Reactions of Alkynols with (Alkynylalkoxycarbene)metal Complexes (Metal = Chromium, Tungsten)

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(Alkynylalkoxycarbene)metal complexes react with alkynols to give different types of products depending fundamentally on the substitution of the triple bond (mono- or disubstituted alkynes) and the spacing between the triple bond and the hydroxy functions.

Since the early work in metal carbene chemistry, the ambivalent electrophilic character of (alkynylalkoxycarbene)metal complexes has been recognized. Under conditions of kinetic control (−80 °C) attack by amines occurs only at the carbene center, but at higher temperatures the product is that arising from amine addition to the triple bond.[1] In addition, carbanions,[2] as well as alcohols, phenols, and thiols,[3] also add readily to the triple bond, giving the corresponding alkenyl complexes. The activated triple bond in these complexes has also been found to readily suffer cycloaddition reactions with a variety of substrates.[4]

The sharp regioselectivity observed in these reactions has been explained on basis of the polarization induced by the metal on the adjacent triple bond.[5]

In the course of our studies on the conjugate addition of alcohols, phenols, and thiols to the triple bond of (alkynylalkoxycarbene)metal complexes, we observed that, when a triple bond was attached to the alcohol at a convenient distance, it could further interact with either the metal–carbene bond or the double bond arising from conjugate addition of the alcohol to the carbene complex to give new types of products.

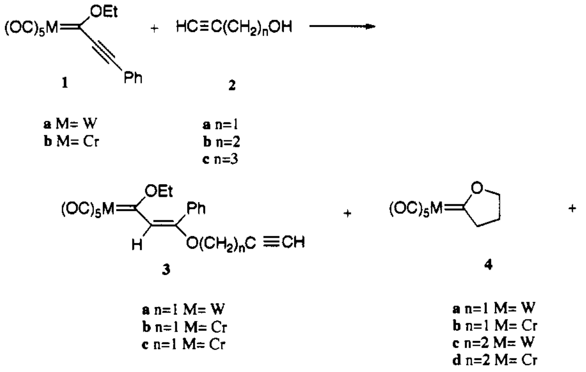
We report here the diverse behavior of alkynols in their reactions with (alkynylalkoxycarbene)metal complexes.

Results and Discussion

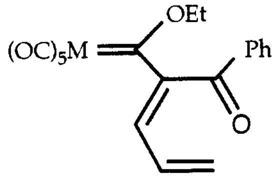
Monosubstituted Alkynols. Reaction of propargyl alcohol with complex **1a** gave, after stirring for 15 min at room temperature in the presence of a substoichiometric amount of DBU, the expected addition product **3a** in good yield (Table 1, entry 1).

Propargyl alcohol also reacted with complex **1b**, giving the corresponding addition product **3b** (as detected by ^{1}H-NMR of the crude reaction mixture). All attempts to isolate and characterize it led to its complete transformation into **5b** (Entry 2).

Table 1. Reaction of Monosubstituted Alkynols with (Alkynylalkoxycarbene)metal (Cr, W) Complexes



entry	starting complex	alkynol	time	temp	products (yield, %)		
1	**1a**	**2a**	15 min	RT	**3a** (75)		
2	**1b**	**2a**	10 min	RT	**3b** (trace)		**5b** (81)
3	**1a**	**2b**	1 h	45 °C	**3c** (8)	**4a** (40)	**6** (2)
4	**1b**	**2b**	1 h	45 °C		**4b** (60)	**6** (30)
5	**1a**	**2c**	1 h	45 °C		**4c** (63)	
6	**1b**	**2c**	1 h	40 °C		**4d** (50)	



5

a M= W
b M= Cr

Figure 1.

When, in a separate experiment, **3a** was dissolved in diethyl ether in the presence of a catalytic amount of trifluoroacetic acid it completely transformed into **5a** (25%) and other polymeric products.

The structures of **5a** and **5b** were determined by spectroscopic data, and they can be thought to originate from an initial [3,3] sigmatropic transformation[6] (a Claisen rearrangement) with consequent [1,3] proton shift to

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⊛ Abstract published in *Advance ACS Abstracts,* May 1, 1994.

[1] (a) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977,** *131,* 57. (b) Duetsch, M.; Lackmann, R.; Stein, F.; De Meijere, A.; *Synlett* **1991,** *5,* 324–326. (c) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; De Meijere, A. *Chem. Ber.* **1992,** *125,* 2051–2065. (d) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993,** *126,* 421–427.

[2] Fischer, H.; Meisner, T.; Hofmann, J. *Chem. Ber.* **1990,** *123,* 1799.

[3] Llebaria, A.; Moretó, J. M.; Ricart, S.; Ros, J.; Viñas, J. M.; Yañez, R. *J. Organomet. Chem.* **1992,** *440,* 79.

[4] (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984,** *106,* 7565–7568. (b) Wulff, W. D.; Batua, W. E.; Kaesler, R. W.; Lankford, D. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990,** *112,* 3642–3659. (c) Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Tetrahedron Lett.* **1990,** 2479. (d) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 1470–1472.

[5] Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986,** *108,* 5229.

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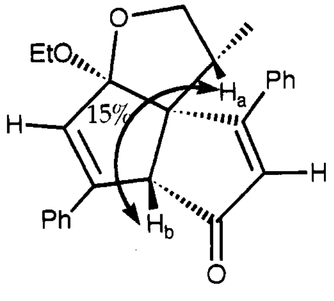
afford the resulting ketone.[7,8] The presence of a different metal in the starting complexes may account for the difference in stability between the two initial propargyl vinyl ethers **3a** and **3b**.

