Activation of Prop-2-yn-1-ols by Metal Carbonyls: Synthesis of (Alkoxyalkenylcarbene)- and (Aminoalkenylcarbene)chromium and -tungsten Complexes

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Received December 12, 1994[⊗]

Fischer type methoxyalkenylcarbene complexes $(CO)_5M{=}C(OMe)(CH{=}CRR')$ have been prepared in one step by photolysis of $M(CO)_6$ [M = Cr, W] in tetrahydrofuran–methanol, in the presence of prop-2-yn-1-ol derivatives $HC{\equiv}CC(OH)(R)(R')$ [R, R′ = Me; R = H, R′ = Me, Ph, C_6H_4-*p*-NMe_2]. Photolysis of a tetrahydrofuran–methanol solution of $M(CO)_6$ with $HC{\equiv}CC(OH)(H)\{(CH{=}CH)_nCH{=}CRR'\}$ [*n* = 0 R, R′ = Me; R = H, R′ = H, Me, Ph, C_6H_4-*p*-NMe_2, C_5H_{11}; *n* = 1 R = H, R′ = Me] provides the new dienyl- and trienylcarbene complexes $(CO)_5W{=}C(OMe)(CH{=}CHCH{=}CRR')$ and $(CO)_5M{=}C(OMe)(CH{=}CHCH{=}CHCH{=}CHMe)$ in 30–70% yields. Alkoxyalkenylcarbene complexes $(CO)_5M{=}C(OCH_2Z)(CH{=}CRR')$ are prepared analogously by using other primary alcohols ZCH_2OH [Z = $CH_2CH(Me)(Et)$, CH_2-$CH_2C{\equiv}CMe$, $CH_2CH_2CH{=}CH_2$, $CH_2CH_2C(Me){=}CH_2$. [(Alkenyloxy)alkenylcarbene]tungsten complexes undergo smooth thermal intramolecular cyclopropanation reactions leading to 1-alkenyl-2-oxabicyclo[3.1.0]hexane compounds. Finally, a series of aminodienylcarbene complexes $(CO)_5W{=}C(NHR')(CH{=}CHCH{=}CHR)$ [R = Ph, C_5H_{11}; R′ = $CHMe_2$, CMe_3, CH_2-$CH{=}CH_2$, CH_2CHMe_2] have been synthesized by aminolysis of the corresponding methoxydienyl carbenes.

Introduction

Fischer type alkenylcarbene complexes of group 6 metals have attracted interest as useful reagents for organic synthesis. Most extensively studied are the annelation,[1–3] cyclopropanation,[4,5] and Diels–Alder reactions.[6,7] They are also precursors to new functionnal organometallic compounds such as bis(carbene)dimetal complexes[8,9] and organometallic polymers.[10] Alkenylcarbene complexes are normally prepared by the Fischer procedure which involves the nucleophilic addition of vinyllithium reagents to a group 6 metal hexacarbonyl followed by O-alkylation of the acylmetalate salts.[11–14] This method has some limitations and is restricted to alkenyl groups which are available from organolithium reagents. An alternative multistep, but more general, procedure requires the synthesis of a methoxymethylcarbene complex and the condensation of an aldehyde,[15] ketone,[16] or enol ether[17] with the corresponding conjugated base $(CO)_5M{=}C(OMe)CH_2^-$. Several other specific methods for the preparation of alkoxyalkenylcarbene complexes, such as the nucleophilic attack of the pentacarbonylchromate dianion on alkenyl acid chlorides followed by alkylation on oxygen,[18] or the insertion of ethoxyacetylene into a metal carbene bond,[19] have been reported.

Another attractive and convenient way to produce metal carbene complexes involves the activation of terminal alkynes by transition metal complexes.[20] This one pot reaction, based on the nucleophilic addition of alcohols to vinylidene species, has been used by Rudler[21]

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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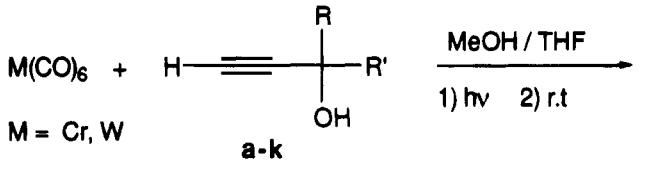
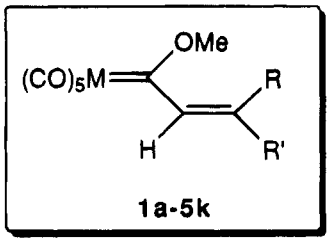
and Dötz[22] to prepare some (alkoxyalkylcarbene)chromium and -tungsten carbene complexes. Our interest in the activation of terminal alkynes with (arene)-ruthenium(II) complexes has already produced evidence for the formation of very reactive vinylidene intermediate precursors of carbene.[23] Furthermore, we have recently reported an easy one step synthesis of novel alkenylcarbene ruthenium cations, *via* allenylidene ruthenium intermediates, by dehydration of propargylic alcohol derivatives.[24] We sought to apply this strategy for the preparation of α,β-unsaturated carbene complexes of group 6 metals. Here we report the results of our studies on the activation of prop-2-yn-1-ols by chromium and tungsten hexacarbonyl in the presence of alcohol nucleophiles. We show that this reaction opens the route to new alkoxypolyenylcarbene complexes. The aminolysis reactions of several methoxydienylcarbenes will also be described. A preliminary account of part of this work has appeared.[25]

Results and Discussion

Our initial experiments were directed toward the synthesis of the known methoxypropenyl-,[26] methoxystyryl-,[15] and methoxyisobutenylcarbene[17] complexes **1a**, **2b**, and **1c**. Photolysis of a 1:2 methanol:tetrahydrofuran solution of $W(CO)_6$ or $Cr(CO)_6$ for 2−3 h at room temperature with a 2-fold excess of prop-2-yn-1-ols **a**−**c** resulted, after further 16 h of stirring, in the formation of complexes **1a**, **2b**, and **1c** in 24−40% yields (eq 1; Table 1, entries 1, 2, and 4). Complex **1a** was



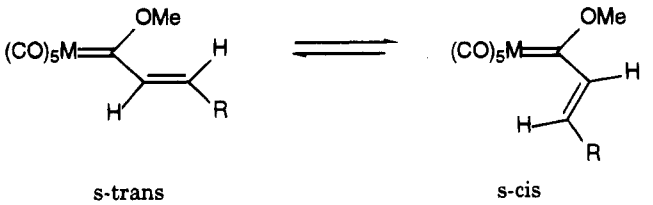


(1)

a [R : H ; R' : Me]
b [R : H ; R' : Ph]
c [R, R' : Me]
d [R : H ; R' : 4-$Me_2NC_6H_4$]
e [R : H ; R' : $CH=CH_2$]
f [R : H ; R' : CH=CHMe]
g [R : H ; R' : CH=CHPh]
h [R : H ; R' : CH=CH(4-$Me_2NC_6H_4$)]
i [R : H ; R' : CH=CH(C_5H_{11})]
j [R : H ; R' : $CH=CMe_2$]
k [R : H ; R' : CH=CHCH=CHMe]

also produced in 60% yield by treatment at room temperature of the photogenerated $W(CO)_5$(THF) with a methanol solution of **a**. When alkyne **d** was irradiated with $M(CO)_6$ (M = Cr and W), the new deep red 4-(dimethylamino)styryl carbene complexes **1d** and **2d** were obtained in *ca.* 50% yield (entries 3 and 5). The synthetic sequence outlined for the preparation of methoxyalkenylcarbene complexes was successfully applied to the synthesis of polyenylcarbene complexes from the readily available alkenyl- and dienyl propargylic alcohol derivatives **e**−**k**.[24] After chromatographic purification (methoxydienylcarbene)tungsten complexes **3e**−**j** and methoxyoctatrienylcarbene complexes **4k** and **5k** were isolated in good yields (entries 6−13).

