Articles

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

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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 Co₂(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 alkenealkyne-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 $(\beta$ -alkoxyvinyl)carbene ligands, ⁶ this approach is unsuccessful in the generation of (allyloxy)-(alkynyl)carbene complexes. Another route to alkoxycarbene 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. 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 acylmetalates.

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

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Scheme 1a

^a Reagents and conditions: (i) n-BuLi, THF, −50 °C; (ii) M(CO)₆, room temperature, 1 h; (iii) H₂C=CHCH₂OTf (1.5 equiv), CCl₄, -10 °C, 15 min; (iv) SiO₂, -10 °C; (v) room temperature.

Scheme 2

$$(CO)_5C_1 \longrightarrow (CO)_5C_1 \longrightarrow (CO)$$

alkylation with allyl triflate occurs remarkably fast, even at temperatures below 0 °C. Above 0 °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 °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 $C_{carbene}$ – $C_{alkynyl}$ and O– C_{allyl} bonds– resulting in a formal retro-Fischer carbene complex synthesis. Whereas the 1,2-addition across a metalcoordinated carbonyl group represents the most efficient synthetic access to Fischer-type alkoxycarbene 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 $\nu(CO)$ absorptions, and an additional stretching frequency is observed near 2150 cm $^{-1}$ (ν (C=C)). The structure of product 3 is deduced from ¹H and ¹³C 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-

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Scheme 3^a

^a Reagent and conditions: (i) Co₂(CO)₈ (1.2 equiv), petroleum ether, room temperature, 30 min; (ii) SiO₂, 0 °C.

trinuclear complexes.9 The alloxy 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 °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 $\nu(CO)$ regions of the IR spectra show a superposition of five bands typical of the Co₂(CO)₆ fragment^{10,11} and three bands characteristic of the (CO)₅M 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 ¹³C 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 heterotrinuclear complexes 5 and 6 above 40 °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 hexacarbonylmetal(0) and dodecacarbonyltetracobalt(0)—the four (alkyne)carbonylcobalt complexes 7-10 (Scheme 4). Neither products bearing a (CO)₅M fragment nor products with a cyclopentenone skeleton could be isolated. Based on cobalt, the total yield of the complexes 7-10is 68% (chromium) and 91% (tungsten), respectively.

Due to their typical $\nu(CO)$ 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 $\nu(CO)$ 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

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 a Conditions: (i) petroleum ether, room temperature, 3 days; (ii) SiO2, 0 °C.

and the allyl functionalities. The substitution of the (allyloxy)carbene metal unit for hydrogen in 7 is established by a singlet in the ¹H NMR spectrum which corresponds to one hydrogen atom resonating at very low field at 6.34 ppm. The coupling constant ${}^{1}J(sp-C.H)$ of 220 Hz is observed in the gated decoupled ¹³C NMR spectrum. As observed for the Co₂(CO)₆ complexes 5, 6, and 8-10, the ¹³C NMR signals attributed to the carbonyl ligands are broadened at room temperature, while all other absorptions are sharp. The structure elucidation of complexes 8-10, whose ¹H and ¹³C{¹H} NMR spectra—except for the CO resonances—are nearly identical with those observed for 4, is mainly based on their IR and mass spectra. The molecular structure of the enynone ligand in 10 is deduced from a gated decoupled ¹³C NMR experiment: the signal for the carbonyl group at 202 ppm appears as a triplet of doublets with ${}^{2}J(C,H) = 6.4 \text{ Hz}$ and ${}^{3}J(C,H) = 2.5 \text{ Hz}$, indicative of its direct connection to both the coordinated triple bond and the allyl group.

