59.01 ($=\text{CH}(\text{OCH}_3)$), 33.58, 30.56, 28.73, 24.80, 24.10, 20.64, and 8.37 ppm. Furthermore, the five CH_2 carbon resonances are observed at δ 70.93 (OCH_2), 48.33, 45.69, 42.97, and 33.04 ppm. The single vinylic resonance (δ 5.83 ppm), the single organic methoxy resonance (δ 3.48 ppm), and the two vinylic carbon resonances (δ 146.32, 107.72 ppm) observed in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) spectra of **9**, respectively, indicated the presence of a vinyl ether moiety which had a hydrogen and a methoxy group on the terminal carbon [7]. Moreover, the internal vinylic quaternary carbon

resonance (δ 107.67 ppm, $C(\text{CH}_3)=$) was absent in the DEPT spectrum (C_6D_6) whereas the terminal vinylic carbon resonance (δ 146.72 ppm, $=\text{CH}(\text{OCH}_3)$) appeared with positive amplitude. Although compound **9** was isolated as one isomer (stereochemical and geometrical), the configuration of the carbon-carbon double bond of the vinyl ether moiety could not be conclusively determined even by a two-dimensional NOESY experiment.

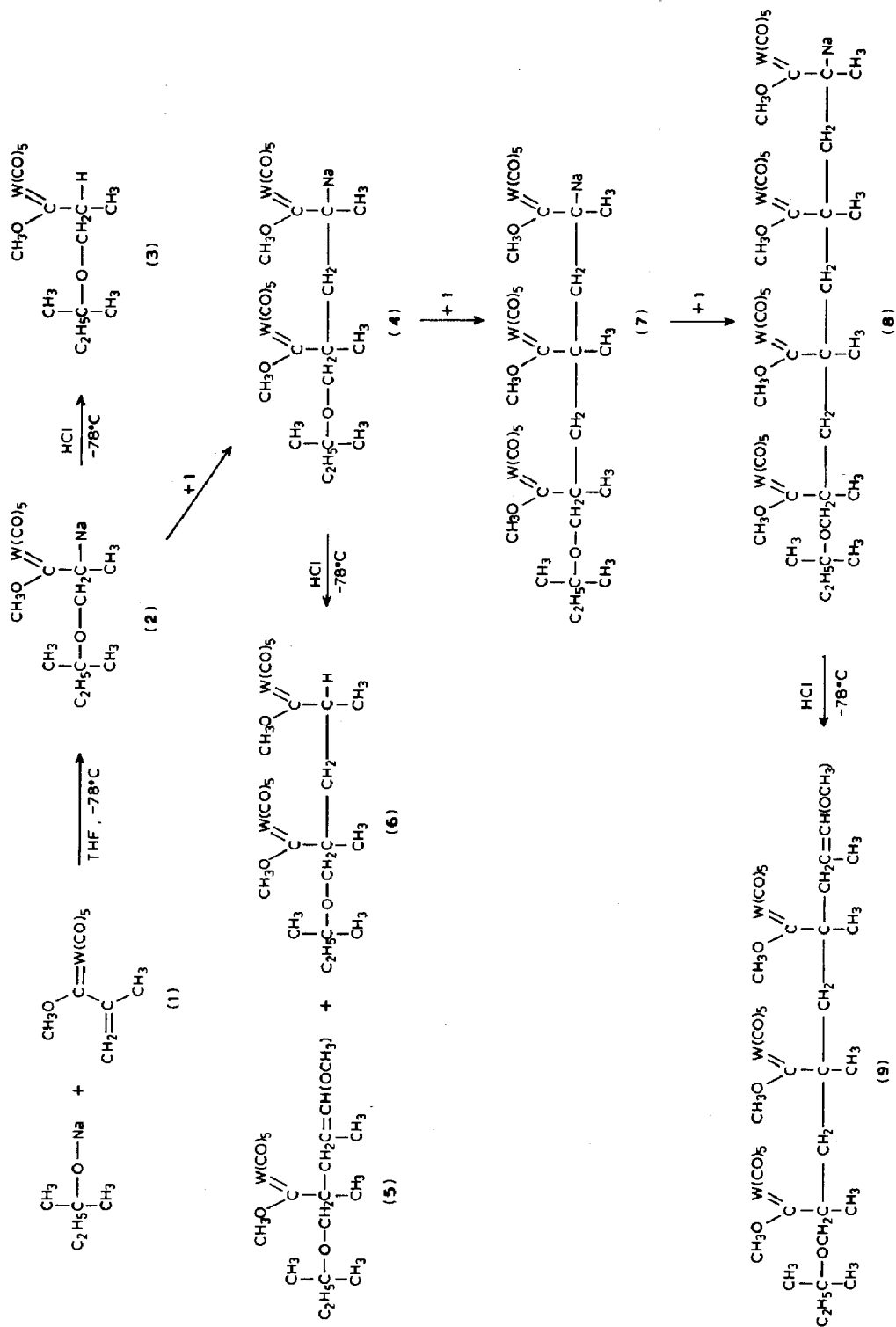
The structure of **9** was further confirmed by its oxidative conversion [8] to the corresponding triester **10** in 80% using PDC/DMSO (eq. 1). Compound **10** was