The higher homologue 3-butyn-1-ol did not react with complex **1a** under the same experimental conditions. However, when the temperature was raised to 45 °C in the presence of DBU, the starting product dissappeared in 1 h and an orange-yellow solution was obtained. After purification of the crude mixture by flash chromatography (hexane/dichloromethane, 9/1) a major yellow product was collected and identified as the oxacycloalkylidene complex **4a**[9] (entry 3). In view of this surprising result, we decided to extend the reaction to other alkynols of type **2** and also to starting complex **1b**.

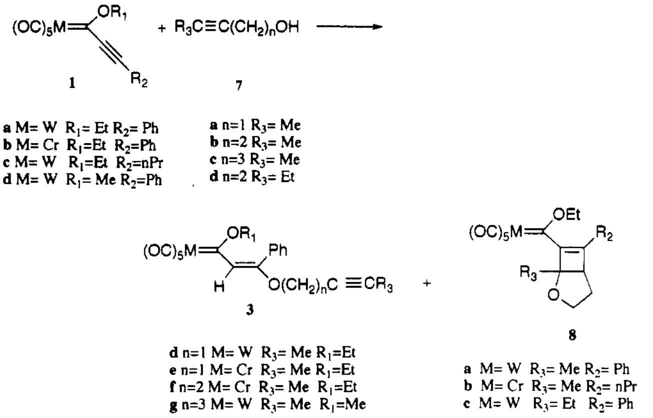
As reflected in Table 1, alkynol homologues with n = 2 and 3 afforded in all cases oxacycloalkylidene complexes **4** as major products in acceptable yields. In all cases, other minor products were also detected in the reaction mixture by TLC. Among them, compound **6**, obtained in the reaction of either **1a** or **1b** with 3-butyn-1-ol, amounted to 5% or 30% respectively. Its basic cyclopentenone structure was deduced from the spectroscopic data (IR strong absorption at 1724 cm^{-1} (strained conjugated carbonyl); ^{1}H-NMR signals at δ 6.28 and 6.42 ppm (vinyl protons) and ^{13}C-NMR quaternary carbon at δ 204 ppm (cyclopentenone carbonyl)). Two-dimensional NMR experiments (COSY and HETCOR) suggested the existence of a tricyclic structure such as **6**. The presence of a bridgehead proton and its ascription from other proton NMR signals was evidenced by a strong NOE effect between protons H_a and H_b (15%) after they could be ascribed in the proton NMR of the product. In addition, a single-crystal diffractometry analysis confirmed the proposed connectivity and stereochemistry. Taking into account the number of new C–C and C–O bonds in this compound, its formation in the reaction is remarkable and points to a strict regioselectivity. In the case of 4-pentyn-1-ol, the only products identified were the corresponding oxacycloalkylidene complexes **4**. Other organic products obtained in very low yield could not be characterized (entries 5, 6). Only traces of products from conjugate addition of type **3** were detected in both cases.



6

Figure 2.

Table 2. Reaction of Disubstituted Alkynols with (Alkynylalkoxycarbene)metal (Cr, W) Complexes



1

a M= W R$_1$= Et R$_2$= Ph
b M= Cr R$_1$=Et R$_2$=Ph
c M= W R$_1$=Et R$_2$=nPr
d M= W R$_1$= Me R$_2$=Ph

7

a n=1 R$_3$= Me
b n=2 R$_3$= Me
c n=3 R$_3$= Me
d n=2 R$_3$= Et

3

d n=1 M= W R$_3$= Me R$_1$=Et
e n=1 M= Cr R$_3$= Me R$_1$=Et
f n=2 M= Cr R$_3$= Me R$_1$=Et
g n=3 M= W R$_3$= Me R$_1$=Me

8

a M= W R$_3$= Me R$_2$= Ph
b M= Cr R$_3$= Me R$_2$= nPr
c M= W R$_3$= Et R$_2$= Ph

entry	starting complex	alkynol	time, h	temp	products (yield, %)	
1	**1a**	**7a**	2.5	RT	**3d** (40)	
2	**1b**	**7a**	2.5	RT	**3e** (62)	
3	**1a**	**7b**	2	RT		**8a** (75)
4	**1b**	**7b**	4	10 °C	**3f** (18)	
5	**1c**	**7b**	1	RT		**8b** (76)
6	**1d**	**7c**	72	RT	**3g** (9)	
7	**1a**	**7d**	2	RT		**8c** (50)

Although the mechanism for the reaction of monosubstituted alkynols with alkynylalkoxycarbene complexes remains unclear, the formation of **6** and other less abundant organic products related to it, which were found difficult to fully characterize, indicated that two (or more) carbene units could react with one alkynol to give the corresponding cyclic organic products while the carbene free metal moiety, "M(CO)$_5$", would bind another alkynol moiety to form the oxacycloalkylidene complexes.[10] Thus, it appears as though the overall reaction consisted of a double trapping on the alkynol: two moieties of carbene on one side and the two remaining pentacarbonylmetal units on the other trapped by two different alkynol molecules.

Disubstituted Alkynols. As from propargyl alcohol, reaction of 2-butyn-1-ol (**7a**) with complexes **1a** and **1b** afforded, after a short reaction time, the corresponding products of conjugate addition **3d** and **3e** (Table 2, entries 1 and 2).

