Propargyl Chlorides as Sources for Cobalt Stabilized γ-Carbonyl Cations[1]

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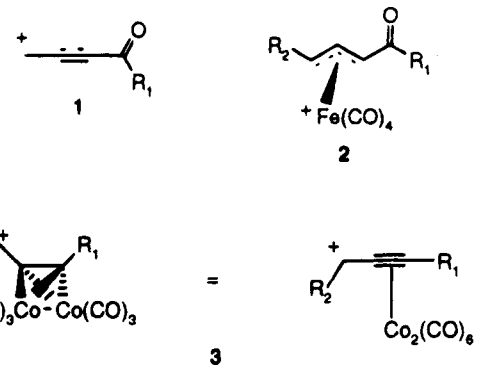
Hexacarbonyldicobalt complexes of γ-chloroalkynones and γ-chloroalkynoates (**5**) were found to undergo silver-mediated Nicholas condensation reactions with silyl enol ethers or silyl ketene acetals (**10**) to give 1,6-dicarbonyl complexes **11** in fair to good yields. Substrates **5** with γ-alkyl substitution formed diastereomeric products with enol silanes **10a** and **10b**. Reactions with propiophenone trimethylsilyl enol ether (**10b**) gave good levels of *syn* diastereoselection, whereas reactions with cyclohexanone trimethylsilyl enol ether (**10a**) were only slightly diastereoselective, favoring the *anti* diastereomer. When conducted in acetonitrile, the silver-mediated reaction of **5e** gave a radical dimerization product **13**, isolated as the *syn* diastereomer.

Introduction

One attractive area of development for new synthetic methods is that of umpolung synthesis, where the normal polar chemistry of carbonyl or related compounds is inverted.[3] Of the various types of umpolung synthesis, that of γ-carbonyl cation equivalents (**1**)[4] has been investigated only sparingly, and each of the reported methods which serve as these equivalents has its limitations. We have been engaged in the investigation of the chemistry of carbonyl-substituted tetracarbonyliron allyl cation complexes and their use as alkenone and alkenoate γ-cation synthons (**2**),[5,6] and we wished to examine closely corresponding γ-alkynone/alkynoate cation equivalents. For this purpose, adaptation of the chemistry of propargyl cation–dicobalt hexacarbonyl complexes **3** was deemed appropriate.[7] Although the formation of **3** or its reactions with nucleophiles (the Nicholas reaction) has seen almost no investigation for alkyne substrates bearing strongly electron withdrawing groups,[8] pK_{R^+} data suggest that the ability to form such cations is not greatly affected by substituents on the alkynyl carbon (R^1).[7c] We therefore considered cation complexes **3** (R^1 = C(O)R^3) good candidates for investigation.



The normal precursors for Nicholas reaction chemistry are the hexacarbonyldicobalt complexes of propargyl alcohols or propargyl ethers. Our initial efforts in this area focused on compounds of this type, and we were able to prepare a number of dicobalt hexacarbonyl complexes of γ-hydroxy- and γ-alkoxy alkynones and alkynoates (**4**). To our surprise, these were totally resistant to Lewis- or Brønsted acid-mediated formation of the corresponding propargyl cation complexes. Based on our belief that the presence of two competitive Lewis basic sites was at least in part responsible for the nonreactivity of **4**, it was decided that substrates amenable to the use of a softer Lewis acid would stand a greater chance of success.

Propargyl chloride–dicobalt hexacarbonyl complexes have been prepared on occasion in the past.[9] The reactivity of such species has not been investigated, however, with the exception of one report including a Zn–acetic acid-induced reduction of the carbon–chlorine bond.[9c] Although concerned that oxidative addition of cobalt(0) into the carbon–chlorine bond might be difficult to suppress, we were intrigued by the prospect of employing silver salts in conjunction with propargyl chloride

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(1) Dedicated to the memory of Prof. Ken Rutherford (1924–1994).

(2) NSERC (Canada) University Research Fellow, 1994–1999.

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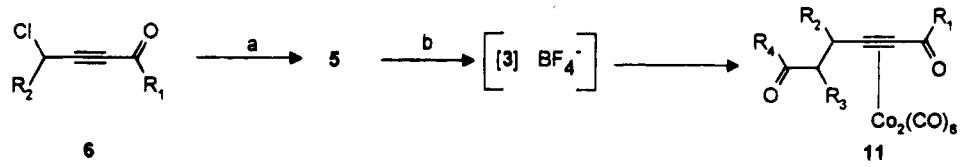
Table 1. Condensation Reactions of Propargyl Chlorides[a]



6 11

propargyl chloride	R_1	R_2	enol silane	product	R_1	R_2	R_3	R_4	yield (%) (*syn/anti*)[b]
6a	OCH_3	H	**10a**	**11a**	OCH_3	H	-$(CH_2)_4$-		69
6a	OCH_3	H	**10b**	**11b**	OCH_3	H	CH_3	Ph	67
6a	OCH_3	H	**10c**	**11c**	OCH_3	H	H	OEt	63
6b	Ph	H	**10a**	**11d**	Ph	H	-$(CH_2)_4$-		70
6b	Ph	H	**10b**	**11e**	Ph	H	CH_3	Ph	63
6b	Ph	H	**10c**	**11f**	Ph	H	H	OEt	74
6c	i-Pr	H	**10c**	**11g**	i-Pr	H	H	OEt	51
6c	OCH_3	CH_3	**10a**	**11h**	OCH_3	CH_3	-$(CH_2)_4$-		62 (1:1.3)
6d	OCH_3	CH_3	**10b**	**11i**	OCH_3	CH_3	CH_3	Ph	82 (8.7:1)
6d	OCH_3	CH_3	**10c**	**11j**	OCH_3	CH_3	H	OEt	61
6e	Ph	CH_3	**10a**	**11k**	Ph	CH_3	-$(CH_2)_4$-		60 (1:1.3)
6e	Ph	CH_3	**10b**	**11l**	Ph	CH_3	CH_3	Ph	60 (6.2:1)
6f	i-Pr	CH_3	**10a**	**11m**	i-Pr	CH_3	-$(CH_2)_4$-		66 (1:2.1)
6f	i-Pr	CH_3	**10b**	**11n**	i-Pr	CH_3	CH_3	Ph	61 (15:1)
6f	i-Pr	CH_3	**10c**	**11o**	i-Pr	CH_3	H	OEt	64
6g	OCH_3	Et	**10b**	**11p**	OCH_3	Et	CH_3	Ph	67 (11:1)

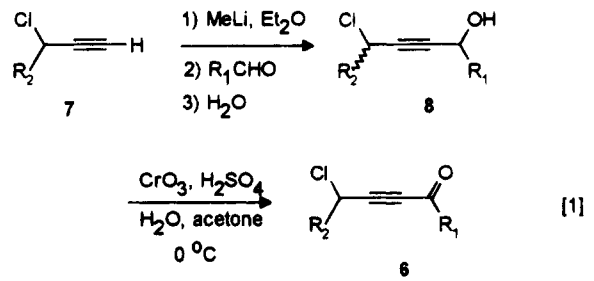
[a] Reagents: (a) $Co_2(CO)_8$, Et_2O, 0 °C; (b) $AgBF_4$, **10**, CH_2Cl_2–MeCN. [b] Based on integration of the ^1H NMR spectra of the crude reaction products.

complexes **5** for the intended Nicholas reaction chemistry.[10]

4 5

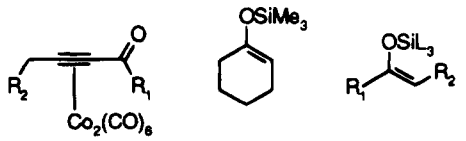
Results and Discussion

A series of γ-chloroalkynones and -alkynoates (**6**) were chosen as appropriate substrates for study. These were available from the corresponding propargyl chlorides by standard transformations involving the corresponding lithium acetylides. The alkynoates were realized by trapping the acetylide anions derived from **7** with methyl chloroformate; the corresponding alkynones were prepared by reaction with one of two aldehydes, followed by Jones oxidation of the resulting propargyl alcohol (**8**) (eq 1).