These compounds were easily characterized on the basis of their IR and ^1H, ^{13}C, and $^1H-^{13}C$ correlated NMR spectra (Table 2). The reaction is completely stereoselective, giving exclusively the *all-trans* isomers for the alkenyl, dienyl, and trienyl substituents, according to the strong vicinal coupling constants ($^3J_{HH} \cong 15$ Hz). Difference NOE experiments were conducted with complexes **1d** and **2b**, in order to establish the conformation of the metal−alkenyl moiety: irradiation of the methoxy protons led to the enhancement of the vinyl H^2C signal [**2b**, 4%; **1d**, 8%] as well as of the H^3C signal [**2b**, 2.5%; **1d**, 4%], consistent with an *s-cis* → *s-trans* equilibrium. This equilibrium has also been suggested by Aumann in the case of the $(CO)_5Cr=C(OEt)-(CH=CHPh)$ complex.[15b]



(Alkenyloxy)- and (alkynyloxy)carbene complexes have found useful applications in organic synthesis such as intramolecular cyclopropanation,[27,28] annelation[29] and Diels−Alder reactions.[7c] They are generally made either by base-catalyzed reaction of ethylene alcohols with methoxycarbene complexes,[27] alcoholysis of (acyloxy)carbene complexes,[28,29] or alkylation of acylmetalates.[14] The success of our strategy to prepare methoxyalkenylcarbene complexes has prompted us to examine the generalization of this simple procedure by using more sophisticated alcohols in place of methanol (eq 2). The chiral [(2-methyl-1-butoxy)pentadienylcar-

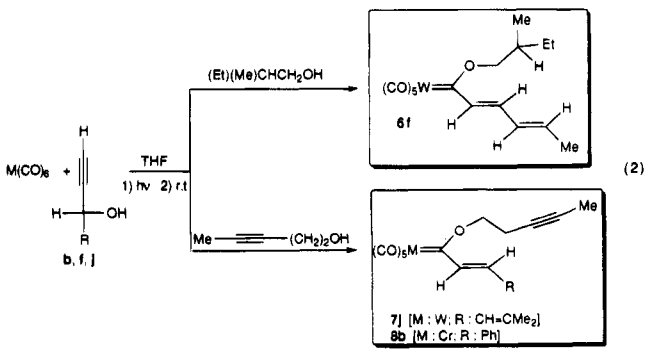


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Table 1. Yields of Alkoxyalkenylcarbene Complexes $(CO)_5M{=}C(OCH_2Z)(CH{=}CRR')$

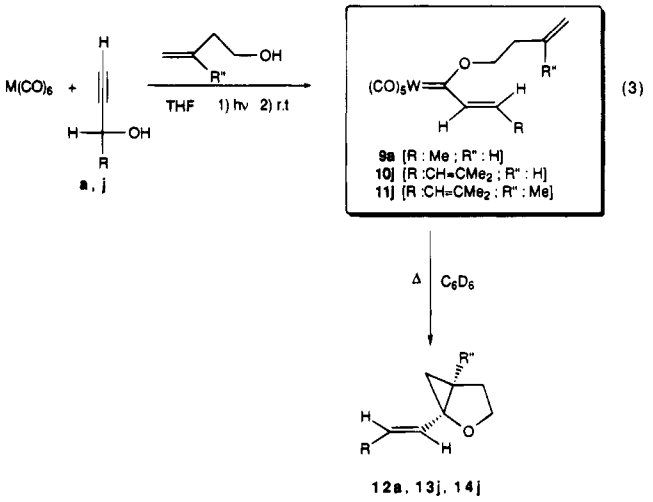
entry	M	CH_2Z	CH=C(R)(R')	complex	% yield
1	W	Me	CH=CH(Me)	**1a**	30 (60[a])
2	W	Me	$CH{=}C(Me)_2$	**1c**	24
3	W	Me	$CH{=}CH(C_6H_4\text{-}p\text{-}NMe_2)$	**1d**	55
4	Cr	Me	CH=CH(Ph)	**2b**	40
5	Cr	Me	$CH{=}CH(C_6H_4\text{-}p\text{-}NMe_2)$	**2d**	50
6	W	Me	$CH{=}CHCH{=}CH_2$	**3e**	50
7	W	Me	CH=CHCH=CH(Me)	**3f**	62
8	W	Me	CH=CHCH=CH(Ph)	**3g**	73
9	W	Me	$CH{=}CHCH{=}CH(C_6H_4\text{-}p\text{-}NMe_2)$	**3h**	30
10	W	Me	$CH{=}CHCH{=}CH(C_5H_{11})$	**3i**	47
11	W	Me	$CH{=}CHCH{=}C(Me)_2$	**3j**	63
12	W	Me	$(CH{=}CH)_3Me$	**4k**	53
13	Cr	Me	$(CH{=}CH)_3Me$	**5k**	46
14	W	$CH_2CH(Me)(Et)$	CH=CHCH=CH(Me)	**6f**	50
15	W	$CH_2CH_2C{\equiv}CMe$	$CH{=}CHCH{=}C(Me)_2$	**7j**	22
16	Cr	$CH_2CH_2C{\equiv}CMe$	CH=CH(Ph)	**8b**	15
17	W	$CH_2CH_2CH{=}CH_2$	CH=CH(Me)	**9a**	59
18	W	$CH_2CH_2CH{=}CH_2$	$CH{=}CHCH{=}CMe_2$	**10j**	69
19	W	$CH_2CH_2CMe{=}CH_2$	$CH{=}CHCH{=}CMe_2$	**11j**	24

[a] From $W(CO)_5(THF)$.

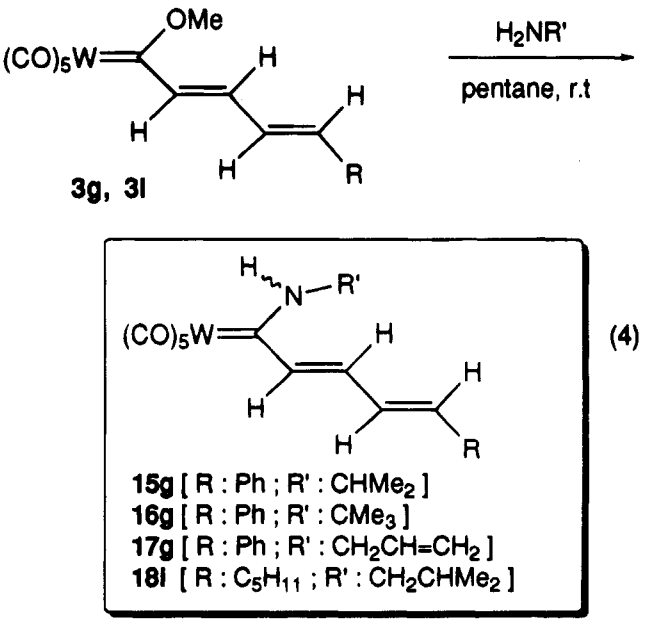
bene]tungsten **6f** was obtained in 50% yield from alkyne **f** and 2-methyl-1-butanol (entry 14). Similarly, the reaction of $M(CO)_6$ with pent-3-yn-1-ol (25 equiv) and alkynes **b** and **j** gave the new (pent-3-yn-1-oxy)alkenylcarbenes **7j** and **8b** in 15–22% yields (entries 15–16).