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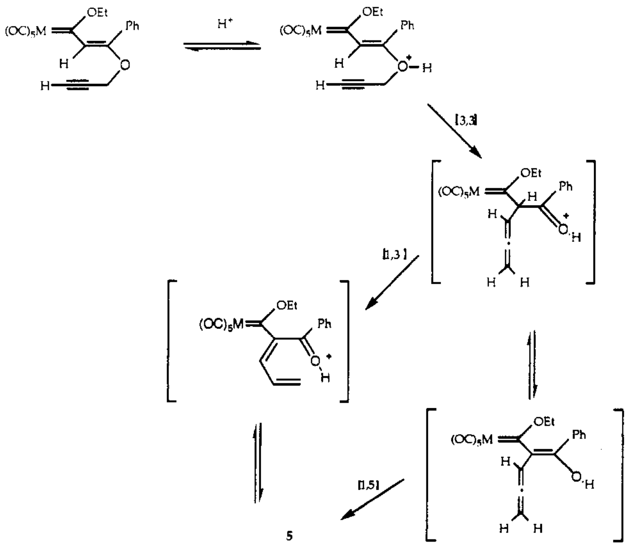
[6] Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205–247.

[7] Black, D. B.; Fomum, Z. T.; Landor, P. D.; Landor, S. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1349–1352.

[8] Alternatively, after the initial [3,3] sigmatropic transformation, a [1,5] proton shift could also explain the resulting product:

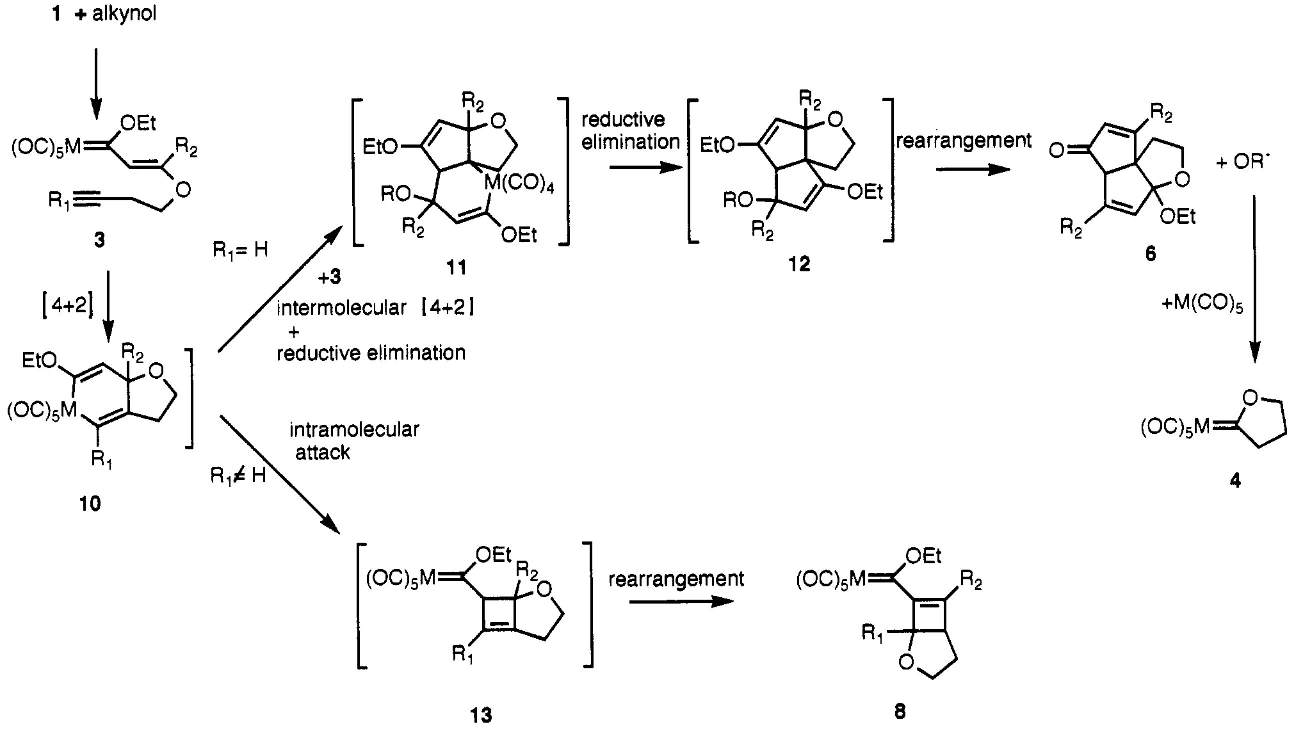


See: Sarcevic, M.; Zsindely, J.; Schmich, H. *Helv. Chim. Acta* **1973**, *56*, 1457.

[9] For alternative formation of oxacycloalkylidenemetal complexes, see: (a) Casey, C. P.; Anderson, R. L. *J. Organomet. Chem.* **1974**, *73*, C28–C30. (b) Dötz, K. H.; Sturm, W. *J. Organomet. Chem.* **1985**, *285*, 205–211. (c) Semmelhack, M. F.; Lee, G. R. *Organometallics* **1987**, *6*, 1839–1844.

[10] Dötz, K. H.; Sturm, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424.

Scheme 1



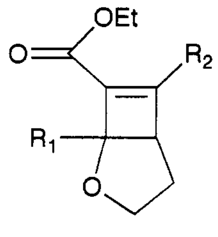


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Figure 3.

Surprisingly, when the reaction was performed with the starting complex **1a** and alkyne **7b**, under the same reaction conditions (DBU, room temperature), only a single product was obtained in good yield. This product was recognized as the new carbene complex **8a** (as evidenced by IR, ^{1}H-NMR, and ^{13}C-NMR). Since an X-ray diffraction study was necessary in order to confirm the proposed structure and no suitable crystals of the complex could be obtained, treatment of **8a** with DMSO afforded the free organic ligand in almost quantitative yield. All spectral data for this organic product correlated perfectly with those of the parent complex, and an X-ray diffractometry study of a single crystal could now be performed, confirming structure **8a** for the product obtained.

