

Articles

Synthesis of (Allyloxy)(alkynyl)carbene Complexes and Their Reaction with Octacarbonyldicobalt: An Unprecedented Retro-Fischer Reaction¹

Jens Christoffers and Karl Heinz Dötz*

*Institut für Organische Chemie und Biochemie, Universität Bonn,
Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany*

Received February 28, 1994[©]

Pentacarbonyl[(allyloxy)((4-methylphenyl)ethynyl)carbene]chromium and tungsten complexes **1** and **2** have been prepared in moderate yields from the corresponding metal hexacarbonyl in a two-step, one-pot, Fischer type nucleophilic/electrophilic addition methodology using allyl triflate as alkylating reagent. As a consequence of its pronounced electrophilicity it also attacks the solvent THF, which results in the formation of the ((allyloxy)butyl)oxy)carbene complex **3** as a byproduct. Both the alkene–alkyne complexes **1** and **2** and their $\text{Co}_2(\text{CO})_6$ adducts fail to undergo intramolecular Pauson–Khand reactions; instead, at room temperature, a 1,2-elimination within the carbene ligand occurs, regenerating the metal hexacarbonyl with predominant formation of the 1,4-enynes **4** and **8–10**. This process corresponds to an unprecedented retroversion of the customary Fischer carbene complex synthesis.

Introduction

Fischer-type carbene complexes are known as valuable reagents for stereoselective carbon–carbon bond formation in organic synthesis. The C–C coupling may occur either at the low-valent metal template or within the carbene ligand.² For instance, the metal carbene functionality is able to activate α,β double or triple bonds toward cycloaddition reactions.³ In this respect, alkene–alkyne-functionalized aminocarbene complexes have been reported to facilitate intramolecular Pauson–Khand reactions.⁴ Since the cobalt-induced Pauson–Khand reaction offers a regioselective access to cyclopentenones, it has been used as an important route to biologically interesting compounds of this structural type.⁵ Aminocarbene complexes containing (allylamino)(alkynyl)carbene ligands undergo cyclization to the cyclopentenone skeleton under extraordinarily mild conditions. We were interested in whether alkene–alkyne-functionalized *alkoxycarbene* complexes are also able to promote the intramolecular Pauson–Khand reaction, and we now report on the synthesis of (allyloxy)-

(alkynyl)carbene pentacarbonyl complexes of chromium and tungsten and their hexacarbonyldicobalt adducts.

Results and Discussion

Synthesis of (Allyloxy)(alkynyl)carbene Complexes. (Allyloxy)carbene complexes are accessible from the base-induced alcoholysis of methoxycarbene complexes using an excess of allyl alcohol. Since the interaction of alcohols with methoxy(alkynyl)carbene complexes leads to addition to the triple bond and thus to the formation of (β -alkoxyvinyl)carbene ligands,⁶ this approach is unsuccessful in the generation of (allyloxy)-(alkynyl)carbene complexes. Another route to alkoxy-carbene complexes with higher alkyl substituents is provided by the alcoholysis of (acyloxy)carbene intermediates. Hegedus reported the synthesis of [(allyloxy)methylcarbene]pentacarbonylchromium(0) from allyl alcohol and the corresponding acetoxycarbene derivative.⁷ Our first attempts to synthesize (alkynyl)(allyloxy)carbene complexes **1** and **2** via allyl alcoholysis of (pivaloyloxy)- or (acetyloxy)carbene species gave only very poor yields of the chromium compound and completely failed for the tungsten analogue. Thus, we focused on the formation of the allyloxy functionality by attack of an electrophilic allyl synthon at the acyl-metalates.

Sequential addition of alkynyllithium and allyl triflate to hexacarbonylchromium and -tungsten affords the (allyloxy)carbene complexes **1** and **2** (Scheme 1). The

* Abstract published in *Advance ACS Abstracts*, August 1, 1994.

(1) Reactions of Complex Ligands. 60. Part 59: Dötz, K. H.; Böttcher, D.; Jendro, M. *Inorg. Chim. Acta*, in press.

(2) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. Hegedus, L. S. *Pure Appl. Chem.* **1990**, *62*, 691. Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, p 1065 ff.