obtained as an analytically pure colorless liquid through chromatography. The ^1H and ^{13}C NMR spectral parameters of **10** were consistent with its proposed structure. For example, the $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) spectrum of **3** exhibited the expected 24 carbon resonances; moreover the resonances at δ 178.48, 178.07, and 176.77 ppm confirmed the presence of three different methoxycarbonyl groups. The singlet at δ 5.84 ppm ($=\text{CH}(\text{OCH}_3)$) in the ^1H NMR (CDCl_3) and the two vinylic carbon resonances (δ 145.11, $=\text{CH}(\text{OCH}_3)$; 109.09, $C(\text{CH}_3)=$) in the $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) of **10** indicated that the vinyl ether moiety had remained intact during oxidation.

A mechanism for the formation of compounds **3**, **5**, **6**, and **9** is proposed in Scheme 1. The first step, which is common to the formation of all the compounds, involves the conjugate addition of $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CONa}$ to **1** which resulted in the intermediate α -carbene anion **2**. There are several literature examples of conjugate additions of anions to α,β -unsaturated carbene complexes [9]. Protonation of anion **2** with HCl leads to compound **3**. Conjugate addition of anion **2** to additional **1** results in **4**, which upon protonation with HCl, leads to **5** and **6**. There are also many examples of α -carbene anions reacting with α,β -unsaturated carbene complexes by a conjugate addition process [3,11]. The vinyl ether moiety in **5** probably arises from protonation of anion **4** at tungsten (as compared to **6**, which arises from protonation at carbon) followed by reductive elimination and loss of a $\text{W}(\text{CO})_5$ fragment. The formation of compound **9** occurs by two successive conjugate additions of α -carbene anions to compound **1**; first **4** adds to **1** to give **7**, and then **7** adds to **1** to give **8**. Protonation of this α -sodio(μ -tetra(carbene))tetratungsten complex **8** at tungsten followed by reductive elimination and loss of one $\text{W}(\text{CO})_5$ fragment leads to **9**. The unidentified compounds formed during the reaction described in Scheme 1 may be stereochemical or geometrical isomers of **5**, **6**, and **9**; moreover, it is possible that other (μ -bis(carbene))ditungsten, (μ -tris(carbene))tritungsten, and (μ -tetra(carbene))tetratungsten complexes could have formed.

A new (μ -bis(carbene))ditungsten complex **11** was also discovered in the course of this study. It was found that if complex **1**, prepared according to the literature procedure [10], was allowed to stand for several weeks at 0°C under a nitrogen atmosphere that ca. a 10% conversion to **11** occurred. Complex **11**, which is more polar than **1**, was isolated by chromatography and purified by crystallization. To date, the mechanism of formation of **11** from **1** is unclear; furthermore, we have not,



Scheme 1

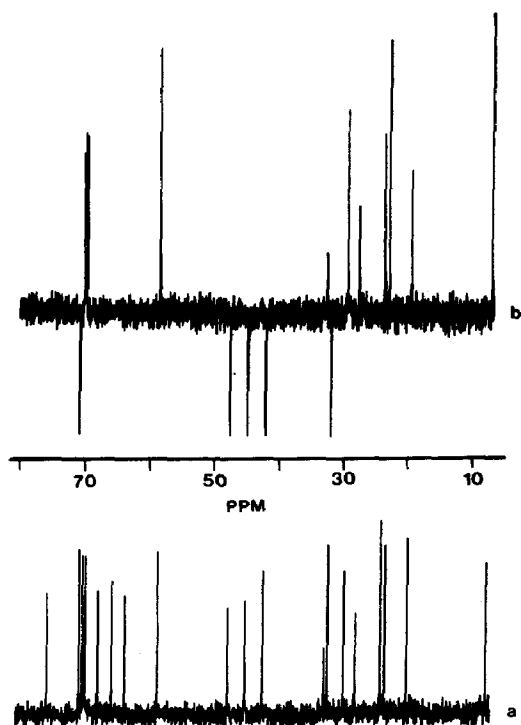
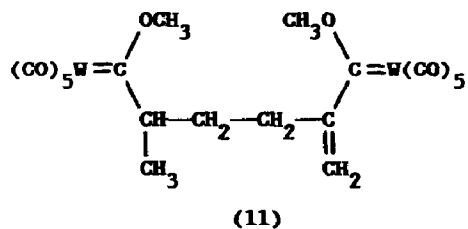