We have extended this simple reaction to synthesize the first (alkenyloxy)alkenylcarbene complexes; [(but-3-en-1-oxy)alkenylcarbene]tungsten complexes **9a** and **10j** were produced in good isolated yields (59 and 69%, respectively) from but-3-en-1-ol in large excess (3 mL) and the propargylic alcohol derivatives **a** and **j** (entries 17 and 18).

The complexes **9a** and **10j** underwent intramolecular cyclopropanation reactions similar to those previously described for [(alkenyloxy)aryl]tungsten[27] and -chromium[28] complexes. The thermolysis, performed at 70 °C for 2 h in benzene-d_6, gave exclusively and quantitatively (NMR yield) the vinylcyclopropanes 1-propenyl-2-oxabicyclo[3.1.0]hexane and 1-(3-methylpentadienyl)-2-oxabicyclo[3.1.0]hexane (**12a** and **13j**), respectively (eq 3). Use of 3-methylbut-3-en-1-ol produced the corresponding carbene complex **11j** in low yield (entry 19). Unlike **9a** and **10j**, which are stable in solution at room temperature, **11j** was readily converted to the cyclopropane derivative **14j** in C_6D_6 at 25 °C. This inherent thermal instability has also been observed by Soderberg and Hegedus for [(3-methylbut-3-en-1-oxy)arylcarbene]-chromium complexes.[28] This reaction appears to be a straightforward entry to bicyclic alkenylcyclopropanes.



Aminoalkenylcarbene complexes are also well-known useful reagents for organic synthesis.[7,30–33] Thus we sought to prepare them by following the same methodology, but with amines as nucleophiles. Our attempts with *tert*-butylamine failed, and the reaction resulted only in the formation of a pentacarbonyltungsten *tert*-butylamine complex, $(CO)_5W(H_2N^tBu)$. These compounds, however, could be easily obtained by the standard aminolysis method[7,33,34] from the readily available methoxyalkenylcarbene complexes synthesized. For example, addition of a variety of primary amines to **3g** and **3i** at room temperature led to the isolation of the aminodienylcarbene complexes **15g–17g** and **18i** in high yields as 1:1 mixtures of *E* and *Z* isomers (eq 4).



These isomers could be easily distinguished by means

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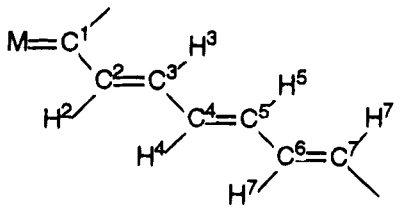
Table 2. Selected ^1H and ^{13}C NMR Data (ppm) for Alkoxyalkenylcarbene Complexes



complex	C^1	C^2 (H^2)	C^3 (H^3)	C^4 (H^4)	C^5 (H^5)	C^6 (H^6)	C^7 (H^7)
1a[a]	309.8	149.3 (7.25)	137.1 (6.58)				
1c[a]	311.7	145.2 (7.35)	146.4				
1d[a]	299.5	140.8 (7.70)	138.4 (7.40)				
2b[b]	333.7	139.6 (7.89)	130.9 (6.89)				
2d[a]	324.1	137.6 (7.72)	134.7 (7.43)				
3e[a]	308.9	147.9 (7.31)	134.8 (6.79)	129.7 (6.40)	136.2 (5.81−5.74)		
3f[a]	307.2	145.7 (7.21)	137.1 (6.88)	131.2 (6.15)	145.6 (6.78)		
3g[b]	305.4	147.0 (7.42)	135.2 (7.05)	127.3 (6.83)	145.0 (7.12)		
3h[a]	300.7	148.0 (7.31)	140.4 (7.20)	122.5 (6.68)	144.4 (7.10)		
3i[a]	307.1	151.3 (7.22)	137.3 (6.88)	129.8 (6.15)	145.7 (6.41)		
3j[b]	306.0	144.9 (7.13)	134.8 (7.29)	125.3 (5.98)	153.3		
4k[a]	305.0	146.8 (7.26)	137.2 (6.95)	129.1 (6.16)	146.4 (6.78)	132.4 (6.23)	137.9 (6.08)
5k[a]	330.6	147.9 (7.42)	138.4 (6.99)	129.6 (6.35)	142.6 (6.99)	132.9 (6.35)	142.1 (6.14)
6f[a]	304.8	145.4 (7.20)	136.1 (6.85)	131.0 (6.85)	144.6 (6.41)		
7j[a]	303.6	144.9 (7.15)	135.0 (7.36)	125.3 (5.99)	153.5		
8b[b]	332.3	140.0 (7.97)	131.3 (7.04)				
9a[c]	307.4	149.8 (7.10)	138.2 (6.28)				
10j[c]	303.7	144.8 (7.10)	134.6 (7.32)	125.1 (5.55)	153.2		

[a] Recorded in CD_2Cl_2. [b] Recorded in $CDCl_3$. [c] Recorded in C_6D_6.

Table 3. Selected ^1H and ^{13}C NMR Data (ppm) for Aminoalkenylcarbene Complexes[a]

complex	C^1	NH	H^2	H^3	H^4	H^5
15g (*Z*)	239.0	8.16	6.88	6.43	6.82	6.83
(*E*)	243.4	8.08	6.68	7.18	6.89	6.94
16g (*Z*)	244.4	8.90	7.13	5.76	6.68	6.72
(*E*)	249.4	8.48	6.93	7.08	6.86	6.86
17g (*Z*)	247.1	8.26	6.83	6.48	6.75	6.77
(*E*)	249.3	8.26	6.59	7.18	6.87	6.88
18i (*Z*)	245.9	8.26	6.65	6.28	6.02	6.02
(*E*)	247.0	8.18	6.44	7.09	6.20	6.20
19a[b] (*Z*)	247.0	8.50	6.75	5.90		
(*E*)	249.3	8.36	6.48	6.67		

[a] In $CDCl_3$. [b] Reference 33.

of their ^1H and ^{13}C NMR chemical shifts (Table 3), which are in good agreement with those recently reported by Wulff for $(CO)_5W{=}C(NHMe)(CH{=}CHMe)$ (**19a**).[33]

A plausible mechanism that can account for the formation of alkoxyalkenylcarbene complexes **1a**−**11j** is presented in Scheme 1. We suggest that photolysis promotes the elimination of one CO ligand to give, *via* a metal carbonyl solvent adduct, the η^2-alkyne intermediate **A**. Then, the mechanism involves the rearrangement of **A** to its η^1-hydroxyvinylidene isomer **B** which readily loses water to afford the allenylidene intermediate **C**.[35] The last step is likely to be the nucleophilic addition of the alcohol. Indeed, several disubstituted allenylidene chromium and tungsten complexes, stabilized by electron-donating groups, have recently been generated by dehydration of 1,1-diarylprop-2-yn-1-ols[36] or by a multistep reaction between dianions $LiC{\equiv}CCR_2OLi$ (R = aryl) and $M(CO)_6$.[37] Other stable (3-aminoallenylidene)chromium and -tungsten complexes are known; they have been prepared either by acid-catalyzed alcohol elimination from ethoxy(2-aminoalkenyl)carbene complexes,[38] *via* a process that is actually the reverse of the **C** → **D** reaction, or by reactions of amines with ethoxyalkynylcarbene complexes.[39]

In summary we have developed a simple route which allows the preparation of alkoxyalkenyl and polyenylcarbene complexes by direct activation of readily available propargylic alcohol derivatives. Moreover this methodology has been extended to a variety of carbene complexes containing "functional" alkoxy groups such as (alkenyloxy)alkenylcarbenes which undergo facile intramolecular cyclopropanation reactions. Finally, aminoalkenylcarbene complexes can be easily obtained by a traditional aminolysis route, thus in two steps from $W(CO)_6$.