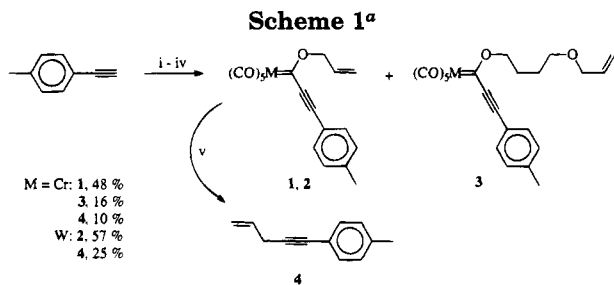
(3) Dötz, K. H.; Noack, R.; Harms, K. *Tetrahedron* **1990**, *46*, 1235. Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642. Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784.

(4) Camps, F.; Moreto, J. M.; Ricart, S.; Vinas, J. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1470. Dötz, K. H.; Christoffers, J. *J. Organomet. Chem.* **1992**, *426*, C58.

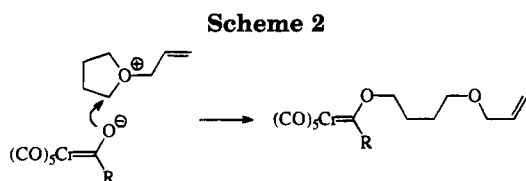
(5) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855. Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. Schore, N. E. *Org. React.* **1991**, *40*, 1.

(6) Camps, F.; Llebaria, A.; Moreto, J. M.; Ricart, S.; Ros, J.; Yanez, R. *J. Organomet. Chem.* **1991**, *401*, C17. Llebaria, A.; Moreto, J. M.; Ricart, S.; Ros, J.; Vinas, J.; Yanez, R. *J. Organomet. Chem.* **1992**, *440*, 79.

(7) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364.



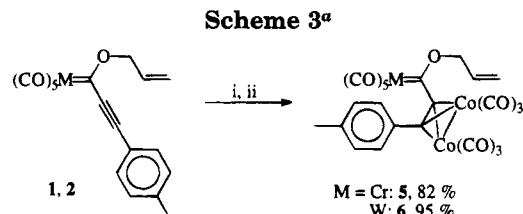
^a Reagents and conditions: (i) *n*-BuLi, THF, $-50\text{ }^{\circ}\text{C}$; (ii) $\text{M}(\text{CO})_6$, room temperature, 1 h; (iii) $\text{H}_2\text{C}=\text{CHCH}_2\text{OTf}$ (1.5 equiv), CCl_4 , $-10\text{ }^{\circ}\text{C}$, 15 min; (iv) SiO_2 , $-10\text{ }^{\circ}\text{C}$; (v) room temperature.



alkylation with allyl triflate occurs remarkably fast, even at temperatures below $0\text{ }^{\circ}\text{C}$. Above $0\text{ }^{\circ}\text{C}$ complexes **1** and **2** slowly decompose with formation of metal hexacarbonyl and enyne **4**, making the acquisition of proper analytical and spectroscopic data difficult. Compounds **1** and **2** can be purified by column chromatography; however, repeated chromatography at $-10\text{ }^{\circ}\text{C}$ after storage always resulted in another fraction of enyne **4**. We assume that the decomposition occurs via β -elimination from the (allyloxy)(alkynyl)carbene ligand—cleavage of the $\text{C}_{\text{carbene}}-\text{C}_{\text{alkynyl}}$ and $\text{O}-\text{C}_{\text{allyl}}$ bonds—resulting in a formal retro-Fischer carbene complex synthesis. Whereas the 1,2-addition across a metal-coordinated carbonyl group represents the most efficient synthetic access to Fischer-type alkoxy carbene complexes, to the best of our knowledge no reverse process has been reported up to now. Chromatography of the crude chromium complex **1** gave a third orange band containing complex **3**, which was identified as the formal insertion product of tetrahydrofuran (THF) into the allyloxy C—O bond of complex **1**. The formation of **3** documents the strong alkylating force of allyl triflate: interaction of allyl triflate with the solvent THF generates the cyclic *O*-allyl oxonium ion, which subsequently undergoes ring opening upon nucleophilic attack by the acyl chromate to form the ((allyloxy)butyl)oxy carbene side chain (Scheme 2).