As reflected in Table 2, the change of the organic moiety of the starting carbene complex (substitution at β-carbene site; cf. entries 3 and 5) did not affect substantially the reaction course. However, change of metal (entries 3 and 4) and/or the number of spacers between the two functionalities in the alkynol did produce a dramatic change in the reaction products or yields. Products **8** can be considered to formally arise from a [2 + 2] cycloaddition[11] of **1** and the cyclic enol ether derived from an intramolecular attack of the alcohol to the triple bond.[12]

Thus, in both cases (mono- and disubstituted alkynols), an initial addition of the alcohol to the triple bond of the carbene complex is liable to be the first reaction step. In subsequent steps, this intermediate could follow two main reaction pathways as reflected in Scheme 1:[13] (a) An intermolecular [4 + 2] cycloaddition followed by a reductive elimination would afford the tricyclic compound **6** and the oxacycloalkylidene complexes **4**; (b) compounds **8** would be formed through an intramolecular insertion and a base-catalyzed rearrangement.[14]

The higher propensity of Cr for carbonyl dissociation to coordinate triple bonds, even at low temperatures, might be the reason for different reaction pathways in chromium *versus* tungsten complexes.[15]

Conclusions. (Alkynylalkoxycarbene)metal complexes react with alkynols to give different types of products depending fundamentally on the substitution of the triple bond (mono- or disubstituted alkynes) and the length of the chain spanning from the triple bond to the hydroxy function which may allow a subsequent reaction to take place.

Thus, while for propargyl alcohol only the product from conjugated addition is isolated, for higher homologues the reaction is driven either to the formation of oxacycloalkylidenemetal complexes or to that of the formal [2 + 2] cycloadduct of the cyclic enol ether derived from the

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[11] (a) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727–8729. (b) Camps, F.; Jordi, L.; Moretó, J. M.; Ricart, S.; Castaño, A. M.; Echavarren, A. M. *J. Organomet. Chem.* **1992**, *436*, 189–198.

[12] It is known that the intramolecular addition of an alcohol or a carboxylic acid to an acetylene is an efficient route to heterocycles: (a) Mercier, F.; Epszttein, R.; *Bull. Soc. Chim. Fr.* **1973**, *12*, 3393–3397. (b) Martin, R.; Schwartz, *J. Am. Chem. Soc.* **1982**, *104*, 5842–5844. (c) Lambert, C.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *45*, 5323–5326. While **1a** was slowly decomposed by the addition of DBU under the general experimental conditions, the starting products were recovered unchanged from the two alternative binary mixtures. This seems to indicate some kind of interaction between the metal and the alkynol "only" in the presence of a base.

[13] We thank the reviewers for helpful suggestions concerning this putative mechanism.

[14] The lack of formation of **8** from pentynols may be explained by an unfavorable entropy contribution relative to butynols.

[15] (a) Foley, H. C.; Strunbinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064–3073. (b) Wulff, W. D.; Kaesler, R. W.; Petersen, G. A.; Tang, P.-C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.

alkynol and the alkynylcarbene complexes, depending on the character of the triple bond (mono- and disubstituted, respectively).

In both cases, the results strongly depend on the metal of the complex. This may be accounted for by the different electronic activation conveyed to the conjugated triple bond and/or the higher lability of the carbonyl ligands bonded to the chromium compared to those of tungsten complexes.

The study of the possible synthetic applications of the ambivalent behavior of alkynylcarbene complexes is currently underway in our laboratory.

Experimental Section

Unless otherwise stated, all common reagents were used as obtained from commercial suppliers without further purification. Solvents were dried and distilled under nitrogen.

NMR spectra were recorded on a Varian Gemini 200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) or a Varian XL-300 apparatus (300 MHz for ^{1}H and 75 MHz for ^{13}C). All samples of carbene complexes were filtered through a pad of Celite prior to recording the spectra. IR spectra were recorded on a Bomen FT-IR M-120 spectrophotometer. Mass spectra were obtained on an AutoSpec-Q mass spectrometer. Elemental analyses were performed using a Carlo Erba 1106 apparatus. Flash column chromatography was performed with "flash grade" silica (SDS 230–400 mesh). Carbene complexes **1a–c** were prepared following literature procedures.[16]

General Procedure. Reaction of 1a with 2-Propyn-1-ol. To a two-neck flame-dried round-bottom flask containing pentacarbonyl[ethoxy(phenylethynyl)carbene]tungsten (**1a**) (482 mg, 1 mmol) were added alkynol **2a** (0.3 mL, 5 mmol) and DBU (1 mL, 0.1 M in toluene, 0.1 mmol). The resulting mixture was stirred under argon at 25 °C for 15 min. Control by TLC (hexanes/CH_2Cl_2, 9/1) showed disappearance of the starting carbene complex. Solvent was removed in the vacuum line, and the resulting crude product was purified by flash chromatography on silica gel. Elution with hexane/CH_2Cl_2 provided a single product identified as **3a** (403 mg, 75%) *E*/*Z* = 7.

3a. MP: 50–51 °C. IR ($CHCl_3$; cm^{-1}) (both isomers): 3309, 2063, 1974, 1932. ^{1}H-NMR ($CDCl_3$): $\delta(E)$ 0.85 (t, J = 6.9 Hz, 3H, CH_3), 2.67 (t, J = 2.4 Hz, 1H, ≡CH), 4.42 (q, J = 6.9 Hz, 2H, OCH_2), 4.73 (d, J = 2.4 Hz, 2H, OCH_2), 7.14 (s, 1H, =CH), 7.24–7.48 (m, 5H, Ph); $\delta(Z)$ 1.69 (t, J = 6.9 Hz, 3H, CH_3), 2.52 (t, J = 2.4 Hz, 1H, =CH), 4.48 (d, J = 2.4 Hz, 2H, OCH_2), 4.92 (q, J = 6.9 Hz, 2H, CH_2), 7.12 (s, 1H, =CH), 7.32–7.62 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$): $\delta(E)$ 13.8 (q), 57.3 (t), 76.4 (s), 77.4 (s), 78.4 (t), 124.9 (d), 128.1 (d), 128.9 (d), 129.8 (d), 136.3 (s), 159.8 (s), 198.1 (cis CO), 203.9 (trans CO), 300.8 (C (carbene C); $\delta(Z)$ 15.2, 59.9, 76.3, 77.7, 79.6, 128.5, 129.1, 130.6, 131.1, 134.0, 155.4, 198.1, 203.9, 301.9. Anal. Calcd for $C_{19}H_{15}O_7W$: C, 42.38; H, 2.60. Found: C, 42.24; H, 2.65.

