Stereoselective Coupling of (Alkynyl acetal)$Co_2(CO)_6$ with Enol Silanes

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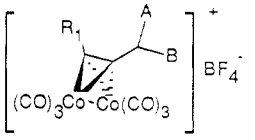
Dicobalt hexacarbonyl complexes of acetylenic acetals **2** react with enol silanes in the presence of $BF_3{\cdot}Et_2O$ to afford β-alkoxyacetylenic ketone derivatives in excellent yield and modest to excellent syn stereoselectivity. The stereochemistry of the diastereomeric products is readily established by ^1H NMR and has been confirmed in one case by X-ray diffraction. In contrast, the corresponding reaction of a noncomplexed acetylenic acetal proceeds with no stereoselectivity. Demetalation of the diastereomeric product complexes provides isomerically pure β-alkoxy-γ-acetylenic ketones.

Introduction

Studies, primarily in this laboratory, have demonstrated the broad synthetic utility of [(propargylium)$Co_2(CO)_6$]BF_4 complexes (**1**) as propargyl cation synthons.[1] Recently, results from Schreiber's group[2,3] and our own[4] have begun to realize the potential of the alkyl- and aryl-substituted complexes **1a** in stereocontrolled C–C bond formation. In



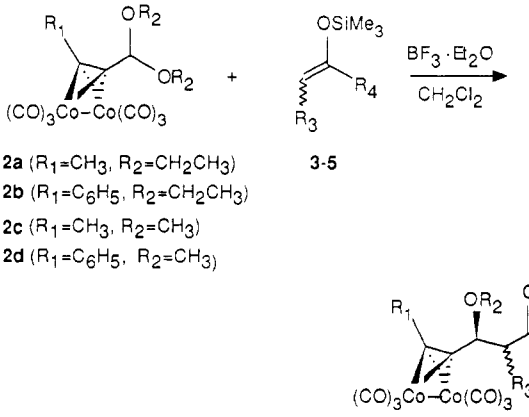
1a (A,B = H or alkyl)
1b (A= OR, B=H or alkyl)

early studies we discovered that the α-alkoxy-substituted complexes **1b** (A = OR) also couple readily with various carbon nucleophiles[5] and that one such reaction with a prochiral enol silane proceeded with a moderate degree of stereoselectivity.[6] In this report we elucidate more generally the stereochemical course of reactions of **1b** and the precursor acetal complexes **2** with enol silanes. These generally have been found to proceed with high stereoselectivity providing (after demetalation) a convenient stereocontrolled route to β-alkoxy-γ-acetylenic ketones.

Results and Discussion

The requisite acetal complexes **2a–d** were conveniently prepared in nearly quantitative yield from the reaction of $Co_2(CO)_8$ with the corresponding acetylenic acetals. The reactions of complexes **2a,b** with the enol trimethylsilanes derived from cyclohexanone (**3**), cycloheptanone (**4**), and 3-pentanone (**5**) were found to occur rapidly (15–60 min) in CH_2Cl_2 at −78 °C in the presence of 1.0 equiv of $BF_3{\cdot}Et_2O$. After base quenching (Et_3N or $NaHCO_3$) and aqueous workup the diastereomeric β-alkoxyacetylenic ketone complexes **6–11** were obtained as dark red oils or crystalline solids in good to excellent yields (eq 1). Structures of the product complexes readily followed from their IR, ^1H NMR, and mass spectra. ^1H NMR analysis of the crude reaction mixture allowed convenient determination of the syn/anti ratio by integration of the widely separated C*H*(OEt) resonances of the diastereomers. Table I summarizes the results of the reactions carried out at −78 and 0 °C.

Stereochemical Assignments. In all cases examined the C*H*(OEt) resonance for the major isomer is deshielded relative to that of the minor one although the magnitude varies significantly (Δδ 0.06–0.36 ppm, Table II). Examination of molecular models of the products derived from



2a (R_1=CH_3, R_2=CH_2CH_3)
2b (R_1=C_6H_5, R_2=CH_2CH_3)
2c (R_1=CH_3, R_2=CH_3)
2d (R_1=C_6H_5, R_2=CH_3)

3-5

6-11, 13, 18 (1)

the cyclic enol silanes (i.e., **6–9**) suggested that the major isomer was of syn (*lk*) stereochemistry since in this isomer the C*H*(OEt) methine proton experiences a deshielding interaction with the ring carbonyl group when the very bulky (alkyne)$Co_2(CO)_6$ group is oriented away from the ring so as to minimize steric repulsions. This assignment was confirmed in the case of the major isomer **7a** (isolated by flash chromatography) by a single-crystal X-ray diffraction study (Figure 1 and Table III). The conformation of the relevant side chain observed in the X-ray structure may be rather similar to that in solution since the H_B–C1′–C2′H_A dihedral angle determined by X-ray diffraction (77°) and that estimated by ^1H NMR from the vicinal coupling constant (ca. 50°) are similar. We have found a similar side-chain orientation in the solid state and solution structures of diastereomeric complexes derived from alkylation of a bicyclic cycloheptylenol silane.[6] All other molecular features found in the X-ray structure of **7a** are unexceptional.[7] It is interesting to note that the magnitude of $\Delta(^2J_{H_A-H_B})$ and Δδ of the C*H*(OEt) resonance for isomeric pairs of **6–9** and **13, 17** show a correlation with the bulk of the acetylenic substituent R_1 (Table II). The phenyl-substituted complexes uniformly exhibit a larger difference of these parameters between the diastereomeric pairs. This probably results from the bent geometry of

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(2) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128.
(3) Schreiber, S. L.; Klimas, M. T.; Sammakia, T. *J. Am. Chem. Soc.* **1987**, *109*, 5749.
(4) (a) Saha, M.; Muchmore, S.; van der Helm, D.; Nicholas, K. M. *J. Org. Chem.* **1986**, *51*, 1960. (b) Saha, M.; Bagby, B.; Nicholas, K. M. *Tetrahedron Lett.* **1986**, *27*, 915.
(5) Montana, A. M.; Nicholas, K. M.; Khan, M. A. *J. Org. Chem.* **1988**, *53*, 5193.
(6) Hodes, H. D. Ph.D. Dissertation, Boston College, 1982.
(7) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248 (supplementary material).

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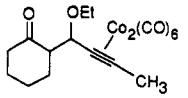
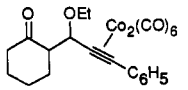
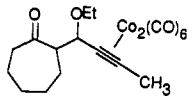
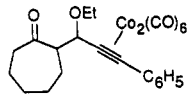
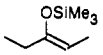
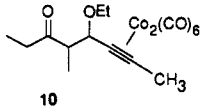
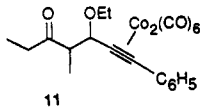
Table I. Alkylation of Enol Silanes by Acetylenic Acetal Complexes 2a and 2b[a]

entry	enol silane	complex	T, °C	product	% yield[b] (syn/anti)
1	 3	2a	−78	 6	89 (8:1)
2			0		91 (9:1)
3		2b	−78	 7	82 (6:1)
4			0		73 (4.5:1)
5	 4	2a	−78	 8	91 (1.1:1)
6			0		72 (1.7:1)
7		2b	−78	 9	76 (1.6:1)
8			0		96 (1.9:1)
9	 5	2a	−78	 10	100 (10.5:1)
10			0		100 (11.2:1)
11		2b	−78	 11	93 (>15:1)
12			0		96 (12.5:1)

[a] All reactions run in CH_2Cl_2 for 15 min with equiv of $BF_3{\cdot}Et_2O$. [b] Yield following workup, determined by NMR.