Fig. 1. (a) Partial $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) spectrum of **9** showing all the CH_3 , CH_2 , and quaternary carbons. (b) Partial DEPT (θ , 135°) $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) spectrum of **9** showing all the CH_3 (positive amplitude) and CH_2 (negative amplitude) carbons.

as yet, found any reagents or conditions that can systematically convert **1** to **11**. We are continuing to investigate the syntheses of new (μ -bis(carbene))dimetallic and (μ -tris(carbene))trimetallic complexes, their mechanisms of formation, and their reactivities.



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 resonance. Low-resolution mass spectra were acquired on a Finnigan 4000 instrument, and spectral data are listed as m/e (intensity of base peak) for

only the tungsten-184 isotope. High-resolution mass spectra were obtained at the Midwest Center for Mass Spectroscopy, Department of Chemistry, University of Nebraska. Elemental analyses were performed by Microlytics, South Deerfield, MA. The DEPT [6] $^{13}\text{C}\{^1\text{H}\}$ NMR experiments were performed in degassed C_6D_6 solutions in sealed NMR tubes using Bruker's software package and pulse sequence program. The pulse flip angle (θ_y) was set at 135° so as to simultaneously observe all but the quaternary carbons.

Tetrahydrofuran was distilled from sodium benzophenoneketyl under nitrogen. Dimethyl sulfoxide was distilled from CaH_2 under vacuum. All reagents and starting materials obtained from commercial sources were used without further purification. Deuterated benzene was dried over CaH_2 followed by vacuum transfer from sodium metal. Flash chromatography [12] was conducted on E. Merck silica gel 60 (40–63 μm).

Reaction of $(\text{CO})_5\text{W}[\text{C}(\text{OCH}_3)\text{C}(\text{CH}_3)=\text{CH}_2]$ (1) with $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CONa}$

To a suspension of $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CONa}$ (0.44 g, 4.0 mmol) in 5 ml of THF, which was cooled to -78°C , was added a precooled solution (-78°C) of **1** [10] (1.63 g, 4.0 mmol) in 5 ml of THF via a cannula over a 10 min period. After the addition was complete the solution was stirred for 5 h at -78°C . The reaction was then quenched with a precooled solution (-78°C) of 1.0 ml of 1.4 M HCl/diethyl ether in 3 ml of THF. The reaction mixture was warmed to 25°C and the solvent removed under aspirator vacuum and the resulting residue chromatographed on silica gel (25 \times 3 cm). The column was washed initially with hexane to afford a red eluent, which upon removal of the solvent under vacuum, gave a trace of unreacted **1**. Further washing with hexane afforded a yellow eluent; the fractions showing a single TLC spot and having an R_f value of 0.4 (hexane) were combined and the solvent removed under vacuum to give 0.02 g (1%) of **3** as an orange liquid; b.p. $48^\circ\text{C}/10^{-3}$ mmHg.

^1H NMR (CDCl_3): δ 4.62 (s, 3 H), 4.42 (sextet, J 7 Hz, 1H), 3.45 (m, 1 H), 3.18 (m, 1 H), 1.43 (q, J 8 Hz, 2H), 1.08 (s, 6 H), 0.93 (d, J 7 Hz, 3H), 0.82 (t, J 8 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 342.81, 204.04, 197.33, 74.82, 70.35, 67.02, 64.31, 32.52, 24.70, 13.58, 8.07 ppm. MS (11 eV): 496 [30%, M^+ (^{184}W)], 468 [22, ($M - \text{CO}$) $^+$], 440 [100, ($M - 2\text{CO}$) $^+$], 412 [23, ($M - 3\text{CO}$) $^+$], 356 [7, ($M - 5\text{CO}$) $^+$]. Found: C, 36.30; H, 4.07. $\text{C}_{15}\text{H}_{20}\text{O}_7\text{W}$ calcd.: C, 36.31; H, 4.06%.