[1]

The γ-chloroalkynones and -alkynoates (**6**) were subjected to treatment with $Co_2(CO)_8$ in Et_2O to form the corresponding hexacarbonyldicobalt complexes **5**. These complexes formed rapidly and were evidenced by a substantial downfield shift of the propargylic hydrogen atoms in the ^1H NMR spectra (δ 4.39 and 5.05 in **6b** and **5b**, respectively) and by a substantial downfield shift in the absorptions of the ketone or ester carbonyl carbon in the ^{13}C NMR spectra (δ 177.1 and 192.9 in **6b** and **5b**, respectively). It soon became clear, however, that **5** did not have the stability of most alkyne–cobalt complexes. Attempted chromatographic purification of these complexes resulted in significant loss of material or the isolation of none at all. Furthermore, allowing this complexation reaction to proceed for extended periods of time at ambient temperature gave material whose ^1H NMR spectral resonances were consistent with the products of dehalogenation (**9**). Nevertheless, conducting the reaction at 0 °C for 1 h resulted in a crude reaction product containing **5** of good purity; spectral data were obtained on these compounds and they were used without further purification.



9 10a

10b, R_1 = Ph, R_2 = Me, L = Me

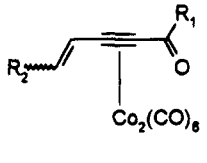
10c, R_1 = OEt, R_2 = H, L_3 = Me_2Bu-t

Dichloromethane solutions of unpurified **5** were then subject to reaction with the requisite silyl enol ether or silyl ketene acetal (**10a–c**) and $AgBF_4$. At −30 to −40 °C, reaction occurred to afford coupling products **11**, through the presumed intermediacy of a cobalt–propargyl cation complex (**3**, R^1 = C(O)R^3) (Table 1). If done in exactly this manner, however, propargyl alcohol complexes (**4**, R^3 = H) were isolated as side products in variable amounts. The most likely cause of **4** was the reaction of adventitious moisture, introduced during the addition of $Co_2(CO)_8$, with the propargyl cation complex. This unwanted process could be suppressed, to no more

(10) This work was presented in preliminary form at the 75th Canadian Chemical Conference, Edmonton, Alberta, May 31–June 4, 1992, Abstr. 547 OR-B5P.

than trace amounts, if molecular sieves (4 Å) were added prior to $AgBF_4$. The temperature of the condensation reaction was less critical, however (stereoselection issues aside), as reactions performed at 0 °C gave almost identical yields of **11**.

The 1,6-dicarbonyl condensation products **11** could be isolated after chromatographic purification as red-brown viscous oils or solids. Provided that the starting propargyl chloride **6** had been distilled shortly before reaction, **11** could be obtained in good yields (Table 1, yields based on **6**). If the propargyl chloride had been stored for a significant period of time after distillation, however, the condensation reaction gave significant amounts of dehalogenation product **9** along with, where possible, elimination product **12**. In such instances, the isolated yields of **11** were significantly lower.



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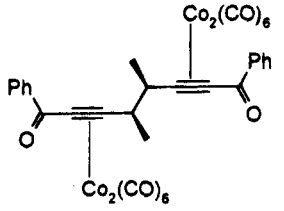


13

In the cases where **5** bearing γ-alkyl substituents (**5d–g**) were allowed to react with propiophenone silyl enol ether (**10b**), diastereomeric products were formed which were substantially enriched in one diastereomer (**11i**, 8.7:1; **11l**, 6.2:1; **11n**, 15:1; **11p**, 11:1). On the basis of literature precedent, these were expected to be the *syn* diastereomer.[7d,8] Nevertheless, the conditions of reaction were sufficiently different from the conventional conditions that independent confirmation was desired. Compound **11i** afforded crystals of suitable quality for X-ray crystallographic analysis, which confirmed *syn*-**11i** as the major diastereomer.[11]

The level of diastereoselection in Nicholas reactions has been found to be dependent on the size of remote acetylenic R substituent (R^1 in **3**).[7d] In view of the relatively small size of acyl groups and the somewhat higher reaction temperature required (−30 °C versus −78 °C) for reaction to take place relative to the cases with oxygen based leaving groups (OH, OMe), the observed levels of diastereoselection in the current work are good. The results with the phenyl ketone are noteworthy, however, in the lower diastereoselectivity of its condensation product (**11l**) relative to the corresponding methyl ester and isopropyl ketone.

The condensation products of **5d–g** with silyl enol ether **10a** also afforded diastereomeric products, but with little selectivity (**11h,k,m**). The assignment of the identity of the diastereomers in these cases was based on their spectroscopic trends. In each of compounds **11h**, **11k**, and **11m**, the ^1H NMR spectral resonances for the propargylic methine protons in the major diastereomer occurred upfield from the corresponding resonances in the minor diastereomer. Conversely, the protons of the methyl substituent resonated relatively downfield in the major diastereomer. Also, the methine-methine ^3J coupling constant in these spectra was observed to be larger for the major diastereomer in each of the cases. A further *upfield* ^1H NMR chemical shift and *smaller* ^3J coupling constant have been associated with the propargylic methine hydrogen atoms in the (major) *syn* diastereomers in the analogous propargyl ether complexes **12**[12] and in the *syn* condensation products with **10b** in the current study. Consequently, we have assigned the major diastereomers as *anti* for **11h**, **11k**, and **11m**.

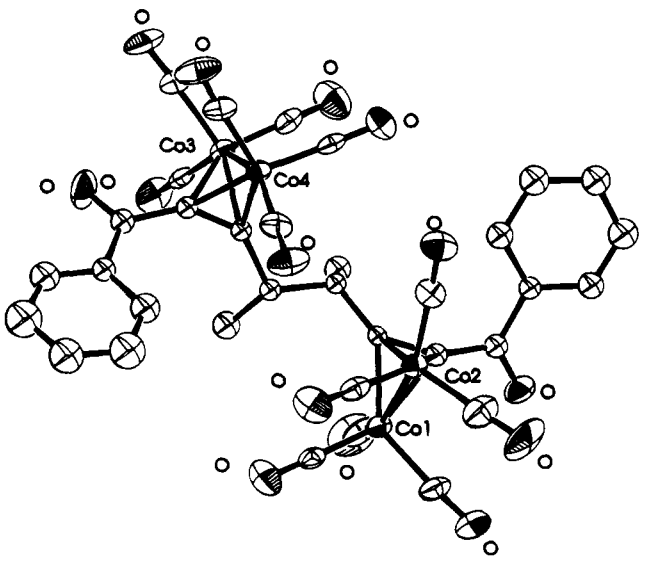


Figure 1. ORTEP drawing of **15** based on X-ray coordinates.