Table II. Stereochemical Correlations by ^1H NMR

product	stereochem	δH_B, ppm	J_{AB}, Hz	$\Delta\delta H_B$
6a	syn	4.98	6.4	
6b	anti	4.83	6.1	0.15
7a	syn	5.41	3.6	
7b	anti	5.06	7.8	0.35
13a	syn	4.96	6.4	
13b	anti	4.80	5.9	0.16
18a	syn	5.30	3.0	
18b	anti	4.94	7.9	0.36
8a	syn	4.80	6.9	
8b	anti	4.74	8.4	0.06
9a	syn	5.23	4.3	
9b	anti	5.05	8.7	0.18
10a	syn	4.72	7.7	
10b	anti	4.47	9.5	0.25
11a	syn	5.10	5.5	
11b	anti	4.78	9.9	0.32

Table III. Selected Bond Lengths (angstrom) 19 and Angles (degrees) for 7a[a]

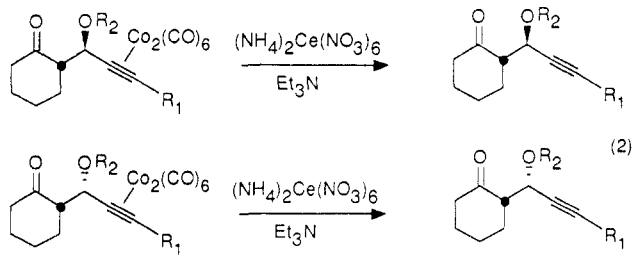
Co(1)–Co(2)	2.468 (2)	O(4)–C(11)	1.11 (1)
Co(1)–C(10)	1.798 (8)	O(5)–C(12)	1.12 (1)
Co(1)–C(11)	1.81 (1)	C(1′)–C(2)	1.52 (1)
Co(1)–C(12)	1.817 (8)	C(1′)–C(2′)	1.50 (1)
O(1)–C(1)	1.21 (1)	C(2′)–C(3′)	1.34 (1)
O(3)–C(10)	1.15 (1)	C(3′)–C(31)	1.48 (1)
C(10)–C(1)–C(11)	98.2 (5)	Co(1)–C(2′)–Co(2)	77.7 (2)
C(10)–Co(1)–C(12)	102.4 (3)	C(1′)–C(2′)–C(3′)	142.1 (5)
C(11)–Co(1)–C(12)	100.3 (4)	Co(1)–C(3′)–Co(2)	77.9 (2)
C(1′)–O(2)–C(1″)	117.4 (7)	C(2′)–C(3′)–C(31)	143.1 (5)
C(2)–C(1′)–C(2′)	112.6 (8)		

[a] Standard deviation for last digit in parenthesis.

the coordinated alkyne unit,[4a] which introduces increased steric interactions between the organometallic side chain and the cycloalkanone unit favoring a great preponderance of a single conformation for each diastereomer.

The assignments of syn (*lk*) stereochemistry to the products **10**, **11** derived from the acyclic *Z*-enol silane **5** likewise follow from an examination of models in conjunction with the deshielded C*H*(OEt) resonances and the values of $^2J_{H_A\text{-}H_B}$ of the major isomers. Models (Figure 2) indicate that in the most stable conformation of each diastereomer the sterically demanding organometallic unit should adopt an anti relationship with the butanoyl chain. For the syn isomers this places the vicinal H's in a gauche relationship (with a smaller coupling constant) as well as the CH_3 and OEt groups (deshielding the former). For the anti isomers $H_{A,B}$ are anti (hence with a larger coupling constant) and H_B, now gauche to OEt, is deshielded (and CH_3 relatively shielded).

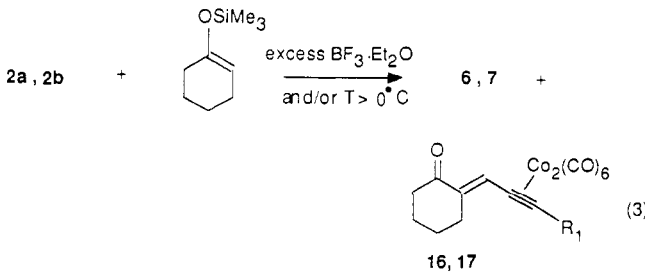
The dominating influence of the bulky (alkynyl)$Co_2(CO)_6$ unit on the preferred conformation of the products is further illustrated by the fact that demetalation of the separated diastereomers **7a,b** using Et_3N-modified ceric ammonium nitrate (eq 2) produces the corresponding diastereomeric free alkynes **12a**, **12b**, whose ^1H NMR spectra have virtually coincident C*H*(OEt) resonances and similar $^2J_{H_A\text{-}H_B}$ values. That no epimerization had occurred during demetalation was apparent from the ^{13}C NMR



7 (R_1=C_6H_5, R_2=CH_2CH_3) 12
6 (R_1=CH_3, R_2=CH_2CH_3) 14
13 (R_1=CH_3, R_2=CH_3) 15

spectra of the individual isomers. Similarly, the complexes **6a** and **13a** (vide infra) were found upon demetalation to afford the free alkynes (**14a,15a**) with stereochemistry intact. The great similarity of the ^1H NMR spectra of the diastereomeric Co-free compounds also points out the difficulties and dangers in stereochemical assignments by ^1H NMR of β-alkoxy carbonyl compounds in which there is no predominant conformation.[7]

Influence of Reaction Parameters on Stereoselectivity. A number of reaction parameters including temperature, BF_3·Et_2O stoichiometry, and reaction time were explored briefly to assess their effects on yields and stereoselectivity. Use of excess BF_3·Et_2O (3 or 6 equiv) or longer reaction times (1–3 h) in the reactions of **2a,b** with enol silane **3** was found to decrease the yield of coupling because of increased formation of elimination products (10–20%), i.e., **16**, **17** (eq 3), and decomposition to inorganic



cobalt salts. A striking temperature effect on the diastereomer ratio was found in the reactions of **2a,b** with enol silane **3** when carried out at room temperature: virtually exclusive formation (>20:1) of the syn isomers **6a** and **7a** occurred accompanied by substantial amounts (20–30%) of the elimination products **16** and **17**. Product stability studies under simulated reaction conditions revealed that this enhanced selectivity was the combined result of isomer equilibration and selective elimination from the anti isomer. Thus, whereas *syn*-**7a** and *anti*-**7b** were unchanged during 1 h at −78 °C in the presence of BF_3·Et_2O, warming to room temperature caused the latter to be substantially converted to the former and elimination product **16**, while *syn*-**7a** still remained largely unaffected. Three reasonable pathways for product isomerization include reversible dealkylation/realkylation (via alkoxy cation complexes **1a** and enol), epimerization via acid-promoted alkoxide loss/readdition, and epimerization via enolization. Conclusions regarding the actual mechanism must await the results of planned crossover and labeling experiments.

Influence of Complex and Substrate Structure. To gain further insight into the nature of the active alkylating species in these reactions the corresponding reactions of the isolated cation salt **1b** (R_1 = Ph, A = OEt, B = H) with silyl enol ether **3** were briefly examined. Runs conducted at −78, 0, and 20 °C in CH_2Cl_2 were found to afford the expected β-alkoxy keto acetylene complex **7** in yields and

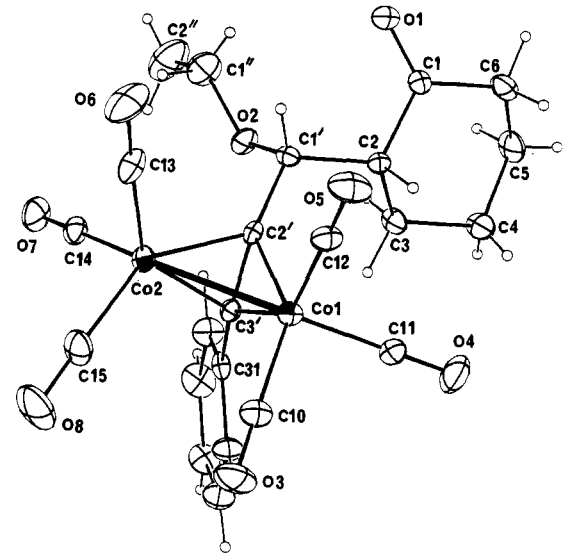


Figure 1. X-ray structure of **7a**. Thermal ellipsoids are shown at the 50% level.

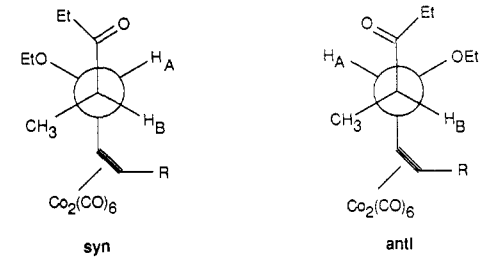


Figure 2. Favored conformations for complexes **10** and **11**.

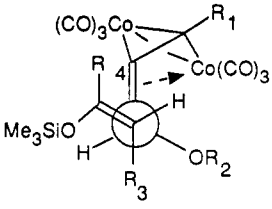
stereoselectivity (3.2:1, 5:1, and >99:1 respectively) very similar to the reactions using acetal **2b**/BF_3·Et_2O. These results suggest strongly that the alkoxy cation complexes **1b** are the active electrophiles in the Lewis acid promoted reactions of the acetal complexes.