Similar to the formation of 4 from 1 to 2, the enyne complex 8 can be regarded as the result of a formal reto-Fischer reaction of 5 or 6 occurring in the presence of the $Co_2(CO)_6$ fragment. The assembly of a $Co_4(CO)_{10}$ cluster in 9 from dinuclear precursors is unprecedented as well. The formation of the enynone ligand in 10 may be rationalized as outlined in Scheme 5: A [3,3]-sigmatropic rearrangement within the ((allyloxy)carbene)metal(0) fragment generates an allylacylpentacarbonylmetal(II) complex intermediate which gives the enynone skeleton upon reductive elimination of the pentacarbonylmetal moiety. Similar rearrangements involving metal carbene structures have been previously suggested for (allyloxy)carbene¹⁴ and (vinylcyclopropyl)carbene complexes.¹⁵

Conclusions. In contrast to (allylamino)carbene complexes the pentacarbonyl (allyloxy)carbene functionality is unable to active an α,β triple bond toward cobaltmediated intramolecular Pauson–Khand reactions. Instead, the reduced thermal stability of oxycarbene complexes results in carbene ligand centered C—C and C—O bond cleavage, regenerating the metal hexacarbonyl and leading predominantly to cobalt-coordinated enynes, a process which can be rationalized in terms of a retro-Fischer carbene synthesis.

Experimental Section

All operations were carried out in flame-dried glassware under an atmosphere of argon. Tetrahydrofuran (THF) was freshly distilled from potassium sodium alloy before use. Tetrachloromethane was dried by distillation from calcium hydride. Petroleum ether (bp 40–60 °C), toluene, and dichloromethane were dried over molecular sieves. All solvents were saturated with argon. Silica gel (Merck, 0.063–0.200 mm) was degassed under high vacuum and stored under argon. p-Tolylacetylene¹⁶ and allyl triflate¹⁷ (0.6 M in tetrachloromethane) were prepared according to literature procedures.

Synthesis of (Allyloxy)(alkynyl)carbene Complexes 1 and 2. A 1.27-mL (1.16-g, 10.0-mmol) amount of p-tolylacetylene was lithiated with 10.0 mmol (12.5 mL of a 1.6 M solution in hexane) of *n*-butyllithium in 50 mL of THF at -50°C. This solution was added to a suspension of 10.0 mmol of hexacarbonylmetal(0) (chromium, 2.20 g; tungsten 3.52 g) in 20 mL of THF at -50 °C. After the mixture was stirred for 1 h at room temperature 15.0 mmol (25.0 mL of a 0.6 M solution in tetrachloromethane) of all vl triflate was added at -10 °C. The mixture was stirred for 10 min at -10 °C and then filtered through silica gel and washed with petroleum ether. After removal of the solvent under reduced pressure chromatography of the residue on silica gel (-10 °C, petroleum ether/ dichloromethane (4:1)) yielded 1.82 g (4.8 mmol, 48%) of the chromium complex 1 as dark violet crystals (slow decomposition at room temperature) and 2.90 g (5.7 mmol, 57%) of the tungsten complex 2 as a dark brown solid (slow decomposition at room temperature), respectively. Further elution gave the enyne 4 (chromium, 0.16 g, 1.0 mmol, 10%; tungsten, 0.38 g, 2.5 mmol, 25%) as a colorless oil. In the case of chromium a third band containing the chromium complex 3 (red oil, 0.70 g, 1.6 mmol, 16%) was eluted with petroleum ether/dichloromethane (1:1).

[(Allyloxy)((4-methylphenyl)ethynyl)carbene]-pentacarbonylchromium(0) (1). Anal. Calcd for $C_{18}H_{12}$ -CrO₆: C, 57.46; H, 3.21. Found: C, 57.08; H, 3.30. MS (FD): m/z 376 (100%, M⁺). FT-IR (petroleum ether): ν 2147 [w, ν -(C=C)], 2062 [m, ν (C=O), A₁¹], 1965 [vs, ν (C=O), E], 1955 [sh, ν (C=O), A₁²] cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 2.41 (s, 3H; CH₃), 5.18 (dt, 3J = 5.48 Hz, 4J = 1.37 Hz, 2H; OCH₂), 5.39 (ddt, 3J = 10.56 Hz, 4J = 1.37 Hz, 2J = 1.17 Hz, 1H; (E)-CHH), 5.50 (ddt, 3J = 17.21 Hz, 4J = 1.37 Hz, 2J = 1.18 Hz, 1H; (Z)-CHH), 6.09 (ddt, 3J = 17.21 Hz, 3J = 10.71 Hz, 3J = 5.45 Hz, 1H; =CH), 7.23–7.25 (m, 2H; Ar H), 7.45–7.48 (m, 2H; Ar H)

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ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 21.89 (1C; CH₃), 79.65 (1C; OCH₂), 92.51 (1C; α -C≡), 119.01 (1C; *ipso* C), 119.74 $(1C; =CH_2), 126.27 (1C; \beta-C=), 129.78 (2C; ortho CH), 131.23$ (1C; =CH), 132.85 (2C; meta CH), 142.99 (1C; para C), 216.31 (4C;cis CO), 225.70 (1C; trans CO), 313.00 (1C; Cr=C) ppm.