Compounds **1–4** have been characterized both by spectroscopic means and by elemental analysis or by high-resolution mass spectroscopy (see Experimental Section). The IR spectra of pentacarbonyl carbene complexes **1–3** show typical $\nu(\text{CO})$ absorptions, and an additional stretching frequency is observed near 2150 cm^{-1} ($\nu(\text{C}\equiv\text{C})$). The structure of product **3** is deduced from ^1H and ^{13}C NMR data. IR and NMR spectra of enyne **4** are identical with those reported in the literature.⁸

Reaction of **1 and **2** with Octacarbonyldicobalt(0).** The reaction of methoxy- and ethoxy(alkynyl)carbene complexes with octacarbonyldicobalt(0) results in complexation of the C—C triple bond to give hetero-



^a Reagent and conditions: (i) $\text{Co}_2(\text{CO})_8$ (1.2 equiv), petroleum ether, room temperature, 30 min; (ii) SiO_2 , $0\text{ }^{\circ}\text{C}$.

trinuclear complexes.⁹ The alkoxy complexes **1** and **2** react readily at room temperature with a small excess of octacarbonyldicobalt(0) with evolution of carbon monoxide (Scheme 3). The trinuclear compounds **5** and **6** are obtained in nearly quantitative yields as crystalline solids; they are stable at room temperature but decompose unspecifically when warmed above $40\text{ }^{\circ}\text{C}$.

The molecular formulas have been established by elemental analysis. Electron impact (EI) mass spectra only show decomposition products; however, an M^+ signal is observed in the field desorption (FD) or fast atom bombardment (FAB) mass spectra. The $\nu(\text{CO})$ regions of the IR spectra show a superposition of five bands typical of the $\text{Co}_2(\text{CO})_6$ fragment^{10,11} and three bands characteristic of the $(\text{CO})_5\text{M}$ fragment. At room temperature, the signals in the ^1H NMR spectra of **5** and **6** are slightly broadened, but all relevant 3J coupling constants can be deduced. In the ^{13}C NMR spectra the signals for the carbonyl ligands attached to the cobalt are broadened, while all other resonances are sharp. The spectroscopic and analytical data are compiled in the Experimental Section.

Thermal Decomposition of Hexacarbonyldicobalt Complexes **5 and **6**.** Warming of the hetero-trinuclear complexes **5** and **6** above $40\text{ }^{\circ}\text{C}$ results in rapid unspecific decomposition. In order to perform an intramolecular Pauson–Khand reaction, a solution of the complexes **5** and **6** was stirred at room temperature until no more educts could be detected by thin-layer chromatography (TLC). Chromatographic workup of the reaction mixture yielded—apart from hexacarbonylmethylmetal(0) and dodecacarbonyltetracobalt(0)—the four (alkyne)carbonylcobalt complexes **7–10** (Scheme 4). Neither products bearing a $(\text{CO})_5\text{M}$ fragment nor products with a cyclopentenone skeleton could be isolated. Based on cobalt, the total yield of the complexes **7–10** is 68% (chromium) and 91% (tungsten), respectively.

Due to their typical $\nu(\text{CO})$ absorptions in the IR spectra, the brown compounds **7**, **8**, and **10** have been identified as (alkyne)hexacarbonyldicobalt(0) complexes. Complex **7** was described earlier by Wotiz.¹² Compound **9**, a blue oil which slowly decomposes at room temperature, shows the typical $\nu(\text{CO})$ pattern of (alkyne)decacarbonyltetracobalt(0) complexes:^{11,13} five bands arising from terminal CO ligands and one absorption at 1877 cm^{-1} due to a bridging CO group. Except for complex **7**, the isolated products have kept both the aryl

(9) Wienand, A.; Reissig, H.-U.; Fischer, H.; Pflumm, D.; Troll, C. *J. Organomet. Chem.* **1992**, *427*, C9. Moldes, I.; Ros, J.; Torres, M. R.; Perales, A.; Mathieu, R. *J. Organomet. Chem.* **1994**, *464*, 219.

(10) Greenfield, H.; Sternberg, H. W.; Friedel, R. A.; Wotiz, J. H.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 120.

(11) Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

(12) Tirpak, M. R.; Hollingsworth, C. A.; Wotiz, J. H. *J. Org. Chem.* **1969**, *25*, 687.

(13) Krüerke, U.; Hübel, W. E. *Chem. Ber.* **1961**, *94*, 2829.

ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 21.89 (1C; CH_3), 79.65 (1C; OCH_2), 92.51 (1C; $\alpha\text{-C}\equiv$), 119.01 (1C; *ipso* C), 119.74 (1C; $=\text{CH}_2$), 126.27 (1C; $\beta\text{-C}\equiv$), 129.78 (2C; *ortho* CH), 131.23 (1C; $=\text{CH}$), 132.85 (2C; *meta* CH), 142.99 (1C; *para* C), 216.31 (4C; *cis* CO), 225.70 (1C; *trans* CO), 313.00 (1C; $\text{Cr}=\text{C}$) ppm.