The effects of a limited set of structural variations of the complex were examined. Unlike the reactions of alkyl-substituted propargylium complexes with silyl enol ethers studied recently by Schreiber[2] in which the steric bulk of the acetylenic substituent has a marked effect on the syn/anti product ratio, the methyl- and phenyl-substituted complexes **2a**, **2b** gave rather similar product distributions. The explanation for this difference is not apparent but could reflect a subtle difference in the structures of the respective cationic complexes or a variable transition state for the two sets of reactions. In some early experiments the *dimethyl* acetal complexes **2c** and **2d** were coupled with enol silane **3** under somewhat different conditions from those in Table I (i.e., 3 equiv of BF_3·Et_2O, 1 h) to afford **13a,b** and **18a,b**. At −78 °C, where diastereomer equilibration does not occur, the stereoselectivity in these reactions was somewhat lower—1.5:1 and 3:1 from 2c and **2d**, respectively—than for the corresponding diethyl derivatives—8:1 and 6:1 from **2a** and **2b**—when carried out at the same temperature and amount of Lewis acid. This modest but significant dependence on the alkoxy substitutent raises the possibility that further improvements in stereoselectivity could result from using even bulkier substituents, a hypothesis we plan to test in future studies.

The stereoselectivity dependence on the structure of the enol silyl ethers is far more dramatic: good to excellent selectivity being observed with the cyclohexanone and 3-pentanone derivatives **3** and **5**, but little selectivity with cycloheptanone enol silane **4** (Table I). The general preference for production of the syn product in these re-

Chart I

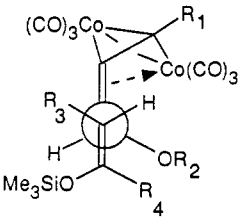
Transition States for Acyclic Enol Ethers



synclinal

A

(producing syn isomer)

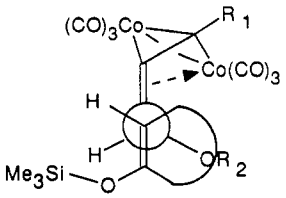


anticlinal

B

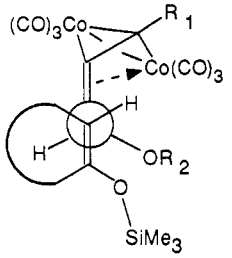
(producing anti isomer)

Transition State for Cyclic Enol Ethers



C

(producing syn isomer)

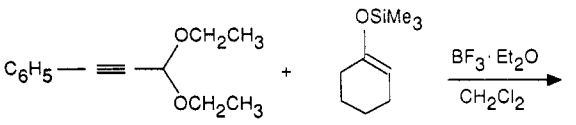


D

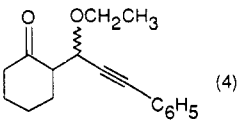
(producing anti isomer)

actions is the same as observed in reactions of the alkyl-substituted complexes **1a** with *acyclic* enol silyl ethers.[2] For the acyclic enol derivative **5** examination of molecular models leads us to propose the *synclinal* and *anticlinal* transition states (A and B, Chart I) as the most stable leading to the syn and anti products respectively for the reactions operating under kinetic control ($T \leq 0$ °C). Although the former appears to be more sterically hindered, it may be favored by a combination of stereoelectronic effects as suggested by Seebach.[8] On the other hand, *synclinal* transition states involving the *cyclic* enol derivatives appear to suffer from severe steric crowding between the bulky (alkyne)$Co_2(CO)_6$ unit and either the ring or the trimethylsilyl group. The less hindered *anticlinal* transition states leading to the diasteromeric products (C and D, Chart I) differ in the extent of crowding and dipolar repulsion between the trimethylsiloxy group and the H and OR groups of the complex. These interactions appear to be minimized in C, favoring formation of the syn products with the cyclic enol derivatives as well. The difference in selectivity observed between the two cyclic enol derivatives is especially striking, an effect not easily accounted for in this simple model.

Although the reactions of organic acetals with enol silanes have been widely studied,[9] those involving *acetylenic* acetals appear to be unknown. To probe the effect of the $Co_2(CO)_6$ unit, the *uncomplexed* acetal **19** was subjected to typical coupling conditions. No reaction was observed at −78 °C, but between −20 and 0 °C reaction did occur, affording the corresponding acetylenic ketone but as a *1:1 mixture of diastereomers* (eq 4). This result is not surprising in view of the minimal steric demand of the free acetylene function. It is clear, therefore, that the metal fragment not only facilitates the coupling but also has a dramatic effect on its diastereoselectivity, an effect that presumably derives from the extremely bulky nature of



19



(4)

(syn:anti = 1)

the complexed acetylenic moiety.

The synthetic potential of these cobalt-mediated reactions is considerable not only because of the enhanced stereoselectivity relative to their uncomplexed counterparts but also because of the additional opportunities for regio- and stereocontrolled elaboration of the resulting β-alkoxy acetylenic ketones, e.g., in the synthesis of polyoxygenated natural products. Studies within this context are underway.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were obtained at 300 and 75.4 MHz, respectively. Deuterated NMR solvents were dried over 4-Å molecular sieves, stored, and handled under N_2. NMR samples of cobalt complexes (10^{-2}–10^{-4} M) were prepared on a vacuum line under prepurified N_2 and filtered (dissolved in the deuterated solvent) through a short pad of dried neutral alumina before use. Analytical gas chromatography was carried out using 5 ft × $^1/_8$ in. OV-101 packed columns. Preparative TLC was performed over silica gel E. Merck (G-60$PF_{254-366}$) with 20 × 20 cm glass plates (1 mm). Flash column chromatography was carried out with oven-dried E. Merck silica gel (230–400 mesh) under 20 psi of N_2. Melting points of solid cobalt complexes were determined in capillaries sealed under 1 atm of CO.

Glassware was oven-dried at 120 °C overnight prior to use; solvents were purified and dried by refluxing over drying agents for 2 h prior to distillation (CH_2Cl_2 and triethylamine from CaH_2; THF, diethyl ether, and pentane from Na/benzophenone; acetone from anhydrous $MgSO_4$). 1,1-Dimethoxy-3-phenyl-2-propyne, 1,1-diethoxy-2-butyne, 1,1-diethoxy-3-phenyl-2-propyne, and 1,1-dimethoxy-2-butyne were obtained commercially. The silyl enol ether of cyclohexanone was prepared according to ref 10. The *Z*-silyl enol ether of 3-pentanone and the silyl enol ether of cycloheptanone were obtained by the procedure described in ref. 11. The purity of all title compounds was judged to be >90% by ^1H and/or ^{13}C NMR determinations. Copies of NMR spectra of **6–12** are provided as supplementary material (see the paragraph at the end of the paper).

Preparation of [RC≡CCH(OR′)$_2$]$Co_2(CO)_6$ (2). In an efficient hood dicobalt octacarbonyl (5.00 g, 14.6 mmol) was dissolved in 250 mL of dry pentane at room temperature under N_2 and 14.5 mmol of the appropriate acetylenic acetal was added dropwise over 10 min. A vigorous evolution of CO was observed, and the reaction mixture was continuously stirred for 1.5 h. When complete complexation was observed by TLC, the dark red solution was filtered under N_2 (by cannula) through a short pad of predried neutral alumina. Solvent was removed by rotatory evaporation, resulting in a dark red oil which was dried under full vacuum for 30 min to remove traces of solvent. The yield in all cases was in the range 95–100%.

Hexacarbonyl[μ-η^4-(1,1-diethoxy-2-butyne)]dicobalt (*Co–Co*) (2a): red oil; IR (film) 2980, 2930, 2900, 2860, 2090, 2040, 2010, 1310, 1140, 1100, 1060, and 1010 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 5.49 (1 H, s, H1), 3.78 (2 H, dq J_1 = 6.8 Hz, J_2 =

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7.9 Hz, H1′), 3.65 (2 H, dq, J_1 = 6.8 Hz, J_2 = 7.9 Hz, H1′), 2.68 (3 H, s, H4), and 1.25 (6 H, t, J = 6.8 Hz, H2′); MS (EI, 12 eV, DIP), m/e (rel intensity) 428 (M^+, 4), 400 (M^+ – CO, 24), 372 (M^+ – 2CO, 52), 344 (M^+ – 3CO, 54), 316 (M^+ – 4CO, 95), 288 (M^+ – 5CO, 100), 260 (M^+ – 6CO, 24), and 97 (80). Anal. Calcd for $C_{14}H_{14}Co_2O_8$: C, 39.3; H, 3.3. Found: C, 39.4; H, 3.2.