[(Allyloxy)((4-methylphenyl)ethynyl)carbene]pentacarbonyltungsten(0) (2). HR-MS (EI): calcd for $C_{18}H_{12}O_6^{182}W$, 506.0116; found, 506.0114 (29%, M⁺). FT-IR (petroleum ether): $\nu 2149 [w, \nu(C=C)], 2069 [m, \nu(C=O), A_1^1],$ 1959 [vs, ν (C=O), E], 1946 [s, ν (C=O), A_1^2] cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 2.39 (s, 3H; CH₃), 5.12 (d, broad, ^{3}J = 5.65 Hz, 2H; OCH₂), 5.40 (ddt, ${}^{3}J = 10.48$ Hz, ${}^{2}J = 1.39$ Hz, ${}^{4}J$ = 1.12 Hz, 1H; (E)-CHH), 5.49 (dtd, ${}^{3}J$ = 17.18 Hz, ${}^{4}J$ = 1.49 Hz, ${}^{2}J = 1.39$ Hz, 1H; (Z)-CHH), 6.11 (ddt, ${}^{3}J = 17.18$ Hz, ${}^{3}J$ = 10.57 Hz, ${}^{3}J = 5.55 \text{ Hz}$, 1H; =CH), 7.24 (m, 2H; Ar H), 7.52 (m, 2H; Ar H)(m, 2H; ArH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3, 100 MHz): δ 22.01 (1C; CH₃), 79.80 (1C; OCH₂), 97.67 (1C; α -C≡), 118.02 (1C; ipso C), 119.95 (1C; =CH₂), 126.48 (1C; β-C≡), 129.98 (2C; ortho CH), 131.07 (1C; =CH), 133.15 (2C; meta CH), 143.14 (1C; para C), 197.60 [s, d, J(183W, 13C) = 129.11 Hz, 4C; cis CO],205.88 (1C; trans CO), 285.18 (1C; W=C) ppm.

[((4-Allyloxy)butyl)oxy)((4-methylphenyl)ethynyl)carbene]pentacarbonylchromium(0) (3). Anal. Calcd for C22-H₂₀CrO₇: C, 58.93; H, 4.50. Found: C, 58.45; H, 4.78. HR-MS (EI): calcd for $C_{22}H_{20}CrO_7$, 448.0614; found, 448.0623 (24%, M⁺). FT-IR (petroleum ether): ν 2151 [vw, ν (C=C)], 2060 [m, ν (C=O), A₁¹], 1994 [vvw, ν (C=O), B₁], 1963 [vs, ν -(C=O), E], 1951 [sh, ν (C=O), A_1^2] cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta 1.78-1.84$ (m, 2H; 2-CH₂), 1.98-2.05 (m, 2H; 3-CH₂), $2.39 (s, 3H; CH_3), 3.52 (t, J = 6.16 Hz, 2H; 4-CH_2), 3.96 (ddd, J)$ $^{3}J = 5.67 \text{ Hz}, ^{4}J_{cis} = 1.57 \text{ Hz}, ^{4}J_{trans} = 1.37 \text{ Hz}, 2H; OCH_{2}),$ $4.70 (t, J = 6.36 \text{ Hz}, 2\text{H}; 1\text{-CH}_2), 5.15 (ddt, {}^3J_{cis} = 10.37 \text{ Hz}, {}^2J_{cis})$ = 1.76 Hz, ${}^{4}J_{\text{trans}}$ = 1.37 Hz, 1H; (E)-CHH), 5.25 (ddt, ${}^{3}J_{\text{trans}}$ = $17.21 \text{ Hz}, {}^{2}J = 1.76 \text{ Hz}, {}^{4}J = 1.57 \text{ Hz}, 1\text{H}; (Z)-\text{C}H\text{H}), 5.89 \text{ (ddt,}$ ${}^{3}J_{\text{trans}} = 17.22 \text{ Hz}, {}^{3}J_{\text{cis}} = 10.37 \text{ Hz}, {}^{3}J = 5.68 \text{ Hz}, 1\text{H}; =\text{CH}),$ 7.22-7.24 (m, 2H; Ar H), 7.44-7.46 (m, 2H; Ar H) ppm. ¹³C-{¹H} NMR (CDCl₃, 100 MHz): δ 21.79 (1C; CH₃), 26.02, 26.41 (2C; 2- and 3-CH₂), 69.42 (1C; 4-CH₂), 71.69 (1C; O-CH₂), 79.73 $(1C; 1-CH_2), 92.29 (1C; \alpha-C=), 116.72 (1C; =CH_2), 117.81 (1C;$ ipso C), 126.19 (1C; β-C≡), 129.67 (2C; ortho CH), 132.81 (2C; meta CH), 134.77 (1C; =CH), 142.84 (1C; para C), 216.33 (4C; cis CO), 225.58 (1C; trans CO), 312.93 (1C; Cr=C) ppm.