In the case of **11l**, an additional product was observed upon switching the reaction solvent from CH_2Cl_2 to 100% CH_3CN. In the latter solvent, only a trace amount of intended Nicholas reaction product was observed, and no evidence existed of products resulting from a Ritter-type reaction of **3** with the solvent.[13] Instead, a significant amount of homocoupling product **13** was isolated, along with the reduction and elimination products (**9** and **12**, respectively). Complete structural assignment of this compound was possible by using spectral techniques, except for the stereochemical disposition of methyl groups about the 4,5-bond. For this purpose, suitable crystals for X-ray crystallographic analysis were grown from hexanes. This revealed a 4,5-*syn* disposition of the methyl groups (Figure 1).[11,14]

The Nicholas group has reported recently that hexacarbonyldicobalt complerxes of propargyl radicals, prepared by reduction of propargyl cation complexes, undergo homocoupling to afford predominantly *syn* dimers.[15] These types of products have also been observed as side products of alkylmetal reactions with the propargyl cation complexes.[15c]

It is likely that the formation of **13** is also the result of a one-electron reduction of propargyl cation complex **3** to give propargyl radical **14** and subsequent dimerization of **14**. The reductant in this process is likely either a Ag-

(11) The authors have deposited atomic coordinates for the structures of **11i** and **13** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

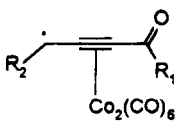
(12) Tester, R.; Varghese, V.; Montana, A. M.; Khan, M.; Nicholas, K. M. *J. Org. Chem.* **1990**, *55*, 186.

(13) Top, S.; Jaouen, G. *J. Org. Chem.* **1981**, *46*, 78.

(14) Compound **13** clung tenaciously to silica during chromatography and was purified by recrystallization after the removal of the other major products. It cannot be claimed that no *anti*-**13** was formed; if present, however, it was in trace amounts.

(15) (a) Melikyan, G. G.; Combs, R. C.; Lamirand, J.; Khan, M.; Nicholas, K. M. *Tetrahedron Lett.* **1994**, *35*, 363. (b) Melikyan, G. G.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1995**, *14*, 2170. (c) Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *212*, 115.

(0) impurity in the $AgBF_4$ source, or Co(0) from either the starting complex **5e** or residual $Co_2(CO)_8$. As the amount of dimerization product was independent of the age of the $AgBF_4$ employed, we consider Co(0) the more probable candidate.[9b,16]



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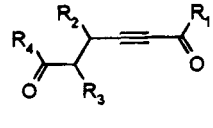

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The solid condensation products (**11h,i,k,n,o**) could be characterized fully. The oils (**11a–g,j,l,m,p**) decomposed slowly in air at room temperature and consequently were converted to the free alkynes for the purposes of their complete characterization. In the event, exposure to ceric ammonium nitrate (CAN, MeOH, silica gel, −78 to −20 °C) afforded **15** in good to excellent yields in all but one of these cases (**11p**). This compound could be demetalated by Me_3NO to give **15p** in excellent yield. In both sets of cases, decomplexation occurred without detectable levels of epimerization of the diastereomers.

In summary, it has proven possible to employ silver-mediated Nicholas reactions of **5** to afford 1,6-dicarbonyl compounds **11** and **15** in fair to good overall yields, despite the relative sensitivity of the hexacarbonyldicobalt–propargyl chloride complexes. As such, these serve as viable umpolung γ-carbonyl cation equivalents. Studies involving the further synthetic application of this methodology are in progress and will be reported in due course.[17]

Experimental Section

General Data. Melting points are uncorrected. Boiling points refer to bulb-to-bulb distillation. ^1H NMR spectra and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise indicated) at 300 and 75 MHz, respectively. Infrared spectra were recorded using neat films on NaCl or KBr plates. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. LSIMS and high resolution mass spectra (EI mode) were recorded at the Department of Chemistry and Biochemistry Mass Spectrometry Facility, University of Windsor.

MeLi was obtained from Aldrich Chemical Co., Ltd. The titer was determined using diphenylacetic acid as standard.[18] Diethyl ether (Et_2O) was distilled from sodium benzophenone ketyl immediately prior to use. Dichloromethane and acetonitrile were distilled from CaH_2 immediately prior to use. Column chromatography on silica gel (Merck, 0.04–0.063 mm) was performed according to the protocol of Still.[19] Methyl 4-chloro-2-butynoate (**6a**)[20] and 4-chloro-1-phenyl-2-butyn-1-one (**6b**)[21] were prepared according to literature procedures.

Methyl 4-Chloro-2-pentynoate (6d). The procedure of Olomucki and Le Gall[20] was employed using 3-chloro-1-butyne (1.99 g) in place of 3-chloropropyne. Bulb-to-bulb distillation of the crude reaction product afforded **6d** (2.30 g, 70%): bp 50–55 °C (0.5 torr); IR (neat, NaCl) ν_{max} 2251, 1716 cm^{-1}; ^1H NMR δ 4.68 (q, J = 7.0, 1H), 3.78 (s, 3H), 1.77 (d, J = 7.0, 3H); ^{13}C NMR 153.3, 85.2, 75.9, 52.9, 41.7, 25.2; MS m/e 146 (M^+); HRMS m/e for $C_6H_7ClO_2$ calcd (M^+) 146.0135, found 146.0130.

Methyl 4-Chloro-2-hexynoate (6g). The procedure of Olomucki and Le Gall[20] was employed using 3-chloro-1-pentyne (0.601 g) in place of 3-chloropropyne. Bulb-to-bulb distillation of the crude reaction product afforded **6g** (1.31 g, 76%): bp 60 °C (0.6 torr); IR (neat, NaCl) ν_{max} 2242, 1722 cm^{-1}; ^1H NMR δ 4.51 (t, J = 6.4, 1H), 3.76 (s, 3H), 1.99 (apparent dq, J = 6.4, 7.3, 2H), 1.09 (t, J = 7.3, 3H); ^{13}C NMR 153.4, 84.4, 76.6, 52.9, 47.9, 31.5, 10.4; MS m/e 160 (M^+), 125 (M^+ − Cl); HRMS m/e for $C_7H_9O_2$ calcd (M^+ − Cl) 125.0603, found 125.0608.

General Procedure for Preparation of γ-Chloro-α,β-alkynones (6). Methyllithium (1.25 equiv) was added to a 0.5 M solution of a propargyl chloride in Et_2O at −50 to −60 °C. The solution was stirred for 30 min, and the appropriate aldehyde (1.3 equiv) was subsequently added. After stirring the solution for a further 20 min at −50 to −60 °C, the cooling bath was removed and the solution allowed to warm to approximately 0 °C. Saturated $NH_4Cl_{(aq)}$ was added, the mixture was extracted several times with Et_2O, and the combined Et_2O layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to bulb-to-bulb distillation and the impure chloroalkynol **8** dissolved in acetone and cooled to 0 °C. Ice-cold Jones reagent (prepared from 67 g of CrO_3, 58 mL of H_2SO_4, and 160 mL of H_2O)[22] was added dropwise until its orange color persisted. The mixture was partitioned between H_2O and CH_2Cl_2. After several extractions with CH_2Cl_2, the combined CH_2Cl_2 layers were dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography (10:1 petroleum ether:Et_2O) afforded **6**.

6-Chloro-2-methyl-4-hexyn-3-one (6c). Propargyl chloride (1.26 mL, 17.4 mmol) afforded **6c** (1.70 g, 68%): bp 35 °C (1.0 torr); IR (neat, NaCl) ν_{max} 2217, 1677 cm^{-1}; ^1H NMR δ 4.23 (s, 2H), 2.62 (septet, J = 7.0, 1H), 1.16 (d, J = 7.0, 6H); ^{13}C NMR 191.0, 86.1, 83.2, 42.9, 29.2, 17.6; MS m/e 144 (M^+); HRMS m/e for C_7H_9ClO calcd (M^+) 144.0342, found 144.0349. Anal. Calcd for C_7H_9ClO: C, 58.14; H, 6.27. Found: C, 58.37, H, 6.33.