Hexacarbonyl[μ-η^4-1,1-diethoxy-3-phenyl-2-propyne)]dicobalt (*Co–Co*) (2b): dark, red oil; IR (film) 3060, 3980, 2970, 2880, 2090, 2050, 2020, 1590, 1570, 1480, 1440, 1400, 1310, 1100, 1050, 760, and 690 cm^{-1}; ^{1}H NMR (C_6D_8, ppm) 7.77 (2 H, d, J = 7.5 Hz, H2′ and H6′), 7.05 (3 H, m, $W_{1/2}$ = 45 Hz, H3′,4′ and 5′), 5.60 (1 H, s, H1), 3.60 (2 H, dq, J_1 = 7.1 Hz, J_2 = 9.0 Hz, H1′), 3.45 (2 H, dq, J_1 = 7.1 Hz, J_2 = 9.0 Hz, H1′), 1.09 (6 H, t, J = 7.1, H2″); MS (EI, 70 eV, DIP), m/e (rel intensity) 490 (M^+, 2.4), 462 (M^+ – CO, 27), 434 (M^+ – 2CO, 36), 406 (M^+ – 3CO, 128), 378 (M^+ – 4CO, 28), 350 (M^+ – 5CO, 98), 322 (M^+ – 6CO, 75), 175 (100). Anal. Calcd for $C_{19}H_{164}Co_2O_8$: C, 46.6; H, 3.4. Found: C, 46.7; H, 3.3.

Hexacarbonyl[μ-η^4-(1,1-dimethoxy-2-butyne)]dicobalt (*Co–Co*) (2c): red oil, IR (film) 2980, 2920, 2890, 2860, 2080, 2050, 2040, 200, 1420, 1370, 1310, 1130, 1100, and 1060 cm^{-1}; ^{1}H NMR (C_6D_6, ppm) 5.17 (1 H, s, H1), 3.14 (6 H, s, OMe), and 2.30 (3 H, s, H4); MS (EI, 12 eV, DIP) m/e (rel intensity) inter alia 400 (M^+, 2), 372 (M^+ – CO, 20), 344 (M^+ – 2CO, 53), 316 (M^+ – 3CO, 65), 288 (M^+ – 4CO, 82), 260 (M^+ – 5CO, 100), and 232 (M^+ – 6CO, 60).

Hexacarbonyl[μ-η^4-(1,1-dimethoxy-3-phenyl-2-propyne)]dicobalt (*Co–Co*) (2d): red oil, IR (film) 3070, 2990, 2980, 2895, 2090, 2045, 2020, 1570, 1550, 1100, 1080, and 1050 cm^{-1}; ^{1}H NMR (C_6D_6, ppm) 7.60 (2 H, d, J = 7.3 Hz, H2′ and H6′), 7.25 (3 H, m, $W_{1/2}$ = 30 Hz, H3′, 4′ and 5′), 5.63 (1 H, s, H1), 3.52 (6 H, s, OCH_3); MS (EI, 12 eV, DIP) m/e (rel intensity) 462 (M^+ – CO, 20), 406 (M^+ – 2CO, 48), 378 (M^+ – 3CO, 60), 350 (M^+ – 4CO, 75), 322 (M^+ – 5CO, 100), and 294 (M^+ – 6CO, 95).

Preparation of Hexacarbonyl[μ-η^4-(1-ethoxy-3-phenyl-2-propyn-1-ylium)]dicobalt (*Co–Co*) Tetrafluoroborate (1b). A mixture of 10.8 g (22 mmol) of complex **2b**, 3 mL of propionic anhydride, and 10 mL of dry ether was stirred and cooled to –45 °C under N_2. Freshly distilled HBF_4·OEt_2 (6 mL, 44 mmol) was added at once with vigorous shaking and then stirred for 30 min. The cooling bath was replaced by ice, and the reaction mixture quenched with 500 mL of cold absolute ether (0 °C). After the cation salt precipitated, the red mother liquor was taken out by cannula. Three more 60-mL aliquots of fresh absolute ether were added and taken out successively, and the red salt was dried by pumping for 1 h, resulting in 9 g (92%) of a loose brownish moisture-sensitive red solid: mp 96–98 °C (dec); IR (CH_2Cl_2) 3100, 3050, 2980, 2105, 2070, 2040, 1550, 1155, 1065, 1030, and 985 cm^{-1}; ^{1}H NMR (CD_2Cl_2, ppm) 9.58 (1 H , s, H1), 7.70 (2 H, d, J = 7.38 Hz, H2′ and H6′), 7.48 (3 H, m, $W_{1/2}$ = 11.9 Hz, H3′, 4′, and 5′), 4.80 (2 H, q, J = 7.1 Hz, H1″), 1.52 (3 H, t, J = 7.1 Hz, H2″).

Alkylation of Silyl Enol Ethers with Acetal Complexes 2. Equimolar amounts of the silylenol ether (**3–5**) and the acetal complex **2** were dissolved in anhydrous CH_2Cl_2 (50 mL/g of complex), cooled to the desired temperature under N_2, and continuously stirred. BF_3·OEt_2 (1–6 equiv) was added by syringe, and the reaction mixture was kept under the established conditions for variable periods of time (monitoring by TLC), quenched with NEt_3 (for –78 °C reactions, 1:1 molar ratio with respect to BF_3·OEt_2) or cold $NaHCO_3$ (for 0 or 20 °C reactions), and washed twice with brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated to dryness at room temperature, resulting in an oily dark red crude mixture. For ^{1}H NMR analysis of the reaction mixture, the crude residue was dissolved in a small volume of diethyl ether, filtered through a short plug of dry neutral alumina, rotary evaporated, dried in vacuo, and dissolved in $CDCl_3$. Isolation of pure products was accomplished by flash column chromatography of the mixture on oven-dried silica gel (60 g of SiO_2/g of crude) with a short precolumn of dry neutral alumina, using mixtures of anhydrous pentane and diethyl ether of increasing polarity as eluents, separating the diastereoisomeric alkylation products from any elimination products and unchanged starting materials.

2,1′-*syn*-Hexacarbonyl{μ-η^4-[2-(1-ethoxy-2-butyn-1-yl)-cyclohexan-1-one]}dicobalt (*Co–Co*) (6a): red oil; IR (neat) 2940, 2900, 2870, 2080, 2050, 2020, 1710, 1450, 1430, 1310, 1260, 1130, 1090, 1070, 1050, and 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$), ppm) 4.98 (1 H, d, J = 6.4 Hz, H1′), 3.78 (1 H, dq, J_1 = 6.9 Hz, J_2 = 7.2 Hz, H1″), 3.62 (1 H, dq, J_1 = 6.9 Hz, J_2 = 7.2 Hz, H1″), 2.60 (1 H, m, $W_{1/2}$ = 20 Hz, H2), 2.42 (s, 3 H, H4′), 2.40 (2 H, m, $W_{1/2}$ = 60 Hz, H6), 2.30–1.20 (6 H, m, $W_{1/2}$ = 290 Hz, H3, H4, and H5), and 1.19 (3 H, t, J = 6.9 Hz, H2″); ^{13}C NMR (C_6D_6, ppm) 209.21 (C1), 200.25 (CoC≡O), 77.15 (C1′), 67.58 (C1″), 58.79 (C2), 42.47 (C6), 30.40 (C3), 28.28 (C5), 25.15 (C4), 21.24 (C4′), and 15.19 (C2″); MS (EI, 12 eV, DIP), m/e (rel intensity) 480 (M^+, 0.5), 452 (M^+ – CO, 5), 424 (M^+ – 2CO, 47), 396 (M^+ – 3CO, 43), 368 (M^+ – 4CO, 78), 340 (M^+ – 5CO, 41), 321 (37), 312 (M^+ – 6CO, 19), 294 (28), 164 (78), and 97 (100).