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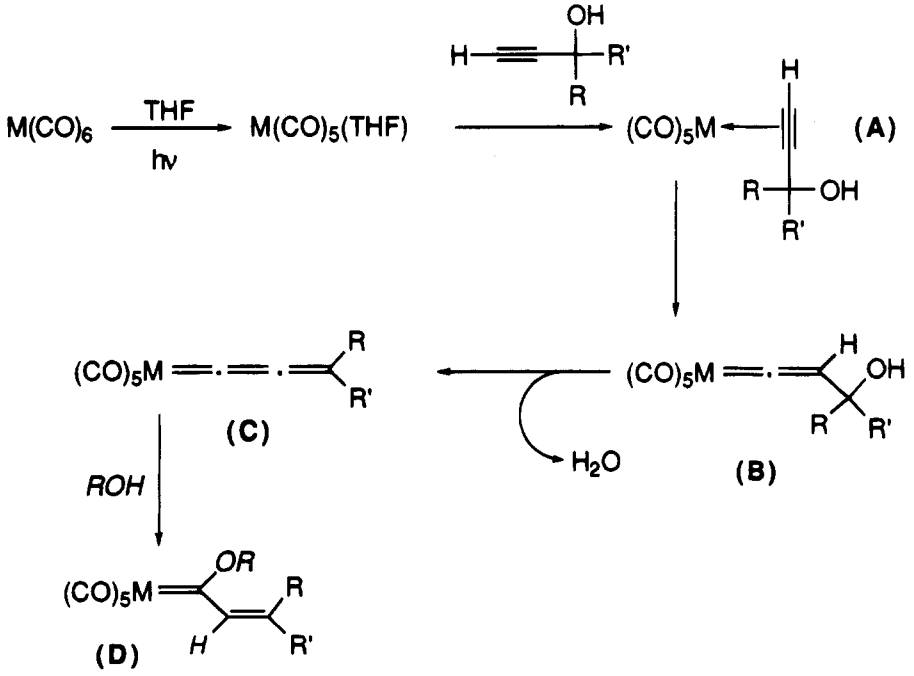
Scheme 1



Experimental Section

General Data. All reactions were conducted under an inert argon or nitrogen atmosphere. The solvents were dried by standard methods. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra were recorded on a Bruker AM 300 spectrometer at 297 K and referenced to TMS. Elemental analyses were performed by the Service Central de Microanalyses du CNRS at Lyon, France. High-resolution mass spectra were obtained on a Varian MAT 311 at CRMPO, University of Rennes. Propargylic alcohols were prepared according to literature procedures.[40,41]

General Procedure for the Synthesis of Methoxyalkenylcarbene Complexes 1–5. A solution of 3 mmol of metal carbonyl [$Cr(CO)_6$ or $W(CO)_6$] and 6 mmol of propyn-1-ol derivatives in 75 mL of a 2/1 mixture of tetrahydrofuran/methanol was irradiated for 2–4 h at room temperature by using a Rayonet photochemical reactor and a Pyrex photochemical cell. The solution was then transferred into a Schlenk flask and stirred for 18 h at room temperature. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel. Elution with dichloromethane/pentane (1/9) followed by evaporation of the solvent gave complexes **1–5** as red solids or oils.

$(CO)_5W$=C(OMe)(CH=CHMe), 1a: yield 0.37 g (30%); IR (Nujol) 2068, 1942, 1610 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.25 (dq, 1H, CH=, ^3J = 15.0 Hz, ^4J = 1.5 Hz), 6.58 (dq, 1H, CH=, ^3J = 15.0 and 7 Hz), 4.57 (3H, OMe), 1.82 (dd, 3H, Me, ^3J = 7.0 Hz, ^4J = 1.5 Hz); ^{13}C NMR (CD_2Cl_2) δ 309.8 (W=C), 203.6 (CO), 197.6 (CO), 149.3 (HC=), 137.1 (HC=), 69.0 (OMe), 18.5 (Me). Anal. Calcd for $C_{10}H_8O_6W$: C, 30.01; H, 1.97. Found: C, 29.44; H, 1.97.

$(CO)_5W$=C(OMe)(CH=CMe_2), 1c: yield 0.31 g (24%); IR (Nujol) 2067, 1939, 1610 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.35 (m, 1H, CH=), 4.59 (3H, OMe), 1.90 (d, 3H, Me, ^4J = 1.0 Hz), 1.86 (d, 3H, Me, ^4J = 1.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 311.7 (W=C), 204.6 (CO), 198.3 (CO), 146,4 (CMe_2), 145.2 (HC=), 69.7 (OMe), 28.6 and 22.6 (Me). Anal. Calcd for $C_{11}H_{10}O_6W$: C, 31.30; H, 2.39. Found: C, 31.01; H, 2.34.

$(CO)_5W$=C(OMe)[CH=C(H)(p-$C_6H_4NMe_2$)], 1d: yield 0.85 g (55%); IR (Nujol) 2061, 1937 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.70 (d, 1H, CH=, ^3J = 15.0 Hz), 7.54 (d, 2H, C_6H_4–, ^3J = 9.0 Hz), 7.40 (d, 1H, CH=, ^3J = 15.0 Hz), 6.67 (d, 2H, C_6H_4–, ^3J = 9.0 Hz), 4.51 (3H, OMe), 3.03 (6H, NMe_2); ^{13}C NMR (CD_2Cl_2) δ 299.5 (W=C), 204.7 (CO), 198.8 (CO), 153.5 (C_6H_4–), 140.8 (CH=), 138.4 (CH=), 132.6, 121.8, 112.5 (C_6H_4–), 68.4 (OMe), 40.3 (NMe_2). Anal. Calcd for $C_{17}H_{16}NO_6W$: C, 39.79; H, 2.95. Found: C, 39.92; H, 3.30.

$(CO)_5Cr$=C(OMe)(CH=CHPh), 2b: yield 0.29 g (40%); IR (Nujol) 2058, 1946 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.82 (d, 1H, CH, ^3J = 15.2 Hz), 7.51–7.10 (m, 5H, C_6H_5), 6.89 (d, 1H, CH=, ^3J = 15.2 Hz), 4.75 (3H, OMe); ^{13}C NMR ($CDCl_3$) δ 333.7 (Cr=C), 224.3 (CO), 216.7 (CO), 139.6 (CH=), 134.4 (C_6H_5), 130.9 (CH=), 129.7, 129.5, 129.1 (C_6H_5), 66.5 (OMe).

$(CO)_5Cr$=C(OMe)[CH=C(H)(p-$C_6H_4NMe_2$)], 2d: yield 0.33 g (50%); IR (Nujol) 2053, 1940 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.72 (d, 1H, CH=, ^3J = 15.0 Hz), 7.52 (d, 2H, C_6H_4–, ^3J = 9.0 Hz), 7.43 (d, 1H, CH=, ^3J = 15.0 Hz), 6.67 (d, 2H, C_6H_4–, ^3J = 9.0 Hz), 4.62 (3H, OMe), 3.03 (6H, NMe_2); ^{13}C NMR (CD_2Cl_2) δ 324.1 (Cr=C), 225.2 (CO), 218.1 (CO), 167.1 (C_6H_4–), 137.6 (CH=), 134.7 (CH=), 132.6, 121.6, 112.4 (C_6H_4–), 65.7 (OMe), 40.3 (NMe_2). HRMS M^+ Calcd for $C_{17}H_{15}NO_6Cr$: 381.0304. Found: 381.0307.