The intermediate chloroalkynol **8c** was characterized spectroscopically: IR (neat, KBr) 3392 (br), 2227 (w) cm^{-1}; ^1H NMR δ 4.21 (dt, J = 5.4, 1.0, 1H), 4.17 (d, J = 1.0, 2H), 2.41 (br, 1H), 1.85 (m, 1H), 0.98 (d, J = 6.9, 3H), 0.97 (d, J = 6.5, 3H).

4-Chloro-1-phenyl-2-pentyn-1-one (6e). 3-Chloro-1-butyne (0.4509 g, 5.09 mmol) was reacted with benzaldehyde and subsequently oxidized, according to the general procedure, to afford **6e** (0.6810 g, 69%): bp 85–90 °C (0.5 torr); IR (neat, NaCl) ν_{max} 2223, 1648 cm^{-1}; ^1H NMR δ 8.13 (d, J = 7.6, 2H), 7.64 (m, 1H), 7.51 (apparent t, J = 7.8, 2H), 4.87 (q, J = 6.9, 1H), 1.89 (d, J = 6.9, 3H); ^{13}C NMR 177.2, 136.3, 134.4, 129.6, 128.7, 91.6, 82.0, 42.4, 25.5; MS m/e 192 (M^+). Anal. Calcd for $C_{11}H_9ClO$: C, 68.58; H, 4.71. Found: C, 68.88, H, 5.01.

The intermediate chloroalkynol **8e** was characterized spectroscopically: IR (neat, KBr) 3394 (br), 2240 (w) cm^{-1}; ^1H NMR δ 7.90 (m, 2H), 7.4–7.5 (m, 3H), 5.51 (br s, 1H), 4.75 (dq, J = 1.5, 6.8, 1H), 2.59 (br, 1H), 1.79 (d, J = 6.8, 3H).

6-Chloro-2-methyl-4-heptyn-3-one (6f). 3-Chloro-1-butyne (0.6176 g, 6.98 mmol) was reacted with isobutyraldehyde and subsequently oxidized, according to the general procedure, to afford **6f** (0.6329, 57%); bp 60–65 °C (0.44 torr); IR (neat, NaCl) ν_{max} 2212, 1681 cm^{-1}; ^1H NMR δ 4.74 (t, J = 6.9, 1H), 2.66 (septet, J = 6.9, 1H), 1.80 (d, J = 6.9, 3H), 1.19 (d, J = 6.9, 6H); ^{13}C NMR 191.3, 90.2, 82.1, 43.0, 42.2, 25.5, 17.7; MS m/e 158 (M^+), 123 (M^+ − Cl); HRMS m/e for $C_8H_{11}O$ calcd (M^+ − Cl) 123.0810, found 123.0805.

The intermediate chloroalkynol **8f** was characterized spectroscopically: IR (neat, KBr) ν_{max} 3383 (br), 2244 (w) cm^{-1}; ^1H NMR δ 4.69 (dq, J = 1.7, 6.8, 1H), 4.22 (br d, J = 5.0, 1H), 2.14 (br, 1H), 1.88 (m, 1H), 1.74 (d, J = 6.5, 3H), 1.00 (d, J =

(16) Cobalt(0) induced dimerization of propargyl halides has been proposed in early work in this area, based upon the amount of CO evolved in the reactions of these halides with $Co_2(CO)_8$.[9b] We have seen no dimerization products in the absence of Ag^+.

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6.6, 3H), 0.99 (d, J = 6.6, 3H); ^{13}C NMR 85.2, 84.9, 67.7, 43.8, 34.4, 26.5, 18.0, 17.4.

General Procedure: Condensation Reactions. To a solution of the propargyl chloride (1 mmol) in Et_2O (10 mL) at 0 °C was added a slight excess of $Co_2(CO)_8$. The solution was stirred for 1 h, filtered through Celite and concentrated on a Schlenk line under reduced pressure. The residue was redissolved in CH_2Cl_2 (8 mL). Molecular sieves (4 Å) and the silyl enol ether (1.5 mmol) was added, and the solution was cooled to −30 °C. $AgBF_4$ (1.25 mmol) was added as a solution in CH_2Cl_2 (2 mL) and CH_3CN (0.5 mL), and the reaction was allowed to stir at −30 °C for 3 h before warming to room temperature. Water was added, and the solution was filtered and subsequently partitioned between CH_2Cl_2 and saturated $NH_4Cl_{(aq)}$. The CH_2Cl_2 layer was separated and the aqueous layer extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography[18] or preparative TLC (10:1 petroleum ether:Et_2O) afforded the products **11**.

Hexacarbonyl[μ-η^4-(methyl 4-chloro-2-butynoate)]dicobalt (Co−Co) (5a): IR (neat, NaCl) ν_{max} 2107, 2073, 2038, 1711 cm^{-1}; ^{1}H NMR δ 4.84 (s, 2H), 3.86 (s, 3H); ^{13}C NMR 197.4 (br), 169.7, 93.8, 78.4, 53.1, 46.3.

Hexacarbonyl[μ-η^4-(4-chloro-1-phenyl-2-butyn-1-one)]dicobalt (Co−Co) (5b): IR (neat, KBr) ν_{max} 2103, 2068, 2037, 1637 cm^{-1}; ^{1}H NMR δ 7.97 (m, 2H), 7.61 (m, 1H), 7.51 (m, 2H), 5.05 (s, 2H); ^{13}C NMR 197.7 (br), 192.9, 137.2, 133.3, 128.7, 128.2, 93.6, 85.6, 47.0.

Hexacarbonyl[μ-η^4-(6-chloro-2-methyl-4-hexyn-3-one)]dicobalt (Co−Co) (5c): IR (neat, NaCl) ν_{max} 2104, 2064, 2034, 1671 cm^{-1}; ^{1}H NMR δ 4.87 (s, 2H), 3.03 (septet, J = 6.0, 1H), 1.25 (d, J = 6.0, 6H); ^{13}C NMR 201.6, 197.8 (br), 108.2, 92.4, 46.0, 41.9, 19.3.

Hexacarbonyl[μ-η^4-(methyl 4-chloro-2-pentynoate)]dicobalt (Co−Co) (5d): IR (neat, NaCl) ν_{max} 2105, 2073, 2036, 1713 cm^{-1}; ^{1}H NMR δ 5.29 (q, J = 6.6, 1H), 3.87 (s, 3H), 1.86 (d, J = 6.6, 3H); ^{13}C NMR 197.6 (br), 169.9, 100.7, 78.4, 58.7, 53.1, 27.3.

Hexacarbonyl[μ-η^4-(4-chloro-1-phenyl-2-butyn-1-one)]dicobalt (Co−Co) (5e): IR (neat, NaCl) ν_{max} 2098, 2060, 2028, 1654 cm^{-1}; ^{1}H NMR δ 7.98 (d, J = 7.3, 2H), 7.58 (t, J = 7.3, 1H), 7.48 (apparent t, J = 7.3, 2H), 5.52 (q, J = 6.5, 1H), 1.91 (d, J = 6.5, 3H); ^{13}C NMR 197.9 (br), 193.3, 137.3, 133.2, 128.5, 128.2, 101.4, 86.2, 58.5, 27.4.

Hexacarbonyl[μ-η^4-(6-chloro-2-methyl-4-heptyn-3-one)]dicobalt (Co−Co) (5f): IR (neat, NaCl) ν_{max} 2102, 2064, 2036, 1670 cm^{-1}; ^{1}H NMR δ 5.30 (q, J = 6.6, 1H), 3.06 (apparent septet, J = 6.8, 1H), 1.87 (d, J = 6.6, 3H), 1.25 (d, J = 6.8, 3H), 1.24 (d, J = 6.7, 3H); ^{13}C NMR 207.6, 198.1 (br), 101.2, 87.8, 57.9, 47.8, 27.4, 19.5.