2,1′-*anti*-Hexacarbonyl{μ-η^4-[2-(1-ethoxy-2-butyn-1-yl)-cyclohexan-1-one]}dicobalt (*Co–Co*) (6b): red oil; IR (neat) 2950, 2910, 2085, 2070, 2050, 2015, 1710, 1480, 1430, 1110, 1080, 1045, and 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$, ppm) 4.83 (1 H, d, J = 6.1 Hz, H1′), 3.64 (2 H, dq, J_1 = 7.0 Hz, J_2 = 7.4 Hz, H1″), 2.50 (1 H, m, $W_{1/2}$ = 30 Hz, H2), 2.30 (3 H, s, H4′), 2.20 (2 H, m, $W_{1/2}$ = 40 Hz, H6), 1.10–1.95 (6 H, m, $W_{1/2}$ = 300 Hz, H3, H4, and H5), and 1.16 (3 H, t, J = 7.0 Hz, H2″); ^{13}C NMR (C_6D_6, ppm) 209.86 (C1), 200.50 (CoC≡O), 79.01 (C1′), 66.78 (C1″), 57.26 (C2), 42.25 (C6), 29.53 (C3), 27.68 (C5), 24.71 (C4), 21.67 (C4′), and 15.32 (C2″); MS (EI, 12 eV, DIP), m/e (rel intensity) 480 (M^+, 0.3), 452 (M^+ – CO, 10), 424 (M^+ – 2CO, 50), 296 (M^+ – 3CO, 60), 368 (M^+ – 4CO, 80), 340 (M^+ – 5CO, 60), 312 (M^+ – 6CO, 80), 294 (30), 164 (90), 148 (60), 120 (40), and 97 (100).

2,1′-*syn*-Hexacarbonyl{μ-η^4-[2-(1-ethoxy-3-phenyl-2-propyn-1-yl)cyclohexan-1-one]}dicobalt (*Co–Co*) (7a): red solid; mp 100–101 °C (ether); IR (KBr) 3050, 129.56 (C2″ 2970, 2950, 2860, 2090, 2050, 2020, 1980, 1710, 1480, 1440, 1315, 1250, 1125, 1080, 1070, 1050, 780, 760, 690, 670, and 620 cm^{-1}; ^{1}H NMR ($CDCl_3$, ppm) 7.51 (2 H, dd, J_1 = 7.2 Hz, J_2 = 2.7 Hz, H2″ and 6″), 7.32 (3 H, m, $W_{1/2}$ = 18 Hz, H3″, 4″, and 5″), 5.41 (1 H, d, J = 3.6 Hz, H1′), 3.70 (2 H, dq, J_1 = 7.1 Hz, J_2 = 8.9 Hz, H1‴), 2.58 (1 H, m, $W_{1/2}$ = 25 Hz, H2), 2.50–2.20 (2 H, m, $W_{1/2}$ = 75 Hz, H6), 2.10–1.50 (6 H, m, $W_{1/2}$ = 150 Hz, H3, 4, and 5), and 1.16 (3 H, t, J = 7.1 Hz, H2‴); ^{13}C NMR ($CDCl_3$, ppm) 210.48 (C1), 199.48 (CoC≡O),148.04 (C3′), 137.91 (C2′), 129.56 (C2″ and C6″), 128.73 (C3″ and C5″), 127.65 (C4″), 98.68 (C1″), 75.98 (C1′), 67.20 (C1‴), 58.28 (C2), 42.15 (C6), 28.38 (C3), 27.35 (C5), 24.78 (C4), and 15.10 (C2‴); MS (EI, 12 eV, DIP) m/e (rel intensity) 542 (M^+, 1.1), 514 (M^+ – CO, 3), 486 (M^+ – 2CO, 46), 458 (M^+ – 3CO, 49), 430 (M^+ – 4CO, 70), 402 (M^+ – 5CO, 63), 374 (M^+ – 6CO, 9), 358 (18), 227 (100), 212 (20), 159 (27), and 131 (17). Anal. Calcd for $C_{23}H_{20}Co_2O_8$: C, 50.9; H, 3.7. Found: C, 51.1; H, 4.0.

2,1′-*anti*-Hexacarbonyl{μ-η^4-[2-(1-ethoxy-3-phenyl-2-propyn-1-yl)cyclohexan-1-one]}dicobalt (*Co–Co*) (7b): red solid; mp 111–112 °C (ether); IR (KBr) 3060, 2980, 2950, 2900, 2870, 2090, 2050, 2030, 2010, 1890, 1710, 1125, 1070, 1000, 840, 760, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, ppm) 7.41 (2 H, d, J = 7.3, H2″ and H6″), 7.20 (3 H, m, $W_{1/2}$ = 24 Hz, H3″, H4″ and H5″), 5.06 (1 H, d, J = 7.8 Hz, H1′), 3.93 (1 H, dq, J_2 = 7.1, J_2 = 8.6, H1‴), 3.85 (1 H, dq, $J1$ = 7.1, J_2 = 8.6, H1‴), 2.73 (1 H, m, $W_{1/2}$ = 18 Hz, H2), 2.3–2.6 (2 H, m, $W_1/_2$ = 92 Hz, H6), 2.10–1.40 (6 H, m, $W_{1/2}$ = 60 Hz, H3, H4, and H5), and 1.19 (3 H, t, J = 7.1 Hz, H2‴); MS (EI, 12 eV, DIP), m/e (rel intensity) 542 (M^+, 1), 414 (M^+ – CO, 1), 486 (M^+ – 2CO, 38), 458 (M^+ – 3CO, 30), 430 (M^+ – 4CO, 52), 402 (M^+ – 5CO, 48), 374 (M^+ – 6CO, 4), 358 (10), 227 (100), 159 (29), and 131 (19). Anal. Calcd for $C_{23}H_{20}Co_2O_8$: C, 50.9; H, 3.7. Found: C, 50.1; H, 3.9.

Hexacarbonyl{μ-η^4-[2-(1-ethoxy-2-butyn-1-yl)cyclohept-1-one]}dicobalt (*Co–Co*) (8): red oil, IR (neat) 2990, 2940, 2970, 2100, 2060, 2030, 1705, 1625, 1460, 1430, 1405, 1370, 1320, 1270, 1230, 1090, 1060, 1040, 1020, 940, 920, and 740 cm^{-1}; ^{1}H NMR ($CDCl_3$, ppm) of the syn-isomer **8a** 4.80 (1 H, d, J = 6.9 Hz, H1′), 3.76 (1 H, dq, J_1 = 7.0 Hz, J_2 = 8.6 Hz, H1), 3.61 (1 H, dq, J_1 = 7.0 Hz, J_2 = 8.6 Hz, H1″), 2.80 (1 H, m, $W_{1/2}$ = 25 Hz, H2), 2.58 (3 H, s, H4′), 2.55 (2 H, m, $W_{1/2}$ = 40 Hz, H7), 2.05–1.20 (8 H, m, H3, H4, H5, and H6), 1.19 (3 H, t, J = 7.0 Hz, H2″); ^{1}H NMR of the anti isomer **8b** inter alia 4.74 (1 H, d, J = 8.4 Hz, H1′), 2.92 (1 H, m, $W_{1/2}$ = 25 Hz, H2), 2.67 (3 H, s, H4′), and 1.12 (3 H, t, J = 7.0 Hz, H4′); MS (EI, 12 eV, DIP) m/e (rel intensity) 494 (M^+, 0.3), 466 (M^+ – CO, 2), 438 (M^+ – 2CO, 48), 410 (M^+ – 3CO, 46), 382 (M^+ – 4CO, 100), 354 (M^+ – 5CO, 88), 326 (M^+ – 6CO, 33), 284 (17), 240 (15), 179 (13), 165 (74), 152 (13), 137 (13), 97 (80), and 69 (14).