5-(4-Methylphenyl)pent-1-en-4-yne (4).8 HR-MS (EI): calcd for C₁₂H₁₂, 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 (CDCl₃, 400 MHz): δ 2.33 (s, 3H; CH₃), 3.18 (ddd, $^3J = 5.23$ Hz, $^4J = 1.82$ Hz, ${}^{4}J = 1.81$ Hz, 2H; CH₂), 5.13 (ddt, ${}^{3}J = 10.00$ Hz, ${}^{2}J =$ 1.71 Hz, ${}^4J = 1.71$ Hz, 1H; (E)-CHH), 5.39 (dtd, ${}^3J = 16.97$ Hz, ${}^{4}J = 1.87$ Hz, ${}^{2}J = 1.60$ Hz, 1H; (Z)-CHH), 5.89 (ddt, ${}^{3}J =$ 16.96 Hz, $^{3}J = 10.03$ Hz, $^{3}J = 5.23$ Hz, 1H; =CH), 7.09 (m, 2H; Ar H), 7.31 (m, 2H; Ar H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 21.32 (1C; CH₃), 23.67 (1C; 3-CH₂), 82.90 (1C; 5-C), 85.66 (1C; 4-C), 116.08 (1C; 1-CH₂), 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.

 $\{\mu$ -(2,3- η):(2,3- η)-[1-(Allyloxy)-3-(4-methylphenyl)prop- ${\bf 2\text{-}yn\text{-}1\text{-}ylidene]} pentacarbonyl chromium (0) \} bis [tri$ carbonylcobalt(0)](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 C24H12-Co₂CrO₁₂: 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, A₁¹), 2043 (s; Co), 2033 (s; Co), 2023 (m; Co), 1962 (s; Cr, E¹), 1954 (s; Cr, E²), 1938 (m; Cr, A_1^2) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 2.36 (s, 3H; CH₃), 5.48 (d, broad, $^3J = 10.4$ Hz, $^1H; (E)$ -CHH), 5.55 (d, broad, 3J = 5.7 Hz, 2H; O-CH₂), 5.56 (d, broad, 3J = 16.6 Hz, 1H: (Z)-

CHH), 6.20 (ddt, ${}^{3}J = 16.6 \text{ Hz}$, ${}^{3}J = 10.3 \text{ Hz}$, ${}^{3}J = 6.0 \text{ Hz}$, 1H; =CH), 7.18-7.20 (m, 2H; Ar H), 7.34-7.36 (m, 2H; Ar H) ppm. $^{13}C\{^{1}H\}$ NMR (CDCl₃, 100 MHz): δ 21.31 (1C; CH₃), 81.54 (1C; OCH₂), 96.92, 101.37 (2C; α - and β -C), 121.29 (1C; =CH₂), 129.29 (2C; meta CH), 129.66 (2C; ortho CH), 130.71 (1C; =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; Cr-C) ppm.