Hexacarbonyl[μ-η^4-(methyl 4-chloro-2-hexynoate)]dicobalt (Co−Co) (5g): IR (neat, NaCl) ν_{max} 2105, 2065, 2033, 1714 cm^{-1}; ^{1}H NMR δ 5.02 (dd, J = 3.5, 9.9, 1H), 3.86 (s, 3H), 2.14 (m, 1H), 1.93 (m, 1H), 1.19 (apparent t, J = 7.2, 3H); ^{13}C NMR 197.6 (br), 170.1, 99.7, 78.8, 66.3, 53.2, 34.2, 12.0.

Hexacarbonyl[μ-η^4-(methyl 4-(2-oxocyclohexyl)-2-butynoate)]dicobalt (Co−Co) (11a). Compound **6a** (0.071 g) was condensed with silyl enol ether **10a** to afford **11a** (0.192 g, 69%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2092, 2070, 2029, 1714 cm^{-1}; ^{1}H NMR δ 3.84 (s, 3H), 3.54 (dd, J = 6.7, 16.4, 1H), 2.71 (partially obscured dd, J = 5.0, 16.4, 1H), 2.66 (m, 1H), 2.10−2.50 (m, 4H), 1.45−2.0 (m, 4H); ^{13}C NMR 211.1, 198.5 (br), 170.5, 97.9, 79.0, 53.0, 52.5, 42.0, 35.1, 33.9, 28.2, 25.3; MS m/e 424 (M$^+$ − 2CO).

Hexacarbonyl[μ-η^4-(methyl 5-methyl-6-oxo-6-phenyl-2-hexynoate)]dicobalt (Co−Co) (11b). Compound **6a** (0.0916 g) was condensed with silyl enol ether **10b** to afford **11b** (0.2379 g, 67%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2101, 2061, 2028, 1716, 1684 cm^{-1}; ^{1}H NMR δ 7.99 (d, J = 7.2, 2H), 7.57 (t, J = 7.2, 1H), 7.48 (m, 2H), 3.77 (m, 1H), 3.70 (s, 3H), 3.66 (dd, J = 8.1, 15.8, 1H), 2.97 (dd, J = 4.7, 15.8, 1H), 1.35 (d, J = 7.1, 3H); ^{13}C NMR 201.2, 198.2 (br), 170.3, 135.6, 133.2, 129.0, 128.4, 97.1, 79.2, 52.8, 42.5, 36.8, 19.0; MS m/e 516 (M$^+$), 460 (M$^+$ − 2CO), 432 (M$^+$ − 3CO).

Hexacarbonyl[μ-η^4-(methyl 6-(ethoxycarbonyl)-2-hexynoate)]dicarbonyl (Co−Co) (11c). Compound **6a** (0.1460 g) was condensed with silyl ketene acetal **10c** to afford **11c** (0.3267 g, 63%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2103, 2062, 2034, 1738, 1711 cm^{-1}; ^{1}H NMR δ 4.18 (q, J = 7.2, 2H), 3.86 (s, 3H), 3.21 (t, J = 7.4, 2H), 2.69 (t, J = 7.4, 2H), 1.28 (t, J = 7.2, 3H); ^{13}C NMR 198.0 (br), 171.9, 170.2, 97.7, 78.4, 60.8, 53.0, 35.1, 28.7, 14.1; MS (LSIMS) m/e 471 (M$^+$ + 1), 414 (M$^+$ − 2CO), 386 (M$^+$ − 3CO).

Hexacarbonyl[μ-η^4-(4-(2-oxocyclohexyl)-1-phenyl-2-butyn-1-one)]dicarbonyl (Co−Co) (11d). Compound **6b** (0.1063 g) was condensed with silyl enol ether **10a** to afford **11d** (0.2210 g, 70%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2096, 2059, 2026, 1715, 1636 cm^{-1}; ^{1}H NMR δ 7.95 (m, 2H), 7.59 (m, 1H), 5.50 (m, 2H), 3.79 (dd, J = 6.4, 15.9, 1H), 2.85 (dd, J = 5.6, 15.9, 1H), 2.64 (m, 1H), 2.35 (m, 1H), 2.3−2.55 (m, 2H), 2.05−2.25 (m, 2H), 1.40−1.95 (m, 3H); ^{13}C NMR 211.0, 198.4 (br), 193.3, 137.2, 133.1, 128.5, 128.4, 97.7, 87.7, 53.1, 42.1, 35.1, 34.0, 28.1, 25.3; MS (LSIMS) m/e 527 (M$^+$ + 1), 470 (M$^+$ − 2CO), 442 (M$^+$ − 3CO), 414 (M$^+$ − 4CO), 386 (M$^+$ − 5CO).

Hexacarbonyl[μ-η^4-(5-methyl-1,6-diphenyl-2-hexyne-1,6-dione)]dicarbonyl (Co−Co) (11e). Compound **6b** (0.0799 g) was condensed with silyl enol ether **10b** to afford **11e** (0.1583 g, 63%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2097, 2059, 2027, 1683, 1636 cm^{-1}; ^{1}H NMR δ 7.98−8.02 (m, 4H), 7.55−7.63 (m, 2H), 7.45−7.54 (m, 4H), 3.80−3.95 (m, 2H), 3.12 (d of $^1/_2$ AB quartet, J = 1.9, 9.3, 1H), 1.38 (d, J = 7.0, 3H); ^{13}C NMR 201.6, 198.5 (br), 193.4, 137.2, 135.4, 133.3, 133.2, 128.8, 128.6, 128.44, 128.40, 105.7, 89.4, 43.0, 36.9, 19.2; MS (LSIMS) m/e 563 (M$^+$ − 1).

Hexacarbonyl[μ-η^4-(ethyl 6-oxo-6-phenyl-4-hexynoate)]diobalt (Co−Co) (11f). Compound **6b** (0.0848 g) was condensed with silyl ketene acetal **10c** to afford **11f** (0.1820 g, 74%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2099, 2060, 2029, 1733, 1651 cm^{-1}; ^{1}H NMR δ 7.94 (d, J = 7.3, 2H), 7.59 (t, J = 7.2, 1H), 7.50 (apparent t, J = 7.3, 2H), 4.17 (q, J = 7.1, 2H), 3.41 (t, J = 7.4, 2H), 2.76 (t, J = 7.4, 2H), 1.28 (t, J = 7.1, 3H); ^{13}C NMR 198.3 (br), 193.0, 171.9, 137.3, 133.2, 128.6, 128.2, 97.4, 86.8, 61.0, 35.5, 29.3, 14.1; MS m/e 516 (M$^+$), 404 (M$^+$ − 4CO).

Hexacarbonyl[μ-η^4-(ethyl 7-methyl-6-oxo-4-octynoate)]dicobalt (Co−Co) (11g). Compound **6c** (0.0739 g) was condensed with silyl ketene acetal **10c** to afford **11g** (0.1251 g, 51%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2099, 2059, 2028, 1735, 1670 cm^{-1}; ^{1}H NMR δ 4.21 (q, J = 7.1, 2H), 3.22 (t, J = 7.4, 2H), 2.96 (septet, J = 6.7, 1H), 2.69 (t, J = 7.4, 2H), 1.28 (t, J = 7.1, 3H), 1.24 (d, J = 6.7, 6H); ^{13}C NMR 207.1, 198.3 (br), 171.9, 98.4, 87.4, 60.9, 41.8, 35.3, 28.7, 19.2, 14.1; MS (LSIMS) m/e 483 (M$^+$ + 1), 426 (M$^+$ − 2CO), 398 (M$^+$ − 3CO), 370 (M$^+$ − 4CO), 342 (M$^+$ − 5CO).