The column was then washed with 10% methylene chloride/hexane to give a moderate amount of a yellow eluent. The fractions showing a single TLC spot with an R_f value of 0.5 (10% methylene chloride/hexane) were combined and the solvent removed under vacuum to afford 0.03 g of a yellow-orange oil. ^1H NMR analysis of this oil showed it to be a ca. 1/1 mixture of **5** and **6** in addition to small amounts of other unidentified compounds. Repeated preparative TLC (10% methylene chloride/hexane) of this mixture provided **5** (ca. 70% pure) and **6** (ca. 90% pure).

^1H NMR of **5** (CDCl_3): δ 5.79 (brs, 1 H), 4.75 (s, 3H), 3.58 (d, J 8 Hz, 1H), 3.51 (s, 3H), 3.22 (d, J 8 Hz, 1H), 2.28 (d, J 13 Hz, 1H), 1.68 (s, 3H), 1.45 (s, 3H), 1.45 (m, 3H), 1.04 (s, 6H), 0.81 (t, J 7 Hz, 3H).

^1H NMR of **6** (CDCl_3): δ 4.77 (s, 3H), 4.59 (s, 3H), 4.03 (m, 1H), 3.42 (d, J 8 Hz, 1H), 3.16 (d, J 8 Hz, 1H), 1.84 (dd, J 16, 10 Hz, 1H), 1.67 (s, 3H), 1.61 (m, 1H), 1.40 (q, J 7 Hz, 2H), 1.04 (s, 6H), 0.90 (d, J 8 Hz, 3H), 0.82 (t, J 7 Hz, 3H).

Continued washing of the column with 10% methylene chloride/hexane provided more yellow eluent, which upon removal of the solvent under vacuum, gave a yellow oil. TLC analysis of this yellow oil showed several spots clustered around an R_f value of 0.3 (10% methylene chloride/hexane). ^1H NMR analysis of this yellow oil confirmed the presence of several compounds, some of which contained tungsten carbene fragments as evidenced by the observation of methoxy resonances as singlets between δ 4.1 and 4.7 ppm. The structures of these compounds have not, as yet, been determined.

The column was then washed with 3% ethyl acetate/hexane to produce a yellow-orange eluent. The fractions showing a single TLC spot having an R_f value of 0.3 (5% ethyl acetate/hexane) were combined and the solvent removed under vacuum. Recrystallization of the residue from 10% methylene chloride/hexane afforded 0.21 g (15%) of **9** as orange crystals; m.p. 125 °C.

^1H NMR (C_6D_6): δ 5.52 (brs, 1H), 4.29 (s, 3H), 4.20 (s, 3H), 4.13 (s, 1H), 3.19 (d, J 7.9 Hz, 1H), 3.10 (s, 3H), 2.91 (d, J 7.9 Hz, 1H), 2.07 (d, J 13.2 Hz, 1H), 1.97 (d, J 13.2 Hz, 1H), 1.88 (d, J 14.5 Hz, 1H), 1.80 (d, J 14.5 Hz, 1H), 1.71 (d, J 7.1 Hz, 1H), 1.68 (d, J 6.7 Hz, 1H), 1.64 (s, 3H), 1.47 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H), 1.32 (q, J 7.4 Hz, 2H), 0.95 (s, 3H), 0.94 (s, 3H), 0.78 (t, J 7.3 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 350.05, 348.57, 347.25, 201.81, 201.36, 201.21, 197.81, 197.75, 197.61, 146.32, 107.72, 75.74, 70.71, 70.53, 70.34, 70.20, 67.72, 65.96, 63.88, 59.31, 48.03, 45.35, 42.72, 33.23, 32.99, 30.53, 28.43, 24.81, 24.07, 20.55, 8.28 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 349.92 (W=C), 348.40 (W=C), 346.97 (W=C), 202.02 (W-CO, *trans*), 201.59 (W-CO, *trans*), 201.49 (W-CO, *trans*), 198.20 (8 W-CO, *cis*), 198.03 (4 W-CO, *cis*), 146.72 (=CH(OCH₃)), 107.67 (C(CH₃)=), 75.78 (C₂H₅(CH₃)₂CO), 70.93 (OCH₂), 70.43 (W=C(OCH₃)), 70.10 (W=C(OCH₃)), 69.95 (W=C(OCH₃)), 68.04 (quaternary), 65.95 (quaternary), 64.00 (quaternary), 59.01 (=CH(OCH₃)), 48.33 (CH₂), 45.69 (CH₂), 42.97 (CH₂), 33.58 (CH₃), 33.04 (CH₂), 30.56 (CH₃), 28.73 (CH₃), 24.80 (CH₃), 24.10 (CH₃), 20.64 (CH₃), 8.37 (CH₃). Found: C, 34.21; H, 3.01. C₄₀H₄₄O₂₀W₃ calcd.: C, 34.41; H, 3.18%.