Hexacarbonyl{μ-η^4-[2-(1-ethoxy-3-phenyl-2-propyn-1-yl)-cycloheptan-1-one]}dicobalt (*Co–Co*) (9): red oil; IR (neat) 3090, 3060, 3020, 2980, 2940, 2870, 2100, 2060, 2030, 1705, 1620, 1480, 1445, 1400, 1370, 1320, 1120, 1080, 935, 770, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) of the syn isomer **9a** 7.49 (2 H, dd, J_1 = 7.3 Hz, J_2 = 1.1 Hz, H2″ and H6″), 7.35 (3 H, m, $W_{1/2}$ = 50 Hz, H3″, H4″, and H5″), 5.23 (1 H, d, J = 4.3 Hz, H1′), 3.65 (1 H, dq, J_1 = 7.1 Hz, J_2 = 8.8 Hz, H1‴), 3.55 (1 H, dq, J_1 = 7.1 Hz, J_2 = 8.8 Hz, H1‴), 2.75 (1 H, ddd, J_1 = 4.3 Hz, J_2 = 3.5 Hz, J_3 = 10.9 Hz, H2), 2.50 (2 H, m, $W_{1/2}$ = 50 Hz, H7), 2.20–1.20 (8 H, m, H3, H4, H5, and H6), and 1.16 (3 H, t, J = 7.1 Hz, H2‴); ^1H NMR ($CDCl_3$, ppm) of the anti isomer **9b** inter alia 5.05 (1 H, d, J = 8.7 Hz, H1′), 3.80 (1 H, dq, J_1 = 7.1 Hz, J_2 = 8.8 Hz, H1‴), 3.60 (1 H, dq, J_1 = 7.1 Hz, J_2 8.8 Hz, H1‴), 2.90 (1 H, m, $W_{1/2}$ = 20 Hz, H2), and 1.13 (3 H, t, J = 7.1 Hz, H2″); MS (EI, 12 eV, DIP), m/e (rel intensity) 556 (M^+ – 0.6), 528 (M^+ – CO, 1.3), 500 (M^+ – 2CO, 35), 472 (M^+ – 3CO, 28), 444 (M^+ – 4CO, 52), 416 (M^+ – 5CO, 52), 388 (M^+ – 6CO, 10), 304 (11), 241 (10), 227 (100), 199 (11), 161 (10), 159 (36), and 131 (23).

Hexacarbonyl[μ-η^4-(5-ethoxy-4-methyloct-6-yn-3-one)]dicobalt (*Co–Co*) (10): red oil; IR (neat) 2990, 2950, 2910, 2890, 2100, 2060, 2030, 1715, 1470, 1430, 1400, 1370, 1090, 1055, and 1020 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) of the syn isomer **10a** 4.72 (1 H, d, J = 7.7 Hz, H5), 3.80 (1 H, dq, J_1 = 6.9 Hz, J_2 = 8.7 Hz, H1′), 3.65 (1 H, dq, J_1 = 6.9 Hz, J_2 = 8.7 Hz, H1′), 2.80 (1 H, dq, J_1 = 7.7 Hz, J_2 = 7.1 Hz, H4), 2.67 (1 H, dq, J_1 = 7.2 Hz, J_2 = 18.8 Hz, H2), 2.45 (1 H, dq, J_1 = 7.2 Hz, J_2 = 18.8 Hz, H2), 2.56 (3 H, s, H8), 1.31 (3 H, d, J = 7.1 Hz, Me-4), 1.22 (3 H, t, J = 6.9 Hz, H2′), and 1.08 (3 H, t, J = 7.2 Hz, H1); ^1H NMR ($CDCl_3$, ppm) of the anti isomer **10b** inter alia 4.47 (1 H, d, J = 9.5 Hz, H5), 3.55 (1 H, dq, J_1 = 6.9 Hz, J_2 = 8.8 Hz, H1′), 3.43 (1 H, dq, J_1 = 6.9 Hz, J_2 = 8.8 Hz, H1′), 2.90 (1 H, dq, J_1 = 9.5 Hz, J_1 = 7.1 Hz, H4), 2.70 (3 H, s, H8), and 1.15 (3 H, d, J = 7.1 Hz, Me-4); MS (EI, 12 eV, DIP), m/e (rel intensity) inter alia 468 (M^+, 0.4), 440 (M^+ – CO, 2.5), 412 (M^+ – 2CO, 64), 384 (M^+ – 3CO, 47), 356 (M^+ – 4CO, 100), 329 (M^+ – 5CO, 92), 300 (M^+ – 6CO, 46), 282 (3), 256 (27), 241 (3), 197 (4), 167 (14), 153 (43), 139 (7), 152 10), 109 (7), 97 (84), and 69 (20).

Hexacarbonyl[μ-η^4-(5-ethoxy-4-methyl-7-phenyloct-6-yn-3-one)]dicobalt (*Co–Co*) (11): red oil; IR (neat) 3080, 3060, 2980, 2950, 3910, 2890, 2100, 2060, 2015, 1715, 1620, 1480, 1445, 1265, 1100, 1080, 1040, 980, 820, 765, 730, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) of the syn isomer **11a** 7.45 (2 H, dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, H2′ and H6′), 7.32 (3 H, m, $W_{1/2}$ = 45 Hz, H3′, H4′ and H5′), 5.10 (1 H, d, J = 5.5 Hz, H5), 3.70 (1 H, dq, J_1 = 7.0 Hz, J_2 = 8.6 Hz, H1″), 3.62 (1 H, dq, J_1 = 7.0, J_2 = 8.6 Hz, H1″), 2.80 (1 H, dq, J_1 = 5.1 Hz, J_2 = 7.1 Hz, H4), 2.53 (1 H, J_1 = 7.2 Hz, J_2 = 18.4 Hz, H2), 2.30 (1 H, dq, J_1 = 7.2 Hz, J_2 = 18.4 Hz, H2), 1.26 (3 H, d, J = 7.1 Hz, H1‴), 1.18 (3 H, t, J = 7.0 Hz, H2″), 0.91 (3 H, t, J = 7.2 Hz, H1); ^1H NMR ($CDCl_3$, ppm) of the anti isomer **11b** inter alia 4.78 (1 H, d, J = 9.9 Hz, H5), 2.90 (1 H, dq, J_1 = 9.9 Hz, J_2 = 6.7 Hz, H4), and 1.10 (3 H, d, J = 6.7 Hz, Me-4); MS (EI, 12 eV, DIP), m/e (rel intensity) 530 (M^+, 0.7), 502 (M^+ – CO, 2), 474 (M^+ – 2CO, 38), 446 (M^+ – 3CO, 26), 418 (M^+ – 4CO, 40), 390 (M^+ – 5CO, 64), 362 (M^+ – 6CO, 2), 246 (2), 229 (100), 215 (21), 201 (21), 187 (12), 171 (8), 169 (5), 159 (64), 143 (7), 131 (46).

2,1′-*syn*-Hexacarbonyl{μ-η^4-[2-(1-methoxy-2-butyn-1-yl)-cyclohexan-1-one]}dicobalt (*Co–Co*) (13a): red oil; IR (neat) 2970, 2930, 2860, 2110, 2080, 2050, 1710, 1100, 1080, 1050 and 760 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 4.96 (1 H, d, J = 6.4 Hz, H1′), 3.36 (3 H, s, OCH_3), 2.54 (3 H, s, H4′), 2.70 (1 H, m, $W_{1/2}$ = 20 Hz, H2), 2.56 (2 H, m, $W_{1/2}$ = 35 Hz, H6), and 2.20–1.20 (6 H, m, $W_{1/2}$ = 100 Hz, H3, H4, and H5); MS (EI, 12 eV, DIP), m/e (rel intensity) inter alia 466 (M^+, 0.5), 451 (10), 438 (M^+ – CO, 15), 435 (25), 410 (M^+ – 2CO, 4O), 382 (M^+ – 3CO, 73), 369 (60), 354 (M^+ – 4CO, 80), 326 (M^+ – 5CO, 100), and 298 (M^+ – 6CO, 70).

2,1′-*anti*-Hexacarbonyl{μ-η^4-[2-(1-methoxy-2-butyn-1-yl)-cyclohexan-1-one]}dicobalt (*Co–Co*) (13b): red oil, IR (neat) 2970, 2930, 2870, 2110, 2080, 2060, 1710, 1110, 1070, 1050, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 4.80 (1 H, d, J = 5.9 Hz, H1′), 3.52 (3 H, s, OCH_3), 2.64 (3 H, s, H4′), 2.76 (1 H, m, $W_{1/2}$ = 18 Hz, H2), 2.56 (2 H, m, $W_{1/2}$ = 30 Hz, H6), and 2.20–1.10 (6 H, m, $W_{1/2}$ = 150 Hz, H3, H4, and H5); MS (EI, 12 eV, DIP), m/e (rel intensity) 466 (M^+, 1), 451 (15), 438 (M^+ – CO, 20), 435 (20), 410 (M^+ – 2CO, 35), 382 (M^+ – 3CO, 70), 369 (78), 354 (M^+ – 4CO, 90), 326 (M^+ – 5CO, 100), and 298 (M^+ – 6CO, 45).