4,1′-*syn*- and 4,1′-*anti*-Hexacarbonyl[μ-η^4-(methyl 4-(2-oxocyclohexyl)-2-pentynoate)]dicobalt (Co−Co) (11h). Compound **6d** (0.2034 g) was condensed with silyl enol ether **10a** to afford **11h** (0.4281 g, 62%) as a 1.3:1 mixture of diastereomers, which was crystallized from petroleum ether at −78 °C to afford red-brown crystals: mp 52−54 °C; IR (neat, NaCl) ν_{max} 2099, 2059, 2028, 1715 cm^{-1}; ^{1}H NMR δ 3.83 and 3.82 (s, 3H), 3.65 (dq, J = 6.1, 7.0) and 3.40 (dq, J = 5.5, 6.9) (1H), 1.6−2.65 (m, 9H), 1.38 (d, J = 6.9) and 1.25 (d, J = 7.0) (3H); ^{13}C NMR 211.2 and 211.1, 198.5 (br), 170.6, 106.0 and 103.6, 79.6 and 79.5, 57.0 and 56.6, 53.0, 42.4 and 42.2, 37.2 and 35.1, 30.8 and 30.3, 28.0 and 27.5, 25.2 and 24.6, 20.7 and 18.7; MS m/e 493 (M$^+$ − 1). Anal. Calcd for $C_{18}H_{16}Co_2O_9$: C, 43.75; H, 3.26. Found: C, 44.13; H, 2.91.

4,5-*syn*-Hexacarbonyl[μ-η^4-(methyl 4,5-dimethyl-6-oxo-6-phenyl-2-hexynoate)]dicobalt (Co−Co) (11i). Compound **6d** (0.2210 g) was condensed with silyl enol ether **10b** to afford **11i** (0.6588 g, 82%), which was crystallized from hexanes to afford red brown crystals: mp 80−82 °C (petroleum ether); IR (neat, NaCl) ν_{max} 2097, 2061, 2028, 2005, 1705, 1681 cm^{-1}; ^{1}H NMR δ 7.98 (d, J = 7.4, 2H), 7.56 (t, J = 7.3, 1H), 7.47 (apparent t, J = 7.4, 2H), 3.72 (dq, J = 6.1, 6.8, 1H), 3.63 (s, 3H), 3.61 (m, obscured, 1H), 1.34 (d, J = 6.8, 3H), 1.26 (d, J = 6.8, 3H); ^{13}C NMR 201.4, 198.3 (br), 170.3, 135.6, 133.0, 128.3, 128.2, 104.6, 79.7, 52.7, 46.6, 38.1, 18.4, 13.9; MS m/e

531 ($M^+ + 1$). Anal. Calcd for $C_{21}H_{16}Co_2O_9$: C, 47.57; H, 3.04. Found: C, 47.44; H, 2.97.

The ^1H NMR spectrum in C_6D_6 gave the following unobscured resonances attributable to the *syn* and *anti* diastereomers (partial spectra):

***syn*-11i**: δ 3.67 (dq, J = 7.0, 6.8, 1H), 3.53 (dq, J = 7.0, 7.0, 1H), 3.21 (s, 3H), 1.20 (d, J = 6.8, 3H), 1.01 (d, J = 7.0, 3H); ***anti*-11i**: δ 3.46 (dq, J = 8.3, 6.7, 1H), 3.34 (s, 3H), 1.33 (d, J = 7.0, 3H), 1.28 (d, J = 6.7, 3H).

The following ^{13}C NMR spectral resonances are attributable to ***anti*-11i**: δ 202.7, 136.5, 133.3, 128.7, 128.2, 104.2, 53.0, 47.3, 40.1, 22.0, 16.9.

Hexacarbonyl[μ-η⁴-(methyl 5-(ethoxycarbonyl)-4-methyl-2-pentynoate)]dicobalt (Co−Co) (11j). Compound **6d** (0.0457 g) was condensed with silyl ketene acetal **10c** to afford **11j** (0.0916 g, 61%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2101, 2062, 2028, 1738, 1713 cm^{-1}; ^1H NMR δ 4.17 (q, J = 7.1, 2H), 3.86 (s, 3H), 3.50 (m, 1H), 2.73 (dd, J = 5.5, 15.7, 1H), 2.43 (dd, J = 8.6, 15.7, 1H), 1.35 (d, J = 6.7, 3H), 1.28 (t, J = 7.1, 3H); ^{13}C NMR 198.2, 171.5, 170.4, 104.7, 78.4, 60.7, 53.0, 42.7, 34.2, 22.2, 14.1; MS *m/e* 428 ($M^+ - 2CO$).

4,1′-Hexacarbonyl[μ-η⁴-(4-(2-oxocyclohexyl)-4-methyl-1-phenyl-2-pentyn-1-one)]dicobalt (Co−Co) (11k). Compound **6e** (0.0650 g) was condensed with silyl enol ether **10a** to afford **11k** (0.1094 g, 60%) as a 1.3:1 mixture of diastereomers, which was crystallized from hexanes to afford red-brown crystals: mp >120 °C dec; IR (neat, NaCl) ν_{max} 2095, 2060, 2017, 1715, 1645 cm^{-1}; ^1H NMR δ 7.95 (d, J = 6.9) and 7.88 (d, J = 7.2, 2H), 7.57 (t, J = 7.4, 1H), 7.48 (apparent t, J = 7.4, 2H), 3.94 (m) and 3.52 (m, 1H), 2.59 (ddd, J = 4.7, 5.4, 12.7) and 2.30 (m, obscured, 1H), 2.30−2.50 (m, 2H), 1.90−2.25 (m, 2H), 1.30−1.80 ppm (m, 4H), 1.48 (d, J = 6.5) and 1.27 (d, J = 7.0, 3H); ^{13}C NMR 211.8 and 211.1, 198.8, 194.2 and 193.6, 137.6 and 137.0, 133.2 and 133.0, 128.56 and 128.5, 128.4 and 128.3, 107.1 and 105.0, 89.8 and 88.4, 58.2 and 57.4, 43.1 and 42.4, 37.0 and 34.6, 33.3 and 30.7, 28.7 and 28.2, 25.3 and 24.7, 22.0 and 19.3; MS (LSIMS) *m/e* 541 ($M^+ + 1$), 484 ($M^+ - 2CO$), 456 ($M^+ - 3CO$), 400 ($M^+ - 5CO$). Anal. Calcd for $C_{23}H_{18}Co_2O_8$: C, 51.13; H, 3.36. Found: C, 51.20; H, 3.30.

4,5-*syn*-Hexacarbonyl[μ-η⁴-(4,5-dimethyl-1,6-diphenyl-2-hexyne-1,6-dione)]dicobalt (Co−Co) (11l). Compound **6e** (0.0559 g) was condensed with silyl enol ether **10b** to afford **11l** (0.1006 g, 60%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2097, 2059, 2027, 1683, 1668 cm^{-1}; ^1H NMR δ 7.95 (m, 4H), 7.35−7.65 (m, 6H), 3.92 (qd, J = 7.1, 7.0, 1H), 3.73 (qd, J = 7.0, 7.0, 1H), 1.38 (d, J = 7.1, 3H), 1.34 (d, J = 7.0, 3H); ^{13}C NMR 201.8, 198.3 (br), 194.2, 137.2, 135.4, 133.2, 133.0, 128.6, 128.4, 128.3, 128.2, 105.7, 89.4, 47.0, 38.0, 22.4, 15.3; MS (LSIMS) *m/e* 577 ($M^+ + 1$), 492 ($M^+ - 3CO$), 464 ($M^+ - 4CO$), 436 ($M^+ - 5CO$).