[(Allyloxy)((4-methylphenyl)ethynyl)carbene]pentacarbonyltungsten(0) (2). HR-MS (EI): calcd for $\text{C}_{18}\text{H}_{12}\text{O}_6^{182}\text{W}$, 506.0116; found, 506.0114 (29%, M^+). FT-IR (petroleum ether): ν 2149 [w, $\nu(\text{C}\equiv\text{C})$], 2069 [m, $\nu(\text{C}=\text{O})$, A_1^{11}], 1959 [vs, $\nu(\text{C}=\text{O})$, E], 1946 [s, $\nu(\text{C}=\text{O})$, A_1^{12}] cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 2.39 (s, 3H; CH_3), 5.12 (d, broad, $^3J = 5.65$ Hz, 2H; OCH_2), 5.40 (ddt, $^3J = 10.48$ Hz, $^2J = 1.39$ Hz, $^4J = 1.12$ Hz, 1H; (*E*)-*CHH*), 5.49 (dtd, $^3J = 17.18$ Hz, $^4J = 1.49$ Hz, $^2J = 1.39$ Hz, 1H; (*Z*)-*CHH*), 6.11 (ddt, $^3J = 17.18$ Hz, $^2J = 10.57$ Hz, $^3J = 5.55$ Hz, 1H; $=\text{CH}$), 7.24 (m, 2H; Ar H), 7.52 (m, 2H; ArH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 22.01 (1C; CH_3), 79.80 (1C; OCH_2), 97.67 (1C; $\alpha\text{-C}\equiv$), 118.02 (1C; *ipso* C), 119.95 (1C; $=\text{CH}_2$), 126.48 (1C; $\beta\text{-C}\equiv$), 129.98 (2C; *ortho* CH), 131.07 (1C; $=\text{CH}$), 133.15 (2C; *meta* CH), 143.14 (1C; *para* C), 197.60 [s, d, $J(^{183}\text{W}, ^{13}\text{C}) = 129.11$ Hz, 4C; *cis* CO], 205.88 (1C; *trans* CO), 285.18 (1C; $\text{W}=\text{C}$) ppm.

[(4-Allyloxy)butyloxy)((4-methylphenyl)ethynyl)carbene]pentacarbonylchromium(0) (3). Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{CrO}_7$: C, 58.93; H, 4.50. Found: C, 58.45; H, 4.78. HR-MS (EI): calcd for $\text{C}_{22}\text{H}_{20}\text{CrO}_7$, 448.0614; found, 448.0623 (24%, M^+). FT-IR (petroleum ether): ν 2151 [vw, $\nu(\text{C}\equiv\text{C})$], 2060 [m, $\nu(\text{C}=\text{O})$, A_1^{11}], 1994 [vww, $\nu(\text{C}=\text{O})$, B_1], 1963 [vs, $\nu(\text{C}=\text{O})$, E], 1951 [sh, $\nu(\text{C}=\text{O})$, A_1^{12}] cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 1.78–1.84 (m, 2H; 2- CH_2), 1.98–2.05 (m, 2H; 3- CH_2), 2.39 (s, 3H; CH_3), 3.52 (t, $J = 6.16$ Hz, 2H; 4- CH_2), 3.96 (ddd, $^3J = 5.67$ Hz, $^4J_{\text{cis}} = 1.57$ Hz, $^4J_{\text{trans}} = 1.37$ Hz, 2H; OCH_2), 4.70 (t, $J = 6.36$ Hz, 2H; 1- CH_2), 5.15 (ddt, $^3J_{\text{cis}} = 10.37$ Hz, $^2J = 1.76$ Hz, $^4J_{\text{trans}} = 1.37$ Hz, 1H; (*E*)-*CHH*), 5.25 (ddt, $^3J_{\text{trans}} = 17.21$ Hz, $^2J = 1.76$ Hz, $^4J = 1.57$ Hz, 1H; (*Z*)-*CHH*), 5.89 (ddt, $^3J_{\text{trans}} = 17.22$ Hz, $^3J_{\text{cis}} = 10.37$ Hz, $^3J = 5.68$ Hz, 1H; $=\text{CH}$), 7.22–7.24 (m, 2H; Ar H), 7.44–7.46 (m, 2H; Ar H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 21.79 (1C; CH_3), 26.02, 26.41 (2C; 2- and 3- CH_2), 69.42 (1C; 4- CH_2), 71.69 (1C; O- CH_2), 79.73 (1C; 1- CH_2), 92.29 (1C; $\alpha\text{-C}\equiv$), 116.72 (1C; $=\text{CH}_2$), 117.81 (1C; *ipso* C), 126.19 (1C; $\beta\text{-C}\equiv$), 129.67 (2C; *ortho* CH), 132.81 (2C; *meta* CH), 134.77 (1C; $=\text{CH}$), 142.84 (1C; *para* C), 216.33 (4C; *cis* CO), 225.58 (1C; *trans* CO), 312.93 (1C; $\text{Cr}=\text{C}$) ppm.