 $\{\mu - (2,3-\eta): (2,3-\eta) - [1-(Allyloxy)-3-(4-methylphenyl)prop {\bf 2\text{-yn-1-ylidene}] pentacar bonyl tung sten (0)} bis [tri$ carbonylcobalt(0)](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 C₂₄H₁₂Co₂O₁₂W: 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, A₁¹), 2062 (vs; Co), 2044 (s; Co), 2035 (s; Co), 2023 (m; Co), 1956 (vs; W, E), 1935 (m; W, A_1^2) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 2.34 (s, 3H; CH₃), 5.38 (ddd, ${}^{3}J = 6.07 \text{ Hz}$, ${}^{4}J = 1.37 \text{ Hz}$, ${}^{4}J = 1.17 \text{ Hz}$, 2H; OCH₂), 5.47 (dtd, ${}^{3}J = 10.37 \text{ Hz}$, ${}^{4}J = 1.37 \text{ Hz}$, ${}^{2}J = 0.98 \text{ Hz}$, 1H; (E)-CHH), 5.54 (dtd, ${}^{3}J = 17.15 \text{ Hz}$, ${}^{4}J = 1.17 \text{ Hz}$, ${}^{2}J = 0.98 \text{ Hz}$, 1H; (Z)-CHH), 6.19 (ddt, ${}^{3}J = 17.22 \text{ Hz}$, ${}^{3}J = 10.37 \text{ Hz}$, ${}^{3}J =$ 6.06 Hz, 1H; =CH), 7.17-7.19 (m, 2H; Ar H), 7.34-7.36 (m, m)2H; Ar H) ppm. ${}^{13}C{}^{1}H}$ NMR (CDCl₃, 100 MHz): δ 21.42 (1C; CH₃), 83.76 (1C; OCH₂), 100.90, 102.11 (2C; α - and β -C), 121.23 (1C; =CH₂), 129.33 (2C; meta CH), 129.77 (2C; ortho CH), 130.58 (1C; =CH), 134.80 (1C; ipso C), 138.62 (1C; para C), 197.14 [s, d, $J(^{13}C,^{183}W) = 127.2$ Hz, 4C; cis W-CO), 198.24(s, broad, 6C; Co-CO), 202.09 (1C; trans W-CO), 306.93 (1C; **W=**C) ppm.

Reaction of the Carbene Metal Alkyne Dicobalt Com**plexes 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 enymone 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.

 $[\mu$ - $(1,2-\eta)$: $(1,2-\eta)$ -(4-Methylphenyl)ethyne]bis[tricarbonylcobalt(0)](Co-Co) (7).13 Anal. Calcd for C15H8-Co₂O₆: C, 44.81; H, 2.01. Found: C, 44.72; 2.15. HR-MS (EI): calcd for $C_{15}H_8Co_2O_6$, 401.8985; found, 401.8987 (1%, M⁺). FT-IR (petroleum ether): ν (C=O) 2094 (s), 2057 (vs), 2031 (vs), 2027 (vs), 2015 (m) cm^{-1} . ¹H NMR (CDCl₃, 400 MHz): δ 2.34 (s, 3H; CH₃), 6.34 (s, 1H; CH), 7.12-7.15 (m, 2H; Ar H), 7.40-7.42 (m, 2H; Ar H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ 21.27 (qt, ${}^{1}J$ = 127.15 Hz, ${}^{3}J$ = 3.81 Hz, 1C; CH₃), $72.46 (d, {}^{1}J = 219.98 Hz, 1C; 2-CH); 90.47 (m, 1C; 1-C), 129.57$ $(dd, {}^{1}J = 158.95 \text{ Hz}, 2C; meta CH), 130.22 ({}^{1}J = 158.94 \text{ Hz}, {}^{2}J)$ = 6.36 Hz, 2C; ortho CH), 134.22 (t, ${}^{2}J$ = 8.27 Hz, 1C; ipso C), 138.31 (sex, ${}^{2}J = 6.36$ Hz, 1C; para C), 199.46 (s, broad, 6C;