$(CO)_5W$=C(OMe)(CH=CHCH=CH_2), 3e: yield 0.63 g (50%); IR (Nujol) 2066, 1941, 1633, 1572 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.31 (dd, 1H, CH=, ^3J = 14.9 Hz, ^4J = 0.4 Hz), 6.79 (m, 1H, CH=, ^3J = 14.8 and 11.0 Hz), 6.40 (m, 1H, CH=), 5.81 (m, 1H, =CH_2, ^3J = 16.9 Hz), 5.74 (m, 1H, =CH_2, ^3J = 9.9 Hz), 4.55 (OMe); ^{13}C NMR (CD_2Cl_2) δ 308.9 (W=C), 203.6 (CO), 197.6 (CO), 147.9 (CH=), 136.2 (CH_2), 134.8 (CH=), 129.7 (CH=), 69.6 (OMe). HRMS M^+ Calcd for $C_{11}H_8O_6W^{182}$: 417.9819. Found: 417.9802.

$(CO)_5W$=C(OMe)(CH=CHCH=CHMe), 3f: yield 0.81 g (62%); IR (Nujol) 2066, 1941, 1610, 1571 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.21 (d, 1H, CH=, ^3J = 14.8 Hz), 6.88 (dd, 1H, CH=, ^3J = 14.8 and 10.9 Hz), 6.78 (dq, 1H, CH=, ^3J = 14.9 and 7.0 Hz), 6.15 (ddq, 1H, CH=, ^3J = 14.7 and 10.9 Hz, ^4J = 1.5 Hz), 4.53 (3H, OMe), 1.83 (d, 3H, Me, ^3J = 7.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 307.2 (W=C), 204.6 (CO), 198.2 (CO), 145,7 (CH=), 145.6 (CH=), 137.1 (CH=), 131.2 (CH=), 69.3 (OMe), 19.8 (Me). Anal. Calcd for $C_{12}H_{10}O_6W$: C, 33.21; H, 2.31. Found: C, 33.12; H, 2.52.

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$(CO)_5W{=}C(OMe)(CH{=}CHCH{=}CHPh)$, 3g: yield 1.09 g (73%); IR (Nujol) 2065, 1942, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42 (d, 1H, CH=, ^3J = 14.6 Hz), 7.53–7.34 (m, 5H, C_6H_5), 7.12 (d, 1H, CH=, ^3J = 15.4 Hz), 7.05 (dd, 1H, CH=, ^3J = 14.6 and 11.1 Hz), 6.83 (dd, 1H, CH=, ^3J = 15.4 and 11.1 Hz), 4.59 (3H, OMe); ^{13}C NMR ($CDCl_3$) δ 305.4 (W=C), 204.0 (CO), 197.7 (CO), 147.0 (CH=), 145.0 (CH=), 136.3 (C_6H_5), 135.2 (CH=), 129.7, 129.0, 127.5, 127.3 (C_6H_5), 68.8 (OMe). HRMS M^+ Calcd for $C_{17}H_{12}O_6W^{186}$: 498.0175. Found: 498.0173.

$(CO)_5W{=}C(OMe)[CH{=}CHCH{=}C(H)(p\text{-}C_6H_4NMe_2)]$, 3h: yield 0.49 g (30%); IR (Nujol) 2061, 1938, 1595, 1552 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.41 (d, 2H, C_6H_4–, ^3J = 9.0 Hz), 7.31 (d, 1H, CH=, ^3J = 14.3 Hz), 7.20 (dd, 1H, CH=, ^3J = 14.3 and 10.8 Hz), 7.10 (d, 1H, CH=, ^3J = 15.1 Hz), 6.68 (dd, 1H, CH=, ^3J = 15.1 and 10.8 Hz), 6.65 (d, 2H, C_6H_4–, ^3J = 9.0 Hz), 4.50 (3H, OMe), 3.00 (6H, NMe_2); ^{13}C NMR (CD_2Cl_2) δ 300.7 (W=C), 204.8 (CO), 198.7 (CO), 152.2 (C_6H_4), 148.0 (CH=), 144.4 (CH=), 140.4 (CH=), 130.0, 124.6 (C_6H_4–), 122.5 (CH=), 112.3 (C_6H_4–), 68.7 (OMe), 40.4 (NMe_2). Anal. Calcd for $C_{19}H_{17}NO_6W$: C, 42.32; H, 3.18; N, 2.60. Found: C, 41.02; H, 3.26; N, 2.59.

$(CO)_5W{=}C(OMe)[CH{=}CHCH{=}C(H)(C_5H_{11})]$, 3i: yield 0.81 g (47%); IR (Nujol) 2065, 1942, 1628, 1571 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.22 (d, 1H, CH=, ^3J = 14.7 Hz), 6.88 (dd, 1H, CH=, ^3J = 14.7 and 10.9 Hz), 6.41 (dt, 1H, CH=, ^3J = 15.0 and 7.0 Hz), 6.15 (ddt, 1H, CH=, ^3J = 15.0 and 10.9 Hz, ^4J = 1.0 Hz), 4.53 (3H, OMe), 2.15 (m, 2H, CH_2–), 1.43 (m, 2H, CH_2–), 1.33–1.22 (m, 4H, CH_2–), 0.86 (t, 3H, Me, ^3J = 7.0 Hz); ^{13}C NMR (CD_2Cl_2) δ 307.1 (W=C), 204.6 (CO), 198.3 (CO), 151.3 (CH=), 145.7 (CH=), 137.3 (CH=), 129.8 (CH=), 69.3 (OMe), 34.2, 31.8, 28.6, 22.9 (CH_2–), 14.2 (Me).

$(CO)_5W{=}C(OMe)(CH{=}CHCH{=}CMe_2)$, 3j: yield 0.85 g (63%); IR (Nujol) 2065, 1939, 1622, 1559 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (dd, 1H, CH=, ^3J = 14.6 and 11.3 Hz), 7.13 (d, 1H, CH=, ^3J = 14.6 Hz), 5.98 (m, 1H, CH=), 4.53 (3H, OMe), 1.90 (3H, Me), 1.88 (3H, Me); ^{13}C NMR ($CDCl_3$) δ 306.0 (W=C), 203.9 (CO), 197.8 (CO), 153.3 (=CMe_2), 144.9 (CH=), 134.8 (CH=), 125.3 (CH=), 68.6 (OMe), 27.5 (Me), 19.6 (Me). Anal. Calcd for $C_{13}H_{12}O_6W$: C, 34.85; H, 2.70. Found: C, 35.06; H, 3.02.

$(CO)_5W{=}C(OMe)(CH{=}CHCH{=}CHCH{=}CHMe)$, 4k: yield 0.73 g (53%); IR (Nujol) 2065, 1941, 1594, 1556 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.26 (d, 1H, CH=, ^3J = 14.6 Hz), 6.95 (dd, 1H, CH=, ^3J = 14.6 and 11.4 Hz), 6.78 (dd, 1H, CH=, ^3J = 14.8 and 10.6 Hz), 6.23 (m, 1H, CH=, ^3J = 15.0 and 10.5 Hz, ^4J = 1.4 and 0.5 Hz), 6.16 (ddd, 1H, CH=, ^3J = 14.8 and 11.4 Hz, ^4J = 0.5 Hz), 6.08 (dq, 1H, CH=, ^3J = 15.0 and 6.8 Hz), 4.53 (3H, OMe), 1.78 (d, 3H, Me, ^3J = 6.7 Hz); ^{13}C NMR (CD_2Cl_2) δ 305.0 (W=C), 204.7 (CO), 198.3 (CO), 146.8 (CH=), 146.4 (CH=), 137.9 (CH=), 137.2 (CH=), 137.4 (CH=), 129.1 (CH=), 69.2 (OMe), 19.1 (Me). Anal. Calcd for $C_{14}H_{12}O_6W$: C, 36.55; H, 2.63. Found: C, 36.57; H, 2.49.