5-(4-Methylphenyl)pent-1-en-4-yne (4).⁸ HR-MS (EI): calcd for $\text{C}_{12}\text{H}_{12}$, 156.0939; found, 156.0933 (100%, M^+). FT-IR (film): ν 3084 (m), 3030 (m), 2921 (m), 2886 (m), 1643 (m), 1511 (s), 990 (m), 917 (m), 818 (s) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 2.33 (s, 3H; CH_3), 3.18 (ddd, $^3J = 5.23$ Hz, $^4J = 1.82$ Hz, $^4J = 1.81$ Hz, 2H; CH_2), 5.13 (ddt, $^3J = 10.00$ Hz, $^2J = 1.71$ Hz, $^4J = 1.71$ Hz, 1H; (*E*)-*CHH*), 5.39 (dtd, $^3J = 16.97$ Hz, $^4J = 1.87$ Hz, $^2J = 1.60$ Hz, 1H; (*Z*)-*CHH*), 5.89 (ddt, $^3J = 16.96$ Hz, $^3J = 10.03$ Hz, $^3J = 5.23$ Hz, 1H; $=\text{CH}$), 7.09 (m, 2H; Ar H), 7.31 (m, 2H; Ar H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 21.32 (1C; CH_3), 23.67 (1C; 3- CH_2), 82.90 (1C; 5-C), 85.66 (1C; 4-C), 116.08 (1C; 1- CH_2), 120.57 (1C; *ipso* C), 128.90 (2C; *ortho* CH), 131.39 (2C; *meta* CH), 132.52 (1C; 2- CH), 137.65 (1C; *para* C) ppm.

$[\mu\text{-}(2,3\text{-}\eta):(2,3\text{-}\eta)\text{-}[1\text{-}(\text{Allyloxy})\text{-}3\text{-}(4\text{-methylphenyl})\text{prop-}2\text{-yn-1-ylidene}]pentacarbonylchromium(0)]bis[\text{tricarboxylcobalt}(0)](\text{Co-Co})$ (5). A solution of 1.82 g (4.84 mmol) of 1 and 1.74 g (5.12 mmol) of octacarbonyldicobalt(0) in 50 mL of petroleum ether was stirred at room temperature for 40 min. After removal of the solvent under reduced pressure, chromatography on silica gel (0 °C, petroleum ether/dichloromethane (5:1)) gave 2.62 g (3.96 mmol, 82%) of the title compound 5 as black crystals. Anal. Calcd for $\text{C}_{24}\text{H}_{12}\text{-Co}_2\text{CrO}_{12}$: C, 43.53; H, 1.83. Found: 43.51; H, 2.02. MS (FD): m/z 661.9 (100%, M^+). FT-IR (petroleum ether): ν 2098 (m; Co), 2064 (vs; Co), 2056 (s; Cr, A_1^{11}), 2043 (s; Co), 2033 (s; Co), 2023 (m; Co), 1962 (s; Cr, E^1), 1954 (s; Cr, E^2), 1938 (m; Cr, A_1^{12}) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 2.36 (s, 3H; CH_3), 5.48 (d, broad, $^3J = 10.4$ Hz, 1H; (*E*)-*CHH*), 5.55 (d, broad, $^3J = 5.7$ Hz, 2H; O- CH_2), 5.56 (d, broad, $^3J = 16.6$ Hz, 1H; (*Z*-

CHH), 6.20 (ddt, $^3J = 16.6$ Hz, $^3J = 10.3$ Hz, $^3J = 6.0$ Hz, 1H; $=\text{CH}$), 7.18–7.20 (m, 2H; Ar H), 7.34–7.36 (m, 2H; Ar H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 21.31 (1C; CH_3), 81.54 (1C; OCH_2), 96.92, 101.37 (2C; α - and β -C), 121.29 (1C; $=\text{CH}_2$), 129.29 (2C; *meta* CH), 129.66 (2C; *ortho* CH), 130.71 (1C; $=\text{CH}$), 134.91 (1C; *ipso* C), 138.43 (1C; *para* C), 198.36 (s, broad, 6C; Co-CO), 216.05 (4C; *cis* Cr-CO), 222.84 (1C; *trans* Cr-CO), 332.49 (1C; $\text{Cr}=\text{C}$) ppm.