2,1′-*syn*-Hexacarbonyl{μ-η^4-[2-(1-methoxy-3-phenyl-2-propyn-1-yl)cyclohexan-1-one]}dicobalt (*Co–Co*) (18a): red oil; IR (neat) 3050, 2960, 2940, 2860, 2090, 2050, 2020, 1980, 1710, 1480, 1430, 1100, 1080, 1050, 780, 690, and 670 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 7.60–7.30 (5 H, m, $W_{1/2}$ = 112 Hz, Ph), 5.30 (1 H, d, J = 3.0 Hz, H1′), 3.53 (3 H, s, OCH_3), 2.73 (1 H, m, $W_{1/2}$ = 19 Hz, H2), 2.65–2.45 (2 H, m, $W_{1/2}$ = 20 Hz, H6), and 2.40–1.20 (6 H, m, H3, H4, and H5); MS EI, 12 eV, DIP), m/e (rel intensity) inter alia 528 (M^+, 0.5), 500 (M^+ – CO, 20), 472 (M^+ – 2CO, 35), 444 (M^+ – 3CO, 50), 416 (M^+ – 4CO, 75), 388 (M^+ – 5CO, 100), and 360 (M^+ – 6CO, 45).

2,1′-*anti*-Hexacarbonyl{μ-η^4-[2-(1-methoxy-3-phenyl-2-propyn-1-yl)cyclohexan-1-one]}dicobalt (*Co–Co*) (18b): red oil; IR (neat); 3060, 2980, 2955, 2910, 2880, 2090, 2050, 2030, 2010, 1710, 1100, 1080, 1050, 840, 760, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 7.65–7.20 (5 H, m, Ph), 4.94 (1 H, d, J = 7.9 Hz, H1′), 3.64 (3 H, s, OCH_3), 2.73 (1 H, m, $W_{1/2}$ = 25 Hz, H2), 2.60–2.20 (2 H, m, H6), and 2.15–1.10 (6 H, m, H3, H4, and H5); MS (EI, 12 eV, DIP), m/e (rel intensity) inter alia 529 (M^+, 0.3), 513 (10), 500 (M^+ – CO, 15), 497 (10), 472 (M^+ – 2CO, 20), 431 (80), 444 (M^+ – 3CO, 60), 416 (M^+ – 4CO, 80), 388 (M^+ – 5CO, 100), 360 (M^+ – 6CO, 60), and 97 (70).

Hexacarbonyl{μ-η^4-[2-(2-butyn-1(*E*)-ylidene)cyclohexan-1-one]}dicobalt (*Co–Co*) (16): red oil; IR (neat); 2940, 2900, 2870, 2090, 2050, 2020, 1990, 1675, 1635, 1555, 1430, 1315, 1260, 1240, 1140, 1060, 1015, 920, 880, 820, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 7.53 (1 H, br, s, $W_{1/2}$ = 5 Hz, H1′), 2.79 (3 H, s, H4′), 2.63 (2 H, m, $W_{1/2}$ = 20 Hz, H6), 1.90 (1 H, m, $W_{1/2}$ = 15 Hz, H3), 1.85 (1 H, m, $W_{1/2}$ = 15 Hz, H3), 1.30 (4 H, m, $W_{1/2}$ = 30 Hz, H4 and H5); MS (EI, 70 eV, DIP), m/e (rel intensity) 434 (M^+, 11), 406 (M^+ – CO, 4), 378 (M^+ – 2CO, 74), 350 (M^+ – 3CO, 79), 322 (M^+– 4CO, 100), 294 (M^+ – 5CO, 100), 266 (M^+ – 6CO, 61), 148 (11).

Hexacarbonyl{μ-η^4-[2-(3-phenyl-2-propyn-1(*E*)-ylidene)-cyclohexan-1-one]}dicobalt (*Co–Co*) (17): red oil; IR (neat) 3080, 3060, 2960,2950, 2870, 2090, 2050, 2040, 2020, 1990, 1670, 1610, 1590, 1550, 1450, 1310, 1255, 1240, 1230, 1115, 880, 820, 770, 735, and 600 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 7.77 (1 H, br s, $W_{1/2}$ = 5 Hz, H1′), 7.50 (2 H, dd, J_1 = 6.2 Hz, J_2 = 2.2 Hz, H2″ and H6″), 7.35 (3 H, m, $W_{1/2}$ = 11 Hz, H3″, H4″, and H5″), 2.53 (2 H, m, $W_{1/2}$ = 20 Hz, H6), 1.90 (1 H, m, $W_{1/2}$ = 15 Hz, H3), 1.75 (1 H, m, $W_{1/2}$ = 15 Hz, H3), 1.28 (4 H, m, $W_{1/2}$ = 35 Hz, H4 and H5); MS (EI, 70 eV, DIP), m/e (rel intensity) 496 (M^+, 3), 468 (M^+ – CO, 7), 440 (M^+ – 2CO, 38), 4.12 (M^+ – 3CO, 36), 384 (M^+ – 4CO, 38), 356 (M^+ – 5CO, 91), 328 (M^+ – 6CO, 11), 210 (100), 182 (17), 167 (14), 154 (11).

X-ray Crystal Structure Determination of 7a. Suitable crystals were obtained by cooling a saturated solution of **7a** in hexane to –20 °C. The crystal selected was mounted on a glass fiber, and the data were collected on an Enraf-Nonius CAD-4 automatic X-ray diffractometer using Mo Kα radiation (λ = 0.71069 Å) by the methods standard in this laboratory.[12] Unit-cell dimensions were obtained by least-squares analysis of the diffractometer angular setting of 25 well-centered reflections (2θ range = 30–40°). The data were corrected for Lorentz and polarization effects; no absorption correction was applied since it was deemed to be negligible. The atomic scattering factors were obtained from ref 13. The structure was solved by the heavy-atom method and refined by least-squares analysis (SHELX76[14]), minimizing $W(|F_o| - |F_c|)^2$. All the non-hydrogens atoms were refined anisotropically, and all the hydrogen atoms were refined isotropically. Selected bond angles and lengths are given in Table III. Tables of crystal data, complete listing of bond lengths and bond angles, thermal parameters, and atomic coordinates are available as Supplementary Material.

Reaction of Silyl Enol Ether 3 with Complex 1b. Salt **1b** (0.18 g, 0.34 mmol) was dissolved in 9 mL of anhydrous CH_2Cl_2 (50 mL/g of **1b**) (R_1 = Me, A = OEt, B = H)) and cooled to the

(12) Khan, M. A.; Taylor, R. W.; Lehn, J.-M.; Dietrich, B. *Acta Crystallogr., Sect. C: Cryst. Struc. Commun.* **1988**, *C44*, 1928.
(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV.
(14) Sheldrick G. M. SHELX76. *Program for Crystal Structure Determination*; Cambridge University, England.

appropriate temperature. Silyl enol ether **3** (70 mg, 0.41 mmol) was then added with vigorous stirring, and the reaction mixture was stirred for 15 min. The reaction was quenched by adding 0.05 mL (9.36 mmol) of NEt_3 (or 1 mL of aqueous 0.5 M $NaHCO_3$), depending on the temperature); the cooling bath was removed, the reaction mixture allowed to warm, and then 20 mL of aqueous 0.5 M $NaHCO_3$ was added. The mixture was stirred for 5 min and transferred to a separatory funnel. The organic layer was separated, and the aqueous layer extracted three times with CH_2Cl_2. All organic fractions were combined, dried over anhydrous Na_2SO_4 (filtered through a short pad of Celite), and stripped of solvent by vacuum, resulting in a dark red oil containing both diasteromeric alkylation products **6a/6b** and, when present, elimination product **16** and/or starting materials.

Demetalation of Complexes 6, 7, and 13 (Exemplified for 7a). Complex **7a** (0.2 g, 0.37 mmol) dissolved in 20 mL of dry acetone containing 0.1 mL of dry NEt_3 was treated with ceric ammonium nitrate (0.6 g, 1.11 mmol) portionwise at 0 °C under anhydrous conditions with vigorous stirring until CO evolution ceased and the reaction mixture turned from dark red to orange (~1 h). The crude mixture was stripped of solvent, quenched with 15 mL of cold 0.5 M $NaHCO_3$, stirred for 5 min, and extracted with ether (four times). All ethereal fractions were combined, washed twice with brine, dried over anhydrous Na_2SO_4, filtered through a short pad of Celite/alumina (1:1), and concentrated to dryness, resulting in 80 mg of a colorless oil (84% yield) of **12a**.