$(CO)_5Cr{=}C(OMe)(CH{=}CHCH{=}CHCH{=}CHMe)$, 5k: yield 0.44 g (46%); IR (Nujol) 2055, 1944, 1594, 1556 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.42 (d, 1H, CH=, ^3J = 14.3 Hz), 6.99 (m, 2H, CH=), 6.35 (m, 2H, CH), 6.14 (dq, 1H, CH=, ^3J = 14.5 and 6.9 Hz), 4.75 (3H, OMe), 1.85 (d, 3H, Me, ^3J = 6.9 Hz); ^{13}C NMR (CD_2Cl_2) δ 330.6 (Cr=C), 225.7 (CO), 218.0 (CO), 147.9 (CH=), 142.6 (CH=), 142.1 (CH=), 138.4 (CH=), 132.9 (CH=), 129.6 (CH=), 66.8 (OMe), 18.9 (Me).

General Procedure for the Synthesis of Alkoxyalkenylcarbene Complexes 6–11. A solution of 2–3 mmol of metal hexacarbonyl, 6–9 mmol of propyn-1-ol derivatives, and 3 mL of the appropriate alcohol in 60 mL of tetrahydrofuran was irradiated for 6–9 h at room temperature. The solution was then transferred into a Schlenk flask and stirred for 18 h at room temperature. After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel. Elution with dichloromethane/pentane (1/9) followed by evaporation of the solvent gave complexes **6–11** as red oils.

$(CO)_5W{=}C[OCH_2CH(Me)(Et)][CH{=}CHCH{=}CHMe]$, 6f: yield 0.74 g (50%) from 1.06 g (3 mmol) of $W(CO)_6$, 0.57 g (6 mmol) of **f**, and 3 mL of 2-methyl-1-butanol; IR (Nujol) 2064, 1937, 1632, 1572 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.20 (d, 1H, CH=, ^3J = 14.8 Hz), 6.85 (dd, 1H, CH=, ^3J = 14.8 and 10.9 Hz), 6.41 (ddq, 1H, CH=, ^3J = 15.0 and 10.9 Hz, ^4J = 1.4 Hz), 4.60 (dd, 1H, OCH_2, ^2J = 10.3 Hz, ^3J = 5.6 Hz), 4.50 (dd, 1H, OCH_2, ^2J = 10.3 Hz, ^3J = 5.6 Hz), 1.98 (m, 1H, –CH–), 1.83 (dd, 3H, Me, ^3J = 7.0 Hz, ^4J = 1.4 Hz) 1.50 (m, 1H, CH_2–), 1.32 (m, 1H, CH_2–), 1.02 (d, 3H, Me, ^3J = 6.8 Hz), 0.96 (d, 3H, Me, ^3J = 7.4 Hz); ^{13}C NMR (CD_2Cl_2) δ 304.8 (W=C), 204.1 (CO), 197.8 (CO), 145.4 (CH=), 144.6 (CH=), 136.1 (CH=), 131.0 (CH=), 87.1 (OCH_2), 35.4 (–CH–), 26.3 (CH_2–), 19.6 (Me), 16.8 (Me), 11.3 (Me). HRMS M^+ Calcd for $C_{16}H_{18}O_6W^{182}$: 488.0585. Found: 488.0591.

$(CO)_5W{=}C(OCH_2CH_2C{\equiv}CMe)(CH{=}CHCH{=}CMe_2)$, 7j: yield 0.22 g (22%) from 0.70 g (2 mmol) of $W(CO)_6$, 0.66 g (6 mmol) of **j**, and 2.5 mL of 3-pentyn-1-ol; IR (Nujol) 2064, 1940, 1623, 1562 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.36 (dd, 1H, CH=, ^3J = 14.5 and 11.6 Hz), 7.15 (d, 1H, CH=, ^3J = 14.5 Hz), 5.99 (dm, 1H, CH=, ^3J = 11.6 Hz), 4.78 (t, 2H, OCH_2–, ^3J = 6.5 Hz), 2.76 (m, 2H, CH_2–), 1.90 (3H, Me), 1.88 (3H, Me), 1.77 (t, 3H, Me, ^5J = 2.5 Hz); ^{13}C NMR (CD_2Cl_2) δ 303.6 (W=C), 203.8 (CO), 197.8 (CO), 153.5 (=C), 144.9 (CH=), 135.0 (CH=), 125.3 (CH=), 79.6 (OCH_2), 77.2 (C≡), 74.3 (C≡), 29.7 (CH_2), 27.5 (Me), 20.1 (Me), 19.5 (Me). Anal. Calcd for $C_{16}H_{13}O_6W$: C, 40.82; H, 3.22. Found: C, 40.41; H, 3.51.

$(CO)_5Cr{=}C(OCH_2CH_2C{\equiv}CMe)(CH{=}CHPh)$, 8b: yield 0.16 g (15%) from 0.66 g (3 mmol) of $Cr(CO)_6$, 0.40 g (3 mmol) of **b**, and 3.0 mL of 3-pentyn-1-ol; IR (Nujol) 2057, 1946, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97 (d, 1H, CH=, ^3J = 15.3 Hz), 7.62–7.41 (m, 5H, C_6H_5), 7.04 (d, 1H, CH=, ^3J = 15.3 Hz), 5.08 (t, 2H, OCH_2–, ^3J = 6.5 Hz), 2.88 (m, 2H, CH_2–), 1.80 (t, 3H, Me, ^5J = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 332.3 (Cr=C), 225.0 (CO), 217.2 (CO), 140.0 (CH=), 134.9 (C_6H_5), 131.3 (CH=), 130.9, 129.9, 129.5 (C_6H_5), 78.4 (OCH_2), 74.5 (C≡), 71.6 (C≡), 29.8 (CH_2–), 20.6 (Me). Anal. Calcd for $C_{19}H_{14}O_6Cr$: C, 58.47; H, 3.62. Found: C, 58.33; H, 3.72.

$(CO)_5W{=}C(OCH_2CH_2CH{=}CH_2)(HC{=}CHMe)$, 9a: yield 1.06 g (59%) from 1.06 g (3 mmol) of $W(CO)_6$, 0.42 g (6 mmol) of **a**, and 2.5 mL of 3-buten-1-ol; IR (Nujol) 2067, 1942, 1611 cm^{-1}; ^1H NMR (C_6D_6) δ 7.10 (dq, 1H, CH=, ^3J = 15.0 Hz, ^4J = 1.5 Hz), 6.28 (dq, 1H, CH=, ^3J = 15.0 Hz, ^3J = 7.0 Hz), 5.55 (m, 1H, CH=), 4.96 (m, 2H, =CH_2), 4.49 (t, 2H, OCH_2, ^3J = 6.5 Hz), 2.16 (m, 2H, CH_2), 1.23 (dd, 3H, CH_3, ^3J = 7.0 Hz, ^4J = 1.5 Hz); ^{13}C NMR (C_6D_6) δ 307.4 (W=C), 204.2 (CO), 198.4 (CO), 149.8 (CH=), 138.2 (CH=), 134.0 (CH=), 118.3 (CH=), 82.2 (OCH_2), 33.9 (CH_2), 18.4 (CH_3). HRMS M^+ Calcd for $C_{13}H_{12}O_6W^{182}$: 446.0124. Found: 446.0115.