$[\mu\text{-}(2,3\text{-}\eta):(2,3\text{-}\eta)\text{-}[1\text{-}(\text{Allyloxy})\text{-}3\text{-}(4\text{-methylphenyl})\text{prop-}2\text{-yn-1-ylidene}]pentacarbonyltungsten(0)]bis[\text{tricarboxylcobalt}(0)](\text{Co-Co})$ (6). A solution of 230 mg (0.453 mmol) of 2 and 260 mg (0.760 mmol) of octacarbonyldicobalt(0) in 15 mL of petroleum ether was stirred for 30 min at room temperature. After removal of the solvent under reduced pressure and chromatography on silica gel (3 °C, petroleum ether/dichloromethane (10:1)), 340 mg (0.428 mmol, 95%) of the title compound 6 was obtained as black crystals. Anal. Calcd for $\text{C}_{24}\text{H}_{12}\text{Co}_2\text{O}_{12}\text{W}$: C, 36.30; H, 1.52. Found: C, 36.55; H, 1.64. MS (FD): m/z 793.9 (100%, M^+). FT-IR (petroleum ether): ν 2098 (m; Co), 2067 (s; W, A_1^{11}), 2062 (vs; Co), 2044 (s; Co), 2035 (s; Co), 2023 (m; Co), 1956 (vs; W, E), 1935 (m; W, A_1^{12}) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 2.34 (s, 3H; CH_3), 5.38 (ddd, $^3J = 6.07$ Hz, $^4J = 1.37$ Hz, $^4J = 1.17$ Hz, 2H; OCH_2), 5.47 (dtd, $^3J = 10.37$ Hz, $^4J = 1.37$ Hz, $^2J = 0.98$ Hz, 1H; (*E*)-*CHH*), 5.54 (dtd, $^3J = 17.15$ Hz, $^4J = 1.17$ Hz, $^2J = 0.98$ Hz, 1H; (*Z*)-*CHH*), 6.19 (ddt, $^3J = 17.22$ Hz, $^3J = 10.37$ Hz, $^3J = 6.06$ Hz, 1H; $=\text{CH}$), 7.17–7.19 (m, 2H; Ar H), 7.34–7.36 (m, 2H; Ar H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 21.42 (1C; CH_3), 83.76 (1C; OCH_2), 100.90, 102.11 (2C; α - and β -C), 121.23 (1C; $=\text{CH}_2$), 129.33 (2C; *meta* CH), 129.77 (2C; *ortho* CH), 130.58 (1C; $=\text{CH}$), 134.80 (1C; *ipso* C), 138.62 (1C; *para* C), 197.14 [s, d, $J(^{183}\text{W}, ^{13}\text{C}) = 127.2$ Hz, 4C; *cis* W-CO], 198.24 (s, broad, 6C; Co-CO), 202.09 (1C; *trans* W-CO), 306.93 (1C; $\text{W}=\text{C}$) ppm.

Reaction of the Carbene Metal Alkyne Dicobalt Complexes 5 and 6. An 820-mg (1.24-mmol) amount of 5 or 800 mg (1.01 mmol) of 6 was dissolved in 50 mL of toluene and stirred 2 days (chromium) or 3 days (tungsten) at room temperature, respectively, until educt 5 or 6 has been completely consumed as detected by TLC. The solvent was removed under reduced pressure, and the residues were purified by chromatography on silica gel at 0 °C. The polarity of the solvent was increased step by step from petroleum ether over petroleum ether/dichloromethane (10:1) to petroleum ether/dichloromethane (1:1). With the tungsten complex 6 as starting material, six bands were eluted and the compounds were isolated according to the following sequence: 200 mg (0.57 mmol) of hexacarbonyltungsten(0), 20 mg (0.05 mmol, 5%) of alkyne complex 7 as black-brown crystals, 160 mg (0.36 mmol, 36%) of alkyne complex 8 as a red-brown oil, 10 mg (0.02 mmol) of dodecacarbonyltetracobalt(0), 150 mg (0.22 mmol, 22%) of alkyne complex 9 as a dark blue oil (slow decomposition at room temperature), and 130 mg (0.28 mmol, 28%) of enynone complex 10 as a red-brown oil. The chromium complex 5 led to the following product distribution: 30 mg (0.07 mmol, 6%) of 7, 60 mg (0.14 mmol, 11%) of 8, 110 mg (0.16 mmol, 13%) of 9, 220 mg (0.47 mmol, 38%) of 10.