Continued washing with 3% ethyl acetate/hexane provided additional yellow-orange eluent, which upon removal of the solvent under vacuum gave a yellow-orange oil. TLC analysis of this material showed several spots clustered around an R_f value of 0.2 (5% ethyl acetate/hexane). ^1H NMR analysis of this yellow oil confirmed the presence of several compounds, some of which contained tungsten carbene fragments as evidenced by the observation of methoxy resonances as singlets between δ 4.1 and 4.8 ppm. The structure of these compounds have not, as yet, been determined.

$\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CO}[\text{CO}(\text{OCH}_3)\text{C}(\text{CH}_3)\text{CH}_2]_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}(\text{OCH}_3)$ (**10**)

To a solution of **9** (0.80 g, 0.57 mmol) in 50 ml of anhydrous dimethyl sulfoxide was added 2.10 g (5.7 mmol) of pyridinium dichromate and the solution stirred for 2 d at 25 °C. The solution was diluted with water and then extracted with diethyl ether. The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and the solvent removed by fractional distillation. The resulting residue was chromatographed on silica gel (25 × 3 cm) by means of 1% ethyl acetate/hexane as the eluent. The fractions showing a single TLC spot having an R_f value of 0.4 (1% ethyl acetate/hexane) were combined and the solvent removed under aspirator vacuum to afford 0.22 g (80%) of **10** as a colorless liquid.

^1H NMR (CDCl_3): δ 5.84 (s, 1H), 3.65 (s, 6H), 3.63 (s, 3H), 3.50 (s, 3H), 3.30 (d, J 10 Hz, 1H), 3.01 (d, J 10 Hz, 1H), 2.37 (d, J 14 Hz, 1H), 2.16–1.87 (m, 5H), 1.42 (brs, 5H), 1.07 (s, 3H), 1.05 (s, 3H), 1.04 (s, 3H), 1.00 (s, 3H), 0.96 (s, 3H), 0.81 (t, J 7 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 178.48, 178.07, 176.77, 145.11, 109.09, 74.40, 69.93, 59.09, 51.90, 51.70, 51.54, 47.47, 45.19, 44.30, 42.77, 33.21, 30.32, 29.70, 24.69, 24.48, 18.67, 17.92, 17.28, 16.80, 7.97 ppm. HRMS, found: 472.3103. $\text{C}_{25}\text{H}_{44}\text{O}_8$ calcd.: 472.3036.

$(\text{CO})_5\text{W}\{\text{C}(\text{OCH}_3)\{\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{C}(\text{=CH}_2)\}\text{C}(\text{OCH}_3)\}\text{W}(\text{CO})_5$ (**11**)

Complex **1** (1.42 g, 3.5 mmol) was allowed to stand at 0°C under a nitrogen atmosphere for ca. 3 weeks; it was noticed after this period that a dark solid residue was present in the sample. Chromatography of this material on silica gel (20×2.5 cm) using hexane as the eluent afforded recovered **1** (0.73 g, 51%). Further elution of the column with 10% methylene chloride/hexane brought down a dark red band which was collected and the solvent removed under vacuum. Recrystallization from 5% methylene chloride/hexane afforded **5** (0.13 g, 9%) as dark red crystals; m.p. 78°C .

^1H NMR (CDCl_3): δ 5.42 (brs, 1H), 5.31 (brs, 1H), 4.61 (s, 6H), 4.06 (sextet, J 8 Hz, 1H), 2.37 (m, 1H), 2.16 (m, 1H), 1.71 (m, 1H), 1.33 (m, 1H), 1.01 (d, J 8 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 341.23, 328.13, 203.24, 203.05, 197.36, 197.19, 164.70, 118.93, 70.71, 69.64, 66.99, 31.64, 30.85, 16.03 ppm. Found: C, 29.57; H, 2.00. $\text{C}_{19}\text{H}_{16}\text{O}_{12}\text{W}_2$ calcd.: C, 29.44; H, 1.98%.

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