Reaction of 1b with 2-Propyn-1-ol. Chromium complex **1b** (350 mg, 1 mmol) and propargyl alcohol **2a** were reacted as described under the general method for **1a**. After 10 min TLC chromatography showed the disappearance of the starting complex **1b**. The ^{1}H-NMR spectrum of the crude reaction mixture revealed the formation of complex **3b** as the only product. Purification by flash chromatography (hexane/CH_2Cl_2, 85/15) of this mixture afforded pure complex **5b** (655 mg, 66%).

3b. ^{1}H-NMR ($CDCl_3$): $\delta(E)$ 0.84 (t, J = 7.2 Hz, 3H, CH_3), 2.67 (t, J = 2.4 Hz, 1H, ≡CH), 4.58 (q, J = 7.2 Hz, 2H, OCH_2), 4.74 (d, J = 2.4 Hz, 2H, OCH_2), 7.17 (s, 1H, =CH), 7.22–7.40 (m, 5H, Ph); $\delta(Z)$ 1.69 (t, J = 7.2 Hz, 3H, CH_3), 2.52 (t, J = 2.4 Hz, 1H, =CH), 5.05 (q, J = 7.2 Hz, 2H, OCH_2), 4.44 (d, J = 2.4 Hz, 2H, CH_2), 7.07 (s, 1H, =CH), 7.32–7.62 (m, 5H, Ph).

5b. IR ($CHCl_3$; cm^{-1}): 2057, 1982, 1944, 1677. ^{1}H-NMR ($CDCl_3$): δ 1.17 (t, J = 7.2 Hz, 3H, CH_3), 4.94 (q, J = 7.2 Hz, 2H, OCH_2), 5.69 (d, J = 10.2 Hz, 1H, =C*H*H), 5.95 (d, J = 16.5 Hz, 1H, =CH*H*), 6.47 (ddd, J = 11.4, 10.2, 16.5 Hz, 1H, CH=), 7.43–7.75 (m, 5H, Ph), 7.68 (d, J = 11.4 Hz, 1H, =CH_2–). ^{13}C-NMR (CD_2Cl_2): δ 14.1 (q), 77.2 (t), 128.7 (d), 130.2 (t), 132.6 (d), 133.4 (d), 136.9 (s), 149.7 (d), 154.2 (s), 195.9 (CO), 216.6 (cis CO), 223.6 (trans CO), 337.5 (carbene).

Reaction of 1a with 3-Butyn-1-ol. Tungsten complex **1a** (484 mg, 1 mmol) and 3-butyn-1-ol (0.76 mL, 10 mmol) were reacted as described under the general method, at 45 °C for 1 h. After this period of time, separation and purification of the crude reaction mixture afforded three products identified as **3c** (44 mg, 8%), **4a** (158 mg, 40%), and **6** (7 mg, 2%).

3c. IR ($CHCl_3$; cm^{-1}): 3313, 2061, 1973, 1936. ^{1}H-NMR ($CDCl_3$): $\delta(E)$ 0.84 (t, J = 7.2 Hz, 3H, CH_3), 2.07 (t, J = 2.6 Hz, 1H, ≡CH), 2.71 (dt, J_d = 2.6 Hz, J_t = 6.8 Hz, CH_2C≡), 4.16 (t, J = 6.8 Hz, 2H, O$CH_2$$CH_2$), 4.40 (q, J = 7 Hz, 2H, OCH_2), 6.90 (s, 1H, C=CH), 7.26–7.42 (m, 5H, Ph); $\delta(Z)$ 1.67 (t, J = 7 Hz, 3H, CH_3), 2.03 (t, J = 2.6 Hz, 1H, =CH), 2.56 (dt, J_d = 2.6 Hz, J_t = 6.8 Hz, 2H, CH_2C=), 3.96 (t, J = 6.8 Hz, 2H, O$CH_2$$CH_2$), 4.90 (q, J = 7.2 Hz, 2H, OCH_2), 6.99 (s, 1H, C=CH), 7.26–7.56 (m, 5H, Ph).

4a. IR ($CHCl_3$; cm^{-1}): 2063, 1980, 1940, 1930. ^{1}H-NMR ($CDCl_3$): δ 1.95 (m, 2H, CH_2), 3.40 (t, J = 7.6 Hz, 2H, W = CCH_2), 4.88 (t, J = 7.6 Hz, 2H, OCH_2). ^{13}C-NMR ($CDCl_3$): δ 21.5 (t), 63.4 (t), 85.3 (t), 197.1 (cis CO), 204.3 (trans CO), 314.5 (carbene). Anal. Calcd for $C_9H_6O_6W$: C, 27.43; H, 1.54. Found: C, 27.62; H, 1.45.