$[\mu\text{-}(1,2\text{-}\eta):(1,2\text{-}\eta)\text{-}(4\text{-Methylphenyl)ethyne}]bis[\text{tricarboxylcobalt}(0)](\text{Co-Co})$ (7).¹³ Anal. Calcd for $\text{C}_{15}\text{H}_8\text{-Co}_2\text{O}_6$: C, 44.81; H, 2.01. Found: C, 44.72; 2.15. HR-MS (EI): calcd for $\text{C}_{15}\text{H}_8\text{Co}_2\text{O}_6$, 401.8985; found, 401.8987 (1%, M^+). FT-IR (petroleum ether): $\nu(\text{C}=\text{O})$ 2094 (s), 2057 (vs), 2031 (vs), 2027 (vs), 2015 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 2.34 (s, 3H; CH_3), 6.34 (s, 1H; CH), 7.12–7.15 (m, 2H; Ar H), 7.40–7.42 (m, 2H; Ar H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ 21.27 (qt, $^1J = 127.15$ Hz, $^3J = 3.81$ Hz, 1C; CH_3), 72.46 (d, $^1J = 219.98$ Hz, 1C; 2-CH); 90.47 (m, 1C; 1-C), 129.57 (dd, $^1J = 158.95$ Hz, 2C; *meta* CH), 130.22 ($^1J = 158.94$ Hz, $^2J = 6.36$ Hz, 2C; *ortho* CH), 134.22 (t, $^2J = 8.27$ Hz, 1C; *ipso* C), 138.31 (sex, $^2J = 6.36$ Hz, 1C; *para* C), 199.46 (s, broad, 6C; CO) ppm.

$[\mu\text{-}(4,5\text{-}\eta):(4,5\text{-}\eta)\text{-}5\text{-}(4\text{-Methylphenyl})\text{pent-1-en-4-yne}]$

bis[tricarbonylcobalt(0)](Co-Co) (8). Anal. Calcd for $C_{18}H_{12}Co_2O_6$: C, 48.90; H, 2.74. Found: C, 48.44; H, 2.80. HR-MS (EI): calcd for $C_{17}H_{12}Co_2O_5$ ($M^+ - CO$), 413.9348; found, 413.9349 (1%, $M^+ - CO$). FT-IR (petroleum ether): $\nu(C=O)$ 2090 (m), 2053 (vs), 2028 (s), 2022 (s), 2009 (w) cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz): δ 2.34 (s, 3H; CH_3), 3.78 (ddd, $^3J = 7.04$ Hz, $^4J = 1.36$ Hz, $^4J = 0.98$ Hz, 2H; 3- CH_2), 5.17 (ddt, $^3J = 9.88$ Hz, $^2J = 1.56$ Hz, $^4J = 0.98$ Hz, 1H; (*E*)-1-*CHH*), 5.27 (ddt, $^3J = 16.87$ Hz, $^2J = 1.57$ Hz, $^4J = 1.37$ Hz, 1H; (*Z*)-1-*CHH*), 6.04 (ddt, $^3J = 16.95$ Hz, $^3J = 9.85$ Hz, $^3J = 7.04$ Hz, 1H; 2-CH), 7.15 (m, 2H; Ar H), 7.41 (m, 2H; Ar H) ppm. ^{13}C - $\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 21.34 (1C; CH_3), 38.55 (1C; 3- CH_2), 90.98 (1C; 4-C), 97.44 (1C; 5-C), 117.48 (1C; 1- CH_2), 129.25 (2C; *meta* CH), 129.60 (2C; *ortho* CH), 134.90 (1C; *ipso* C), 135.75 (1C; 2-CH), 137.96 (1C; *para* C), 199.65 (s, broad, 6C; Co-CO) ppm.