$(CO)_5W{=}C(OCH_2CH_2CH{=}CH_2)(HC{=}CHHC{=}CHMe_2)$, 10j: yield 0.68 g (69%) from 0.70 g (2 mmol) of $W(CO)_6$, 0.66 g (6 mmol) of **j**, and 2.5 mL of 3-buten-1-ol; IR (Nujol) 2064, 1940, 1623, 1560 cm^{-1}; ^1H NMR (C_6D_6) δ 7.32 (dd, 1H, CH=, ^3J = 14.5 and 11.6 Hz), 7.10 (d, 1H, CH=, ^3J = 14.5 Hz), 5.57 (m, 1H, CH=), 5.55 (dm, 1H, CH=, ^3J = 11.6 Hz) 4.98 (m, 2H, =CH_2), 4.48 (t, 2H, OCH_2, ^3J = 6.3 Hz), 2.12 (m, 2H, CH_2), 1.47 (3H, CH_3), 1.38 (3H, CH_3); ^{13}C NMR (C_6D_6) δ 303.7 (W=C), 203.9 (CO), 197.9 (CO), 153.2 (=CMe_2), 144.8 (CH=), 134.6 (CH=), 133.7 (CH=), 125.1 (CH=), 117.9 (=CH_2), 80.7 (OCH_2), 33.9 (CH_2), 27.4 (CH_3), 19.5 (CH_3). Anal. Calcd for $WC_{16}H_{16}O_6$: C, 39.74; H, 3.25. Found: C, 39.37; H, 3.30. HRMS M^+ calcd for $C_{16}O_6H_{16}W^{184}$: 488.04546. Found: 488.04526.

$(CO)_5W{=}C[OCH_2CH_2C(Me){=}CH_2][CH{=}CHHC{=}CMe_2]$, 11j: yield 0.48 g (24%) from 1.41 g (4 mmol) of $W(CO)_6$, 1.32 g (12 mmol) of **j**, and 4 mL of 3-methyl-3-buten-1-ol; IR (Nujol) 2064, 1939, 1620, 1560 cm^{-1}. HRMS M^+ calcd for $C_{17}H_{18}O_6W^{182}$: 500.05849. Found: 500.0585. **11j** decomposes to **14j** at 25 °C in C_6D_6.

Thermolysis of 9a, 10j, and 11j. The thermolyses were carried out in NMR tubes. A solution of 25 mg of **9a** and **10j** in 0.6 mL of C_6D_6 was heated at 60–70 °C for 2 h. The red solution gradually darkened. The ^1H NMR spectra of the

samples showed total conversion of **9a** and **10j** to **12a** and **13j**, respectively. The conversion of **11j** to **14j** was obtained at 25 °C in C_6D_6.

12a: ^{1}H NMR (C_6D_6) δ 5.64 (dq, 1H, CH=, ^3J = 15.2 Hz, ^3J = 6.4 Hz), 5.45 (dq, 1H, CH=, ^3J = 15.2 Hz, ^4J = 1.5 Hz), 4.00 (ddd, 1H, OCH_2–, ^2J = 9.1 Hz, ^3J = 9.1 Hz, ^3J = 2.3 Hz), 3.48 (ddd, 1H, OCH_2–, ^2J = 9.1 Hz, ^3J = 9.1 Hz, ^3J = 7.3 Hz), 2.06 (m, 1H, CH_2–), 1.87 (ddd, 1H, CH_2–, ^3J = 9.1 Hz, ^3J = 7.3 Hz, ^3J = 2.3 Hz), 1.67 (dd, 3H, CH_3, ^3J = 6.4 Hz, ^4J = 1.5 Hz), 1.39 (m, 1H, –CH–), 1.0 (dd, 1H, CH_2 cyclopropyl, ^2J = 5.6 Hz, ^3J = 5.6 Hz), 0.68 (dd, 1H, CH_2 cyclopropyl, ^3J = 8.9 Hz, ^3J = 5.6 Hz).

13j: ^{1}H NMR (C_6D_6) δ 6.99 (dd, 1H, CH=, ^3J = 15.1 Hz, ^3J = 11.2 Hz), 5.99 (d, 1H, CH=, ^3J = 11.2 Hz), 5.50 (d, 1H, CH=, ^3J = 15.1 Hz), 3.89 (ddd, 1H, OCH_2–, ^2J = 9.0 Hz, ^3J = 9.0 Hz, ^3J = 2.3 Hz), 3.31 (ddd, 1H, OCH_2–, ^2J = 9.0 Hz, ^3J = 9.0 Hz, ^3J = 7.3 Hz), 1.75 (m, 1H, CH_2–), 1.65 (3H, CH_3), 1.63 (3H, CH_3), 1.48 (m, 1H, CH_2–), 1.20 (m, 1H, –CH–), 0.99 (dd, 1H, CH_2 cyclopropyl, ^2J = 6.0 Hz, ^3J = 6.0 Hz), 0.60 (ddd, 1H, CH_2 cyclopropyl, ^3J = 8.9 Hz, ^2J = 6.0 Hz, ^4J = 0.3 Hz).

14j: ^{1}H NMR (C_6D_6) δ 7.00 (dd, 1H, CH=, ^3J = 15.1 Hz, ^3J = 11.1 Hz), 5.99 (dm, 1H, CH=, ^3J = 11.1 Hz), 5.53 (d, 1H, CH=, ^3J = 15.1 Hz), 3.83 (ddd, 1H, OCH_2–, ^2J = 9.0 Hz, ^3J = 9.0 Hz, ^3J = 2.5 Hz), 3.26 (ddd, 1H, OCH_2–, ^3J = 10.2 Hz, ^2J = 9.0 Hz, ^3J = 7.5 Hz), 1.66 (m, 1H, CH_2–), 1.65 (d, 3H, CH_3, ^4J = 0.5 Hz), 1.63 (d, 3H, CH_3, ^4J = 1.0 Hz), 1.60 (m, 1H, CH_2–) 1.15 (d, 1H, CH_2 cyclopropyl, ^2J = 6.1 Hz), 1.01 (3H, CH_3), 0.43 (dd, 1H, CH_2 cyclopropyl, ^2J = 6.1 Hz, ^4J = 1.4 Hz).

General Procedure for the Aminolysis of (Methoxyalkenylcarbene)tungsten Complexes. A solution of 1 mmol of complex **3g** or **3i** in 50 mL of pentane was treated with 0.5 mL of amine (5–7 equiv) at room temperature. The color rapidly changed from red to orange. After stirring for 1 h (the reaction was slower with tert-butylamine and needed 18 h of stirring), the solvent was removed and the crude product was chromatographed on silica gel using pentane/dichloromethane (1/1) as eluent. Evaporation of the solvent gave complexes **15**–**18** as orange solids.