6. IR ($CHCl_3$; cm^{-1}): 1704. ^{1}H-NMR ($CDCl_3$): δ 1.06 (t, J = 6.9 Hz, 3H, CH_3), 1.98 (ddd, J = 13.1, 6.0, 2.1 Hz, 1H, CH_2), 2.71 (ddd, J = 13.1, 10.8, 8.1 Hz, 1H, CH_2), 3.65 (dq, J = 9.0, 6.9 Hz, 1H, OCH_2), 3.73 (ddd, J = 10.8, 9.0, 6.0 Hz, 1H, CH_2), 3.86 (dq, J = 9.0, 6.9 Hz, 1H, OCH_2), 3.88 (d, J = 1.5 Hz, 1H, CH), 4.24 (ddd, J = 9.0, 8.1, 2.1 Hz, 1H, CH_2), 6.28 (d, J = 1.5 Hz, 1H, =CH), 6.42 (s, 1H, =CH), 7.32–7.90 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): δ 15.6 (q), 36.7 (t), 60.8 (t), 65.4 (d), 65.5 (d), 118.4 (s), 123.2 (d), 127.5 (d), 128.1 (d), 128.3 (d), 128.7 (d), 129.0 (d), 130.1 (s), 130.2 (d), 133.4 (s), 143.8 (s), 174.9 (s), 204.0 (CO). MS (EI): *m/z* 358 (M$^+$, 100%), 330 (30.9%), 314 (82.2%), 285 (74.4%), 257 (26.8%), 255 (22.4%).

Reaction of 1b with 3-butyn-1-ol. Chromium complex **1b** (350 mg, 1 mmol) and 3-butyn-1-ol (0.76 mL, 10 mmol) were reacted as described under the general method. After 1 h at 45 °C, the reaction was stopped and the crude reaction mixture purified by flash chromatography. Two products were identified, **4b** (157 mg, 60%) and **6** (107 mg, 30%).

4b. IR ($CHCl_3$; cm^{-1}): 2063, 1990, 1922. ^{1}H-NMR ($CDCl_3$): δ 1.94 (m, 2H, CH_2), 3.65 (t, J = 8.0 Hz, 2H, Cr=CCH_2), 4.92 (t, J = 8.0 Hz, 2H, OCH_2). ^{13}C-NMR ($CDCl_3$): δ 20.9 (t), 60.7 (t), 85.5 (t), 216.3 (cis CO), 223.4 (trans CO), 342.2 (carbene). Anal. Calcd for $C_9H_6CrO_6$: C, 41.20; H, 2.29. Found: C, 41.42; H, 2.27.

Reaction of 1a with 4-Pentyn-1-ol. Tungsten complex **1a** (484 mg, 1 mmol) and 4-pentyn-1-ol (0.92 mL, 10 mmol) were reacted as described under the general method. After 1 h at 45 °C, the reaction was stopped and the crude reaction mixture purified. A single orange complex **4c** was identified, (257 mg, 63%).

4c. IR ($CHCl_3$; cm^{-1}): 2062, 1970, 1935. ^{1}H-NMR ($CDCl_3$): δ 1.62 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 3.31 (t, J = 6.8 Hz, 2H, W=CCH_2), 4.55 (t, J = 5.8 Hz, 2H, OCH_2). ^{13}C-NMR: δ 15.7 (t), 21.2 (t), 54.9 (t), 74.5 (t), 197.9 (cis CO), 204.9 (trans CO), 328.7 (carbene). Anal. Calcd for $C_{10}H_8O_6W$: C, 29.43; H, 1.98. Found: C, 29.67; H, 2.06.

Reaction of 1b with 4-Pentyn-1-ol. Chromium complex **1b** (350 mg, 1 mmol) and 4-pentyn-1-ol (0.92 mL, 10 mmol) were reacted as described under the general method for 1 h at 40 °C. After separation and purification by flash chromatography, a single orange complex **4d** was obtained (135 mg, 50%).

4d. IR ($CHCl_3$; cm^{-1}): 2052, 1982, 1940. ^{1}H-NMR ($CDCl_3$): δ 1.64 (m, 2H, CH_2), 1.88 (m, 2H, CH_2), 3.51 (t, J = 6.8 Hz, 2H, Cr=CCH_2), 4.63 (t, J = 6.0 Hz, 2H, OCH_2). ^{13}C-NMR ($CDCl_3$): δ 16.3 (t), 21.8 (t), 53.3 (t), 75.3 (t), 217.2 (cis CO), 224.4 (trans CO).

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[16] Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23–C26.

Reaction of 1a with 2-Butyn-1-ol. Tungsten complex **1a** (482 mg, 1 mmol) and 2-butyn-1-ol (0.37 mL, 5 mmol) were reacted as described under the general method. After 2.5 h at 25 °C, the reaction was stopped and the crude reaction mixture purified by flash chromatography. A single orange-yellow product was obtained and identified as **3d** (212 mg, 40%, *E/Z* = 10).

3d. IR ($CHCl_3$; cm^{-1}): 2250, 2061, 1978, 1934. ^1H-NMR ($CDCl_3$): $\delta(E)$ 0.90 (t, J = 7.2 Hz, 3H, CH_3), 1.92 (t, J = 2.0 Hz, 3H, $\equiv CCH_3$), 4.35 (q, J = 7.2 Hz, 2H, OCH_2), 4.68 (q, J = 2.0 Hz, 2H, OCH_2), 7.15–7.50 (m, 6H, Ph, =CH); $\delta(Z)$ 1.69 (t, J = 7.2 Hz, 3H, CH_3), 1.86 (t, J = 2.0 Hz, 3H, $\equiv CCH_3$), 4.40 (q, J = 2.0 Hz, 2H, OCH_2), 4.88 (q, J = 7.2 Hz, 2H, OCH_2), 7.10–7.65 (m, 6H, Ph, =CH). ^{13}C-NMR ($CDCl_3$): δ 3.6 (q), 13.8 (q), 58.1 (t), 72.0 (s), 78.1 (t), 85.9 (s), 124.6 (d), 127.9 (d), 128.6 (d), 129.6 (d), 136.5 (s), 160.6 (s), 198.0 (cis CO), 203.9 (trans CO). Anal. Calcd for $C_{20}H_{16}O_7W$: C, 43.49; H, 2.89. Found: C, 43.58; H, 2.93.