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

bis[tricarbonylcobalt(0)](Co-Co) (8). Anal. Calcd for C₁₈-H₁₂Co₂O₆: 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): ν (C=O) $2090\ (m),\, 2053\ (vs),\, 2028\ (s),\, 2022\ (s),\, 2009\ (w)\ cm^{-1}. \ ^{1}H\ NMR$ (CDCl₃, 400 MHz): δ 2.34 (s, 3H; CH₃), 3.78 (ddd, $^3J = 7.04$ Hz, ${}^{4}J = 1.36 Hz$, ${}^{4}J = 0.98 Hz$, 2H; $3-CH_2$), $5.17 (ddt, {}^{3}J =$ 9.88 Hz, $^{2}J = 1.56$ Hz, $^{4}J = 0.98$ Hz, 1H; (E)-1-CHH), 5.27 (ddt, $^{3}J = 16.87 \text{ Hz}$, $^{2}J = 1.57 \text{ Hz}$, $^{4}J = 1.37 \text{ Hz}$, 1H; (Z)-1-CHH), 6.04 (ddt, ${}^{3}J = 16.95 \text{ Hz}$, ${}^{3}J = 9.85 \text{ Hz}$, ${}^{3}J = 7.04 \text{ Hz}$, 1H; 2-CH), 7.15 (m, 2H; Ar H), 7.41 (m, 2H; Ar H) ppm. ¹³C- ${^{1}H}$ NMR (CDCl₃, 100 MHz): δ 21.34 (1C; CH₃), 38.55 (1C; 3-CH₂), 90.98 (1C; 4-C), 97.44 (1C; 5-C), 117.48 (1C; 1-CH₂), 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)pent1-en-4-yne]tetracobalt(0) (9). HR-MS (EI): calcd for C₂₂H₁₂-Co₄O₁₀, 671.7758; found, 671.7776 (3%, M⁺). FT-IR (PE): ν (C=O) 2089 (m), 2052 (vs), 2039 (s), 2030 (s), 1988 (w), 1877 (m) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 2.28 (s, 3H; CH₃), 3.46 (d, br, 3J = 7.23 Hz, 2H; 3-CH₂), 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. ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 20.98 (1C; CH₃), 52.76 (1C; 3-CH₂), 117.02 (1C; 1-CH₂), 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 C₁₉H₁₂Co₂O₇: 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): ν (C=O) 2099 (m), 2064 (vs), 2039 (sh), 2035 (s), 2024 (sh), 1679 (w) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 2.34 (s, 3H; CH₃), 3.57 (dt, 3J = 6.65 Hz, $^{4}J = 1.37 \text{ Hz}, 2\text{H}; 4\text{-CH}_{2}), 5.18 (dq, ^{3}J = 17.02 \text{ Hz}, ^{2}J = 1.37$ Hz, ${}^{4}J = 1.37$ Hz, 1H; (Z)-6-CHH), 5.23 (dq, ${}^{3}J = 10.18$ Hz, ${}^{2}J$ = 1.37 Hz, ${}^{4}J$ = 1.37 Hz, 1H; (E)-6-CHH), 6.06 (ddt, ${}^{3}J$ = 17.02 Hz, $^{3}J = 10.17$ Hz, $^{3}J = 6.85$ Hz, 1H; 5-CH), 7.14-7.17 (m, 2H; Ar H), 7.43-7.46 (m, 2H; Ar H) ppm. 13C NMR (CDCl₃, 100 MHz): δ 21.42 (qt, ${}^{1}J$ = 126.7 Hz, ${}^{3}J$ = 4.5 Hz, 1C; CH₃), $48.13 \text{ (tm, } ^{1}J = 127.8 \text{ Hz, } 1C; 4-CH_{2}), 86.47 \text{ (s, } 1C; 2-C), 93.06$ (m, 1C; 1-C), 118.96 (tm, ${}^{1}J = 157.0 \text{ Hz}$, 1C; 6-CH₂), 129.54 $(dd, {}^{1}J = 158.9 \text{ Hz}, {}^{2}J = 6.4 \text{ Hz}, 2C; ortho CH), 129.81 (dm, {}^{1}J)$ = 157.7 Hz, 2C; meta CH), 130.56 (dtd, ${}^{1}J$ = 158.9 Hz, ${}^{2}J$ = 6.4 Hz, $^{2}J = 2.5$ Hz, 1C; 5-CH), 133.46 (t, $^{2}J = 8.3$ Hz, 1C; ipso C), 139.04 (sex, $^2J = 6.8$ Hz, 1C; para C), 198.18 (s, broad, 6C; Co-CO), 201.69 (td, ${}^{2}J = 6.4 \text{ Hz}$, ${}^{3}J = 2.5 \text{ Hz}$, 1C; 3-CO) ppm.

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