The following spectroscopic data could be ascribed to ***anti*-11l**: ^1H NMR δ 7.94 (d, J = 7.6, 4H), 7.4−7.65 (m, 6H), 3.73 (qd, J = 6.4, 9.9, 1H), 3.38 (qd, J = 6.9, 9.9, 1H), 1.38 (d, J = 6.4, 3H), 1.11 (d, J = 6.9, 3H); ^{13}C NMR 202.8, 198.8 (br), 193.4, 136.7, 136.5, 133.3, 128.9, 128.6, 128.5, 128.4, 104.4, 90.6, 48.2, 40.0, 22.5, 17.6.

6,1′-*syn*- and 6,1′-*anti*-Hexacarbonyl[μ-η⁴-(6-(2-oxocyclohexyl)-2-methyl-4-heptyn-3-one)]dicobalt (Co−Co) (11m). Compound **6f** (0.0425 g) was condensed with silyl enol ether **10a** to afford **11m** (0.0896 g, 66%) as a red-brown oil in a 1.3:1 mixture of diastereomers. Repeated preparative TLC (10:1 petroleum ether:Et_2O) afforded the diastereomers separately, each as a viscous red-brown oil, in the order of presentation.

***syn*-11m**: IR (neat, NaCl) ν_{max} 2095, 2057, 2024, 1712, 1666 cm^{-1}; ^1H NMR δ 3.69 (dq, J = 5.7, 6.7, 1H), 3.01 (apparent septet, J = 6.8, 1H), 2.55 (dt, J = 12.9, 5.5, 1H), 2.3−2.5 (m, 2H), 1.85−2.3 (m, 3H), 1.4−1.8 (m, 3H), 1.25 (d, J = 7.0, 3H), 1.23 (d, J = 6.7, 3H), 1.20 (d, J = 6.9, 3H); ^{13}C NMR 211.2, 208.9, 198.7 (br), 107.9, 88.9, 56.8, 42.3, 41.7, 35.0, 30.3, 28.0, 25.2, 19.7, 19.3, 19.0; MS (LSIMS) *m/e* 506 (M^+).

***anti*-11m**: IR (neat, NaCl) ν_{max} 2096, 2057, 2026, 1713, 1666 cm^{-1}; ^1H NMR δ 3.32 (dq, J = 6.1, 6.9, 1H), 2.99 (apparent septet, J = 6.8, 1H), 2.25−2.5 (m, 3H), 1.55−2.1 (m, 6H), 1.39 (d, J = 6.8, 3H), 1.23 (d, J = 6.9, 3H), 1.20 (d, J = 6.7, 3H); ^{13}C NMR 211.2, 208.7, 198.8 (br), 105.8, 89.5, 57.2, 42.5, 41.8, 37.6, 31.8, 27.8, 24.7, 20.8, 20.0, 19.4; MS (LSIMS) *m/e* 506 (M^+).

2,3-*syn*-Hexacarbonyl[μ-η⁴-(2,3,7-trimethyl-1-phenyl-4-octyne-1,6-dione)]dicobalt (Co−Co) (11n). Compound **6f** (0.2035 g) was condensed with silyl enol ether **10b** to afford **11n** (0.4331 g, 61%), which could be recrystallized from hexanes to give red-brown crystals: mp 61−62.5 °C (hexanes); IR (neat, NaCl) ν_{max} 2097, 2059, 2027, 1683, 1668 cm^{-1}; ^1H NMR δ 7.96 (d, J = 7.8, 2H), 7.56 (m, 1H), 7.46 (apparent t, J = 7.5, 2H), 3.71 (m, 1H), 3.66 (m, 1H), 3.00 (m, 1H), 1.32 (d, J = 6.8, 3H), 1.26 (d, J = 7.0, 3H), 1.22 (d, J = 7.0, 3H), 1.19 (d, J = 6.7, 3H); ^{13}C NMR 208.5, 201.6, 198.6 (br), 135.6, 133.2, 128.7, 128.4, 106.4, 89.5, 46.8, 41.8, 38.2, 19.7, 19.5, 19.1, 14.0; MS (LSIMS) *m/e* 541 ($M^+ - 1$), 484 ($M^+ - 2CO$), 428 ($M^+ - 4CO$), 400 ($M^+ - 5CO$). Anal. Calcd for $C_{23}H_{20}Co_2O_6$: C, 50.94; H, 3.72. Found: C, 50.86, H, 3.78.

The ^1H NMR spectrum in C_6D_6 gave the following unobscured resonances attributable to the *syn* and *anti* diastereomers (partial spectra):

***syn*-11n**: 3.65 (dq, J = 7.1, 7.1, 1H), 3.49 (dq, J = 7.1, 7.1, 1H), 1.14 (d, J = 7.1, 3H), 0.98 (d, J = 7.1, 3H); ***anti*-11n**: 3.38 (dq, J = 8.8, 6.8, 1H), 1.30 (d, J = 6.6, 3H).

Hexacarbonyl[μ-η⁴-(ethyl 3,7-dimethyl-6-oxo-4-octynoate)dicobalt (Co−Co) (11o). Compound **6f** (0.1065 g) was condensed with silyl ketene acetal **10c** to afford **11o** (0.2130 g, 64%), which could be recrystallized from hexanes at −78 °C to give red-brown crystals mp 31−33 °C; IR (neat, NaCl) ν_{max} 2097, 2059, 2024, 1735, 1668 cm^{-1}; ^1H NMR δ 4.15 (q, J = 7.1, 2H), 3.49 (m, 1H), 2.98 (septet, J = 7.0, 1H), 2.66 (dd, J = 5.3, 15.6, 1H), 2.43 (dd, J = 8.6, 15.6, 1H), 1.32 (d, J = 6.7, 3H), 1.26 (t, J = 7.1, 3H), 1.23 (d, J = 6.8, 6H); ^{13}C NMR 208.0, 198.5 (br), 171.4, 106.3, 88.2, 60.7, 43.0, 41.8, 34.2, 22.7, 19.5, 19.4, 14.1; MS (LSIMS) *m/e* 497 ($M^+ + 1$). Anal. Calcd for $C_{18}H_{18}Co_2O_9$: C, 43.57; H, 3.66. Found: C, 43.41, H, 3.57.

4,5-*syn*-Hexacarbonyl[μ-η⁴-(methyl 4-ethyl-5-methyl-6-oxo-6-phenyl-2-hexynoate)]dicobalt (Co−Co) (11p). Compound **6g** (0.0488 g) was condensed with silyl enol ether **10b** to afford **11p** (0.1104 g, 67%) as a viscous red-brown oil: IR (neat, NaCl) ν_{max} 2099, 2060, 2028, 1715, 1683 cm^{-1}; ^1H NMR δ 7.92 (d, J = 7.7, 2H), 7.54 (t, J = 7.2, 1H), 7.44 (apparent t, J = 7.4, 2H), 3.82 (m, 1H), 3.76 (s, 3H), 3.33 (m, 1H), 1.86 (m, 1H), 1.59 (m, 1H), 1.27 (d, J = 6.6, 3H), 0.96 (t, J = 7.4, 3H); ^{13}C NMR 202.2, 198.4 (br), 170.7, 136.1, 133.0, 128.7, 128.3, 103.2, 80.7, 53.1, 46.6, 45.0, 25.9, 12.7, 12.3; MS (LSIMS) *m/e* 544 (M^+).

The following spectroscopic data could be ascribed to ***anti*-11p**: ^1H NMR δ 3.84 (s, 3H), 3.31 (m, 1H), 1.09 (t, J = 7.4, 3H).