Reaction of 1b with 2-Butyn-1-ol. Chromium complex **1b** (350 mg, 1 mmol) and 2-butyn-1-ol (0.37 mL, 5 mmol) were reacted as described for 2.5 h at 25 °C; subsequent separation protocol rendered a product which was identified as **3e** (190 mg, 62%, *E/Z* = 8.5).

3e. IR ($CHCl_3$; cm^{-1}): 2054, 1965, 1934. ^1H-NMR ($CDCl_3$): $\delta(E)$ 0.94 (t, J = 7.0 Hz, 3H, CH_3), 1.91 (t, J = 2.2 Hz, 3H, $\equiv CCH_3$), 4.58 (q, J = 7.0 Hz, 2H, OCH_2), 4.71 (q, J = 2.2 Hz, 2H, OCH_2), 7.20–7.60 (m, 6H, Ph, =CH); $\delta(Z)$ 1.50 (t, J = 7.0 Hz, 3H, CH_3), 1.79 (t, J = 2.2 Hz, 3H, $\equiv CCH_3$), 4.43 (q, J = 2.2 Hz, 2H, OCH_2), 5.05 (q, J = 7.0 Hz, 2H, OCH_2), 7.05 (s, 1H, =CH), 7.20–7.90 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$): δ 3.7 (q), 13.8 (q), 58.2 (t), 72.0 (s), 75.6 (t), 85.8 (s), 121.5 (d), 128.0 (d), 128.8 (d), 129.6 (d), 136.4 (s), 157.4 (s), 217.2 (cis CO), 224.1 (trans CO), 325.9 (carbene). Anal. Calcd for $C_{20}H_{16}CrO_7$: C, 57.14; H, 3.81. Found: C, 56.99; H, 3.80.

Reaction of 1a with 3-Pentyn-1-ol. Tungsten complex **1a** (482 mg, 1 mmol) and 3-pentyn-1-ol (0.46 mL, 5 mmol) were reacted as described under the general method. After 2 h at 25 °C, the reaction was stopped and the crude reaction mixture purified by flash chromatography. The product was identified as **8a** (424 mg, 75%).

8a. IR ($CHCl_3$; cm^{-1}): 2070, 1985, 1940, 1210. ^1H-NMR ($CDCl_3$): δ 1.62 (t, J = 7.2 Hz, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.90 (m, 2H, CH_2), 3.39 (dd, J = 3.6, 4.2 Hz, 1H, CH), 4.14 (m, 2H, OCH_2), 4.79 (q, J = 7.2 Hz, 2H, OCH_2), 7.32 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$): δ 14.9 (q), 21.1 (q), 27.1 (t), 50.1 (d), 68.0 (t), 78.2 (t), 89.0 (s), 128.0 (d), 128.6 (d), 128.7 (s), 129.0 (d), 131.9 (s), 136.2 (s), 197.0 (cis CO), 203.6 (trans CO), 318.3 (carbene).

Reaction of 1b with 3-Pentyn-1-ol. Chromium complex **1b** (350 mg, 1 mmol) and 3-pentyn-1-ol (0.46 mL, 5 mmol) were reacted as described under the general method. After 4 h at 10 °C, the reaction was stopped and the crude reaction mixture purified by flash chromatography. One single product was obtained and identified as the very unstable complex **3f** (80 mg, 18.5%, *E/Z* = 5.6).

3f. IR ($CHCl_3$; cm^{-1}): 2054, 1970, 1938. ^1H-NMR ($CDCl_3$): $\delta(E)$ 0.83 (t, J = 7.2 Hz, 3H, CH_3), 1.81 (t, J = 2.6 Hz, 3H, $\equiv CCH_3$), 2.64 (qt, J_t = 6.8, J_q = 2.6 Hz, 2H, $CH_2C\equiv$), 4.11 (t, J = 6.8 Hz, 2H, OCH_2), 4.55 (q, J = 7.2 Hz, 2H, OCH_2), 6.95 (s, 1H, =CH), 7.20–7.50 (m, 5H, Ph); $\delta(Z)$ 1.66 (t, J = 7.2 Hz, 3H, CH_3), 1.76 (t, J = 2.6 Hz, 3H, $\equiv CCH_3$), 2.50 (m, 2H, $CH_2C\equiv$), 3.88 (t, J = 6.8 Hz, 2H, OCH_2), 5.02 (q, J = 7.2 Hz, 2H, OCH_2), 7.20–7.60 (m, 5H, Ph).

Reaction of 1c with 3-Pentyn-1-ol. Tungsten complex **1c** (448 mg, 1 mmol) and 3-pentyn-1-ol (0.46 mL, 5 mmol) were reacted as described under the general method. After 1 h at 25 °C, the reaction was stopped and the crude reaction mixture purified by flash chromatography. A single product was obtained and identified as **8b** (404 mg, 76%).