2,1′-*syn*-2-(1-Ethoxy-3-phenyl-2-propyn-1-yl)cyclohexan-1-one (12a): colorless oil; IR (neat) 3060, 3030, 2990, 2970, 2870, 2365, 1710, 1600, 1570, 1490, 1445, 1360, 1320, 1140, 1100, 1070, 760, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 7.43 (2 H, dd, J_1 = 7.3 Hz, J_2 = 2.4 Hz, H2″ and H6″), 7.30 (3 H, m, $W_{1/2}$ = 10 Hz, H3″, H4″, and H5″), 4.75 (1 H, d, J = 4.6 Hz, H1′), 3.86 (1 H, dq, J_1 = 9.3 Hz, J_2 = 7.1 Hz, H1‴), 3.55 (1 H, dq, J_1 = 9.3 Hz, J_2 = 7.1 Hz, H1‴), 2.65 (1 H, m, $W_{1/2}$ = 22 Hz, H2), 2.50–2.24 (2 H, m, $W_{1/2}$ = 78 Hz, H6), 2.10–1.60 (6 H, m, $W_{1/2}$ = 150 Hz, H3, H4, and H5), and 1.21 (3 H, t, J = 7.1 Hz, H2‴); ^{13}C NMR ($CDCl_3$, ppm) 209.16 (C1), 131.75 (C2″ and C6″), 128.24 (C3″, C4″, and C5″), 122.82 (C1″), 88.01 (C3′), 85.31 (C2′), 67.49 (C′), 65.01 (C1‴), 55.47 (C2), 42.06 (C5), 27.63 (C3), 29.91 (C5), 24.58 (C4), and 15.06 (C2‴); MS (EI, 70 eV, DIP), m/e (rel intensity) 256 (M^+, 6), 227 (M^+ – Et, 96), 199 (25), 159 (34), 131 (100), 129 (36), 115 (40), 103 (39), 91 (20), and 77 (50); HRMS (EI, 70 eV, DIP) calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1468. Anal. Calcd: C, 79.7; H, 7.8. Found: C, 79.2; H, 7.9.

2,1′-*anti*-2-(1-Ethoxy-3-phenyl-2-propyn-1-yl)cyclohexan-1-one (12b): colorless oil; IR (neat) 3080, 3060, 3020, 2970, 2930, 2870, 2370, 1710, 1600, 1575, 1490, 1450, 1340, 1320, 1130, 1100, 1035, 760, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 7.44 (2 H, dd, J_{21} = 7.6 Hz, J_2 = 2.2 Hz, H2″ and H6″), 7.30 (3 H, m, $W_{1/2}$ = 10 Hz, H3″, H4″, and H5″), 4.78 (1 H, d, J = 6.1 Hz, H1′), 3.88 (1 H, dq, J_1 = 7.1 Hz, J_2 = 9.3 Hz, H1‴), 3.56 (1 H, dq, J_1 = 7.1 Hz, J_2 = 9.3 Hz, H1‴), 2.75 (1 H, m, $W_{1/2}$ = 25 Hz, H2), 2.40 (2 H, m, $W_{1/2}$ = 50 Hz, H6), 2.3–1.6 (6 H, m, $W_{1/2}$ = 210 Hz, H3, H4, and H5), and 1.24 (3 H, t, J = 7.1 Hz, H2‴); ^{13}C NMR ($CDCl_3$, ppm) 209.77 (C-1), 131.82 (C2″ and C6″), 128.25 (C3″, C4″ and C5″), 122.79 (C1″), 86.97 (C2′ or C3′), 86.70 (C2′ or C3′), 68.69 (C1′); 64.86 (C1‴), 55.32 (C2), 42.21 (C6), 29.76 (C3), 27.73 (C5), 24.63 (C4), and 15.21 (C2‴); MS (EI, 70 eV, DIP), m/e (rel intensity) 256 (M^+, 5), 227 (M^+ – Et, 96), 199 (26), 159 (36), 131 (100), 129 (38), 115 (38), 103 (35), 77 (44); HRMS (EI, 70 eV, DIP) calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1470.

2,1′-*syn*-2-(1-Ethoxy-2-butyn-1-yl)cyclohexan-1-one (14a): colorless oil; IR (neat) 2990, 2960, 2870, 2350, 1710, 1480, 1440, 1135, 1090, 1075, and 760 cm^{-1}; ^1H NMR (C_6D_6, ppm) 4.76 (1 H, dq, J_1 = 5.1 Hz, J_2 = 2.1 Hz, H1′), 3.86 (1 H, dq, J_1 = 7.1 Hz, J_2 = 7.9 Hz, H1″), 3.47 (1 H, dq, J_1 = 7.1 Hz, J_2 = 7.9 Hz, H1″), 2.54 (1 H, m, $W_{1/2}$ = 25 Hz, H2), 2.27 (2 H, m, $W_{1/2}$ = 50 Hz, H6), 1.51 (3 H, d, J = 2.1 Hz, H4′), 1.12 (3 H, t, J = 7.1 Hz, H2″), and 1.90–1.20 (6 H, m, H3, H4, and H5); ^{13}C NMR (C_6D_6, ppm) 207.41 (C1), 80.91 (C2′), 78.87 (C3′), 67.57 (C1′), 64.82 (C1″), 55.73 (C2), 41.87 (C6), 27.41 (C3), 26.75 (C5), 24.64 (C4), 15.28 (C2″), and 3.28 (C4′); MS (EI, 70 eV, DIP), m/e (rel intensity) 194 (M^+, 2), 165 (M^+ – Et, 68), 149 (10), 137 (23), 125 (13), 105 (11), 97 (81), 91 (23), 79 (23), and 69 (100).

2,1′-*syn*-2-(1-Methoxy-2-butyn-1-yl)cyclohexan-1-one (15a): colorless oil; IR (neat) 2970, 2935, 2870, 1430, 1380, 1710, 1105, 1070, 1050, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 4.37 (1 H, dq, J_1 = 2.1 Hz, J_2 = 4.2 Hz, H1′), 3.38 (3 H, s, OCH_3), 2.50 (1 H, m, $W_{1/2}$ = 30 Hz, H2), 2.45–2.20 (2 H, m, $W_{1/2}$ = 80 Hz, H6), 1.83 (3 H, d, J = 2.1 Hz, H4′), and 2.10–1.50 (6 H, m, H3, H4, and H5); ^{13}C NMR ($CDCl_3$, ppm) 209.46 (C1), 81.85 (C2′), 76.99 (C3′), 68.95 (C1′), 56.84 (C2), 55.41 (OCH_3), 41.96 (C6), 27.26 (C3), 26.86 (C5), 24.52 (C4) and 3.54 (C4′); MS (EI, 70 eV, DIP), m/e (rel intensity) inter alia 180 (M^+, 2), 165 (20), 149 (50), 83 (100), and 79 (80).

Reaction of 1-(Trimethylsiloxy)cyclohexene with 1,1-Diethoxy-3-phenyl-2-propyne. The enol silane (0.17 g, 1.0 mmol) and acetal (0.20 g, 1.0 mmol) were dissolved in 10 mL of dry CH_2Cl_2 and cooled to −78 °C. $BF_3{\cdot}Et_2O$ (0.14 g, 1.0 mmol) was added by syringe. Monitoring by GC indicated a reaction occuring at ca. −20 °C. After the reaction mixture stirred at 0 °C for 1 h, 10 mL of saturated $NaHCO_3$ solution was added, and the layers were separated. The organic phase was washed three times with $NaHCO_3$, dried over $MgSO_4$, and concentrated to give 0.27 g of an oil whose GC (6-ft OV 101, 90–225 °C) showed only one peak but whose ^1H NMR spectrum revealed a 1:1 mixture of diastereomeric acetylenic ketones (cf. with spectra of demetalated isomers **12a**, **12b** above).

Stability of Complexes 7a and 7b. In separate vessels 5 mL of a CH_2Cl_2 solution containing 0.10 g (0.20 mmol) of the isomeric products **7a** and **7b** and 0.20 mmol of (trimethylsiloxy)cyclohexene was cooled to −78 °C. $BF_3{\cdot}Et_2O$ (1 equiv) was added, and the reaction was monitored by TLC. After ca. 1 h at −78 °C only the original complexes were present. After being warmed to 20 °C for 15 min, the mixture containing the major isomer **7a** showed a trace (<10%) of the minor isomer **7b** present; the mixture originally containing the minor isomer **7b** had been substantially converted to a mixture of the major isomer **7a** and the elimination product **16**.

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Supplementary Material Available: NMR spectra of title compounds and crystal data, complete listings of bond lengths and angles, thermal parameters, and atomic coordinates for **7a** (23 pages). Ordering information is given on any current masthead page.