Decacarbonyl[μ -(4,5- η):(4,5- η)-5-(4-methylphenyl)pent-1-en-4-yne]tetracobalt(0) (9). HR-MS (EI): calcd for $C_{22}H_{12}Co_4O_{10}$, 671.7758; found, 671.7776 (3%, M^+). FT-IR (PE): $\nu(C=O)$ 2089 (m), 2052 (vs), 2039 (s), 2030 (s), 1988 (w), 1877 (m) cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz): δ 2.28 (s, 3H; CH_3), 3.46 (d, br, $^3J = 7.23$ Hz, 2H; 3- CH_2), 4.85 (dd, $^3J = 16.82$ Hz, $^2J = 1.37$ Hz, 1H; (*Z*)-1-*CHH*), 5.05 (dd, $^3J = 9.78$ Hz, $^2J = 0.98$ Hz, 1H; (*E*)-1-*CHH*), 5.37 (ddt, $^3J = 16.82$ Hz, $^3J = 9.78$ Hz, $^3J = 7.24$ Hz, 1H; 2-CH), 6.99 (s, 4H; Ar H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 20.98 (1C; CH_3), 52.76 (1C; 3- CH_2), 117.02 (1C; 1- CH_2), 127.35 (2C; *meta* CH), 128.60 (2C; *ortho* CH), 138.46 (1C; *ipso* C), 139.63 (1C; 2-CH), 147.52 (1C; *para* C), 203.34 (s, broad, 10C; CO) ppm (4-C and 5-C not observed).

[μ -(1,2- η):(1,2- η)-1-(4-Methylphenyl)hex-5-en-1-yn-3-one]-

bis[tricarbonylcobalt(0)](Co-Co) (10). Anal. Calcd for $C_{19}H_{12}Co_2O_7$: C, 48.54; H, 2.57. Found: C, 48.70; H, 2.75. HR-MS (EI): calcd for $C_{19}H_{12}Co_2O_7$, 469.9247; found, 469.9234 (0.3%, M^+). FT-IR (petroleum ether): $\nu(C=O)$ 2099 (m), 2064 (vs), 2039 (sh), 2035 (s), 2024 (sh), 1679 (w) cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz): δ 2.34 (s, 3H; CH_3), 3.57 (dt, $^3J = 6.65$ Hz, $^4J = 1.37$ Hz, 2H; 4- CH_2), 5.18 (dq, $^3J = 17.02$ Hz, $^2J = 1.37$ Hz, $^4J = 1.37$ Hz, 1H; (*Z*)-6-*CHH*), 5.23 (dq, $^3J = 10.18$ Hz, $^2J = 1.37$ Hz, $^4J = 1.37$ Hz, 1H; (*E*)-6-*CHH*), 6.06 (ddt, $^3J = 17.02$ Hz, $^3J = 10.17$ Hz, $^3J = 6.85$ Hz, 1H; 5-CH), 7.14–7.17 (m, 2H; Ar H), 7.43–7.46 (m, 2H; Ar H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.42 (qt, $^1J = 126.7$ Hz, $^3J = 4.5$ Hz, 1C; CH_3), 48.13 (tm, $^1J = 127.8$ Hz, 1C; 4- CH_2), 86.47 (s, 1C; 2-C), 93.06 (m, 1C; 1-C), 118.96 (tm, $^1J = 157.0$ Hz, 1C; 6- CH_2), 129.54 (dd, $^1J = 158.9$ Hz, $^2J = 6.4$ Hz, 2C; *ortho* CH), 129.81 (dm, $^1J = 157.7$ Hz, 2C; *meta* CH), 130.56 (dtd, $^1J = 158.9$ Hz, $^2J = 6.4$ Hz, $^3J = 2.5$ Hz, 1C; 5-CH), 133.46 (t, $^2J = 8.3$ Hz, 1C; *ipso* C), 139.04 (sex, $^2J = 6.8$ Hz, 1C; *para* C), 198.18 (s, broad, 6C; Co-CO), 201.69 (td, $^2J = 6.4$ Hz, $^3J = 2.5$ Hz, 1C; 3-CO) ppm.

Acknowledgment. Support from the Deutsche Forschungsgemeinschaft (Grant No. SFB 260), the Graduiertenkollegs "Metallorganische Chemie" and "Spektroskopie isolierter und kondensierter Moleküle", and the Fonds der Chemischen Industrie is gratefully acknowledged.

OM9401519