8b. IR ($CHCl_3$; cm^{-1}): 2060, 1975, 1932. ^1H-NMR ($CDCl_3$): δ 0.97 (t, J = 7.0 Hz, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.6 (t, J = 7.1 Hz, 3H, CH_3), 1.8 (m, 4H), 2.7 (m, 3H), 3.9 (m, 2H), 4.81 (q, J = 7.1 Hz, 2H, OCH_2). ^{13}C-NMR ($CDCl_3$): δ 14.2 (q), 15.1 (q), 20.5 (q), 21.1 (t), 26.7 (t), 31.4 (t), 32.2 (t), 51.4 (d), 67.3 (t), 78.6 (t), 86.7 (s), 153.6 (s), 161.6 (s), 197.6 (cis CO), 203.2 (trans CO), 306.4 (carbene). Anal. Calcd for $C_{18}H_{20}O_7W$: C, 40.62; H, 3.79. Found: C, 40.68; H, 3.79.

Reaction of 1d with 4-Hexyn-1-ol. Tungsten complex **1d** (482 mg, 1 mmol) and 4-hexyn-1-ol (0.54 mL, 5 mmol) were reacted for 72 h at 25 °C and the mixture purified. A single product was obtained and identified as **3g** (52 mg, 9%).

3g. IR ($CHCl_3$; cm^{-1}): 2063, 1988, 1935. ^1H-NMR ($CDCl_3$): δ 1.78 (t, J = 2.2 Hz, 3H, CH_3), 2.01 (m, 2H, CH_2), 2.30 (m, 2H, CH_2), 4.03 (s, 3H, OCH_3), 4.17 (t, 2H, OCH_2), 6.90 (s, 1H, =CH), 7.2–7.4 (m, 5H, Ph).

Reaction of 1a with 3-Hexyn-1-ol. Tungsten complex **1a** (482 mg, 1 mmol) and 3-hexyn-1-ol (0.46 mL, 5 mmol) were reacted as described under the general method. After 2 h at 25 °C, the reaction was stopped and the crude reaction mixture purified by flash chromatography. A single product was obtained and identified as **8c** (290 mg, 50%).

8c. IR ($CHCl_3$; cm^{-1}): 2067, 1986, 1945. ^1H-NMR ($CDCl_3$): δ 0.98 (t, J = 7.0 Hz, 3H, CH_3), 1.60 (t, J = 7.0 Hz, 3H, CH_3), 2.91 (m, 4H), 3.42 (m, 1H, CH), 4.15 (m, 2H), 4.77 (q, J = 7.0 Hz, OCH_2), 7.09–7.30 (m, 5H, Ph). ^{13}C-NMR ($CDCl_3$): δ 9.5 (q), 15.0 (q), 27.4 (t), 27.8 (t), 47.9 (d), 68.1 (t), 78.3 (t), 93.2 (s), 128.1 (d), 128.7 (d), 128.5 (s), 129.0 (d), 132.0 (s), 136.9 (s), 197.1 (cis CO), 203.6 (trans CO), 318.5 (carbene). Anal. Calcd for $C_{22}H_{20}O_7W$: C, 45.54; H, 3.47. Found: C, 45.71; H, 3.49.

Reaction of 3a with Trifluoroacetic Acid. To a flame-dried round-bottom flask containing **3a** (538 mg, 1 mmol) in 10 mL of CH_2Cl_2 was added 1 mL (13.7 mmol) of trifluoroacetic acid. The resulting mixture was stirred under argon at 25 °C for 2 h. Control by TLC (hexane/CH_2Cl_2, 85/15) showed disappearance of the starting carbene complex. The solvent was removed in the vacum line, and the resulting crude product was purified by flash chromatography on silica gel. Only a single product **5a** (133 mg, 25%) could be identified in the reaction mixture.

5a. IR ($CHCl_3$; cm^{-1}): 2063, 1978, 1936. ^1H-NMR ($CDCl_3$): δ 1.17 (t, J = 7.2 Hz, 3H, CH_3), 4.75 (q, J = 7.2, 2H, OCH_2), 5.76 (d, J = 10.2 Hz, 1H, =C*H*H), 5.99 (d, J = 16.4 Hz, 1H, =CH*H*), 6.48 (ddd, J = 16.4, 10.2, 11.2 Hz, 1H, CH=), 7.67 (d, J = 11.2 Hz, 1H, CH=), 7.42–7.77 (m, 5H, Ph).

Oxidation of 14a with DMSO. A mixture of 200 mg (0.36 mmol) of **9a** in 8 mL of diethyl ether and a few drops of DMSO were allowed to react during 10 min at room temperature. After this period, the solvent was removed by vacuum, and the resulting crude product was extracted with water/pentane. The organic layer was dried, filtered, and concentrated in vacuum. Purification of the resulting mixture by flash chromatography on silica gel afforded a single product **9** (87 mg, 95%) as a white solid.

9. IR ($CHCl_3$; cm^{-1}): 1698, 1630, 1187, 1018. ^1H-NMR ($CDCl_3$): δ 1.36 (t, J = 7.2 Hz, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.89 (m, 2H, CH_2), 3.30 (d, J = 7.8 Hz, 1H, CH), 3.85 (m, 1H, CH_2), 4.19 (m, 1H, CH_2), 4.22 (dq, J = 7.2, 10.8 Hz, 1H, CH_2), 4.36 (dq, J = 7.2, 10.8 Hz, 1H, CH_2), 7.42 (m, 3H, Ph), 8.11 (m, 2H, Ph). ^{13}C-NMR: δ 14.3 (q), 19.7 (q), 27.0 (t), 50.6 (d), 60.2 (t), 67.1 (t), 83.8 (s), 128.2 (d), 129.7 (d), 129.3 (s), 130.8 (d), 131.5 (s), 151.0 (s), 162.6 (CO). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.56; H, 7.05.

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Supplementary Material Available: Tables of X-ray experimental details, crystallographic data, positional parameters, bond distances, bond angles, torsion angles, root-mean-square amplitudes of anisotropic displacement, and general anisotropic displacement parameter expressions, ORTEP diagrams, and packing diagrams (22 pages). Ordering information is given on any current masthead page.

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