$(OC)_5W$=C(NHCHMe$_2$)(CH=CHCH=CHPh), 15g: yield 0.45 g (86%) from 0.5 g (1 mmol) of **3g** and 0.5 mL (5.8 mmol) of isopropylamine; IR (Nujol) 2061, 1925, 1614, 1590 cm^{-1}. Anal. Calcd for $WC_{19}H_{17}NO_5$: C, 43.59; H, 3.28; N, 2.68. Found: C, 43.56; H, 3.30; N, 2.67. (*Z*): ^{1}H NMR ($CDCl_3$) δ 8.16 (s broad, 1H, NH), 7.46–7.27 (m, 5H, C_6H_5), 6.88 (d, 1H, CH=, ^3J = 15.0 Hz), 6.83 (d, 1H, CH=, ^3J = 15.7 Hz), 6.82 (dd, 1H, CH=, ^3J = 15.7 Hz, ^3J = 10.1 Hz), 6.43 (m, 1H, CH=), 4.60 (m, 1H, N–CH), 1.42 (d, 6H, CH_3, ^3J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 239.0 (W=C), 203.3 (CO), 196.7 (CO), 145.2 (CH=), 138.9 (CH=), 136.3 (C_6H_5), 131.6 (CH=), 128.8 (CH=), 128.8, 126.9, 126.8 (C_6H_5), 57.3 (N–C), 21.1 (CH_3). (*E*): ^{1}H NMR ($CDCl_3$) δ 8.08 (s broad, 1H, NH), 7.46–7.27 (m, 5H, C_6H_5), 7.18 (m, 1H, CH=), 6.94 (d, 1H, CH=, ^3J = 15.5 Hz), 6.89 (dd, 1H, CH=, ^3J = 15.5 Hz, ^3J = 12.0 Hz), 6.68 (d, 1H, CH=, ^3J = 14.2 Hz), 4.07 (m, 1H, N–CH), 1.28 (d, 6H, CH_3, ^3J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 243.4 (W=C), 201.5 (CO), 197.8 (CO), 49.2 (N–C), 21.2 (CH_3).

$(OC)_5W$=C(NHCMe$_3$)(CH=CHHC=CHPh), 16g: yield 0.32 g (60%) from 0.5 g (1 mmol) of **3g** and 0.5 mL (4.8 mmol) of *tert*-butylamine; IR (Nujol) 2061, 1933, 1618, 1590 cm^{-1}. Anal. Calcd for $WC_{20}O_5H_{19}N$: C, 44.72; H, 3.56; N, 2.61. Found: C, 44.90; H, 3.81; N, 2.54. (*Z*): ^{1}H NMR ($CDCl_3$) δ 8.90 (s broad, 1H, NH), 7.46–7.27 (m, 5H, C_6H_5), 7.13 (d, 1H, CH=, ^3J = 14.7 Hz), 6.72 (d, 1H, CH=, ^3J = 15.5 Hz), 6.68 (dd, 1H, CH=, ^3J = 15.5 Hz, ^3J = 12.0 Hz), 5.76 (m, 1H, CH=), 1.57 (9H, CH_3); ^{13}C NMR ($CDCl_3$) δ 244.4 (W=C), 203.4 (CO), 198.7 (CO), 58.1 (N–C), 30.3 (CH_3). (*E*): ^{1}H NMR ($CDCl_3$) δ 8.48 (s broad, 1H, NH), 7.46–7.27 (m, 5H, C_6H_5), 7.08 (m, 1H, CH=), 6.93 (d, 1H, CH=, ^3J = 14.6 Hz), 6.86 (m, 1H, CH=), 6.86 (m, 1H, CH=), 1.45 (9H, CH_3); NMR ^{13}C{^{1}H} ($CDCl_3$) δ 249.4 (W=C), 203.0 (CO), 199.4 (CO), 60.7 (N–C), 30.6 (CH_3).

$(OC)_5W$=C(NHCH$_2$CH=CH$_2$)(HC=CHHC=CHPh), 17g: yield 0.41 g (82%) from 0.5 g (1 mmol) of **3g** and 0.5 mL (6.7 mmol) of allylamine; IR (Nujol) 2061, 1927, 1612, 1590 cm^{-1}. (*Z*): ^{1}H NMR ($CDCl_3$) δ 8.26 (s broad, 1H, NH), 7.46–7.27 (m, 5H, C_6H_5), 6.83 (d, 1H, CH=, ^3J = 15.0 Hz), 6.77 (m, 1H, CH=), 6.75 (m, 1H, CH=), 6.48 (m, 1H, CH=), 5.93 (m, 1H, CH=), 5.28 (m, 2H, =CH_2), 4.44 (m, 2H, NCH_2); ^{13}C NMR ($CDCl_3$) δ 247.1 (W=C), 203.0 (CO), 198.2 (CO), 57.1 (–CH_2N). (*E*): ^{1}H NMR ($CDCl_3$) δ 8.26 (s broad, 1H, NH), 7.46–7.27 (m, 5H, C_6H_5), 7.18 (m, 1H, CH=), 6.87 (m, 1H, CH=), 6.88 (m, 1H, CH=), 6.59 (d, 1H, CH=, ^3J = 14.7 Hz), 5.82 (m, 1H, CH=), 5.28 (m, 2H, =CH_2), 4.01 (m, 2H, NCH_2); ^{13}C NMR ($CDCl_3$) δ 249.3 (W=C), 203.3 (CO), 199.1 (CO), 51.3 (–CH_2N).

$(OC)_5W$=C(NHCH$_2$CHMe$_2$)(HC=CHHC=CHC$_5$H$_{11}$), 18i: yield 0.49 g (92%) from 0.49 g (1 mmol) of **3i** and 0.5 mL (5.9 mmol) of isopropylamine; IR (Nujol) 2060, 1926, 1636, 1596 cm^{-1}. Anal. Calcd for $C_{19}H_{15}NO_5W$: C, 42.96; H, 4.74. Found: C, 41.56; H, 4.38. (*Z*): ^{1}H NMR ($CDCl_3$) δ 8.26 (s broad, 1H, NH), 6.65 (d, 1H, CH=, ^3J = 14.9 Hz), 6.28 (m, 1H, CH=), 6.02 (m, 1H, CH=), 6.02 (m, 1H, CH=) 3.63 (m, 2H, N–CH_2), 2.12 (m, 2H, CH_2), 1.92 (sept, 1H, –CH–, ^3J = 6.7 Hz), 1.38 (2H, CH_2, ^3J = 7.2 Hz, ^3J = 7.2 Hz), 1.29–1.18 (m, 4H, CH_2), 1.00 (d, 6H, CH_3, ^3J = 6.7 Hz), 0.82 (t, 3H, CH_3, ^3J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 245.9 (W=C), 203.3 (CO), 198.4 (CO), 143.6 (HC=), 143.4 (HC=), 133.1 (HC=), 128.7 (HC=), 62.1 (CH_2), 33.1 (CH_2), 31.4 (CH_2), 28.7 (CH), 28.4 (CH_2), 22.5 (CH_2), 20.1 (CH_3), 14.0 (CH_3). (*E*): ^{1}H NMR ($CDCl_3$) δ 8.18 (s broad, 1H, NH), 7.09 (dd, 1H, CH=, ^3J = 14.8 Hz, ^3J = 9.5 Hz), 6.44 (d, 1H, CH=, ^3J = 14.8 Hz), 6.20 (m, 1H, CH=), 6.20 (m, 1H, CH=), 3.20 (m, 2H, N–CH_2), 2.12 (m, 2H, CH_2), 1.92 (sept, 1H, CH, ^3J = 6.7 Hz), 1.38 (tt, 2H, CH_2, ^3J = 7.2 Hz, ^3J = 7.2 Hz), 1.29–1.18 (m, 4H, CH_2), 0.96 (d, 6H, CH_3, ^3J = 6.7 Hz), 0.83 (t, 3H, CH_3, ^3J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 247.0 (W=C), 202.8 (CO), 199.3 (CO), 152.5 (HC=), 145.6 (CH=), 133.1 (CH=), 129.7 (CH=), 56.2 (CH_2), 33.2 (CH_2), 31.4 (CH_2), 28.7 (CH), 28.4 (CH_2), 22.5 (CH_2), 20.0 (CH_3), 14.0 (CH_3).

Acknowledgment. This work was supported by the CNRS. We thank J. P. Guégan for NMR technical assistance, the European ERASMUS program for a grant to I.D.R., the University of Oviedo (Spain), and the European Union (CHM program, contract CHRXCT 940501) for financial support.

OM9409433