Dodecacarbonyl[μ⁴-η²,η²,η²,η²-4,5-dimethyl-1,8-diphenyl-2,6-octadiyne-1,8-dione]tetracobalt (2 Co−Co) (13). To a solution of **6e** (0.1066 g, 0.553 mmol) in Et_2O (10 mL) at 0 °C was added a slight excess of $Co_2(CO)_8$. The solution was stirred for 1 h, filtered through Celite, and concentrated on a Schlenk line under reduced pressure. The residue was redissolved in CH_3CN (4 mL). Molecular sieves (4 Å) and the silyl enol ether (1.5 mmol) were added, and the solution was cooled to −30 °C. $AgBF_4$ (1.25 mmol) was added as a solution in CH_3CN (0.5 mL), and the reaction was allowed to stir at −30 °C for 3 h before warming to room temperature. Water was added, and the solution was filtered and subsequently subjected to a conventional workup (see general conditions for condensation reactions). Flash chromatography (10:1 petroleum ether:Et_2O) removed the nonpolar byproducts, and elution with 100% acetone followed. Concentration of the acetone fractions and recrystallization from hexanes provided ***syn*-13** (0.0780 g, 16%): mp 153−155 °C dec; IR (neat, NaCl) ν_{max} 2098, 2057, 2019, 1636 cm^{-1}; ^1H NMR δ 7.97 (d, J = 7.3, 4H), 7.58 (t, J = 7.4, 2H), 7.45 (apparent t, J = 7.4, 4H), 3.74 (q, J = 6.9, 2H), 1.39 (d, J = 6.9, 6H); ^{13}C NMR 198.5 (br), 193.4, 137.1, 133.4, 128.6, 128.2, 105.1, 88.4, 43.3, 17.2; MS *m/e* 888 ($M^+ + 2$). Anal. Calcd for $C_{34}H_{18}Co_4O_{14}$: C, 46.08; H, 2.05. Found: C, 46.47, H, 1.96.

General Procedure for CAN Decomplexation of Cobalt−alkyne Complexes. To solution of complex **11** (0.4

mmol) and silica gel (2 g) in MeOH, cooled to −78 °C, was added ceric ammonium nitrate (CAN) (0.4 g). The reaction was stirred as the bath temperature was gradually allowed to warm to −20 °C over 2 h. Water was added, and the mixture filtered through Celite. The filtrate was extracted several times with Et_2O, and the combined Et_2O layers were dried over $MgSO_4$ and concentrated under reduced pressure. The pure alkyne **15** was obtained after distillation or preparative TLC (petroleum ether:Et_2O, 2:1).

Methyl 4-(2-Oxocyclohexyl)-2-butynoate (15a). Reaction of **11a** (0.0489 g) with CAN according to the general procedure gave **15a** (0.0177 g, 90%) after preparative TLC (petroleum ether:Et_2O, 2:1): bp 100−105 °C (0.29 torr); IR (neat, NaCl) ν_{max} 2238, 1714 cm^{-1}; ^1H NMR δ 3.72 (s, 3H), 2.74 (dd, J = 4.5, 17.5, 1H), 2.55 (m, 1H), 2.25−2.50 (m, 3H), 2.30 (dd, J = 8.6, 17.5, 1H), 2.09 (m, 1H), 1.90 (m, 1H), 1.55−1.80 (m, 2H), 1.39 (m, 1H); ^{13}C NMR 209.7, 153.9, 87.7, 73.8, 52.4, 48.7, 41.7, 33.3, 27.6, 24.9, 19.0; MS *m/e* 194 (M^+); HRMS *m/e* for $C_{11}H_{14}O_3$ calcd (M^+) 194.0943, found 194.0934.

Methyl 5-Methyl-6-oxo-6-phenyl-2-hexynoate (15b). Reaction of **11b** (0.2361 g) with CAN according to the general procedure gave **15b** (0.757 g, 72%) after preparative TLC (petroleum ether:Et_2O, 2:1): bp 100−105 °C (0.8 torr); IR (neat, NaCl) ν_{max} 2239, 1716, 1683 cm^{-1}; ^1H NMR δ 7.95 (d, J = 7.1, 2H), 7.59 (t, J = 7.2, 1H), 7.48 (apparent t, J = 7.1, 2H), 3.74 (s, 3H), 3.73 (m, obscured, 1H), 2.77 (dd, J = 5.6, 17.5, 1H), 2.57 (dd, J = 8.3, 17.4, 1H), 1.34 (d, J = 7.1, 3H); ^{13}C NMR 201.1, 153.8, 135.3, 133.3, 128.7, 128.3, 87.4, 73.9, 52.4, 39.6, 22.0, 17.6; MS *m/e* 230 (M^+). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.08, H, 6.18.

Methyl 6-(Ethoxycarbonyl)-2-hexynoate (15c). Reaction of **11c** (0.0586 g) with CAN according to the general procedure gave **15c** (0.0195 g, 85%) after preparative TLC (petroleum ether:Et_2O, 2:1): bp 60−65 °C (0.8 torr); IR (neat, NaCl) ν_{max} 2242, 1733, 1716 cm^{-1}; ^1H NMR δ 4.17 (q, J = 7.1, 2H), 3.57 (s, 3H), 2.66 (m, 2H), 2.59 (m, 2H), 1.27 (t, J = 7.1, 3H); ^{13}C NMR 170.9, 153.8, 87.2, 73.1, 60.8, 52.4, 32.1, 14.4, 14.0; MS *m/e* 184 (M^+). Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.90, H, 6.48.

4-(2-Oxacyclohexyl)-1-phenyl-2-butynone (15d). Reaction of **11d** (0.2114 g) with CAN according to the general procedure gave **15d** (0.0863 g, 89%) after distillation: bp 130−135 °C (0.8 torr); IR (neat, NaCl) ν_{max} 2237, 2205, 1712, 1643 cm^{-1}; ^1H NMR δ 8.12 (m, 2H), 7.60 (t, J = 7.4, 1H), 7.49 (m, 2H), 2.91 (dd, J = 4.7, 17.3, 1H), 2.68 (m, 1H), 2.3−2.6 (m, 4H), 2.17 (m, 1H), 1.95 (m, 1H), 1.45−1.85 (m, 3H); ^{13}C NMR 210.0, 178.0, 136.8, 133.9, 129.5, 128.4, 94.6, 80.5, 49.0, 41.8, 33.5, 27.7, 25.0, 19.6; MS *m/e* 240 (M^+). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.83, H, 6.60.

5-Methyl-1,6-diphenyl-2-hexyne-1,6-dione (15e). Reaction of **11e** (0.1862 g) with CAN according to the general procedure gave **15e** (0.782 g, 85%) after preparative TLC (petroleum ether:Et_2O, 2:1): bp 125−130 °C (0.68 torr); IR (neat, NaCl) ν_{max} 2236, 2201, 1683, 1651 cm^{-1}; ^1H NMR δ 8.07 (d, J = 7.2, 2H), 7.99 (d, J = 7.2 2H), 7.4−7.65 (m, 6H), 3.84 (ddq, J = 6.2, 7.6, 7.1, 1H), 2.94 (dd, J = 6.2, 17.3, 1H), 2.75 (dd, J = 7.6, 17.3, 1H), 1.40 (d, J = 7.1, 3H); ^{13}C NMR 201.5, 177.9, 136.7, 135.4, 133.9, 133.4, 129.5, 128.8, 128.44, 128.37, 94.0, 80.6, 39.8, 22.8, 17.9; MS *m/e* 276 (M^+). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.31, H, 6.08.

Ethyl 6-Oxo-6-phenyl-4-hexynoate (15f). Reaction of **11f** (0.1786 g) with CAN according to the general procedure gave **15f** after distillation (0.0754 g, 95%): bp 110 °C (0.1 torr); IR (neat, NaCl) ν_{max} 2238, 2206, 1733, 1650 cm^{-1}; ^1H NMR δ 8.12 (m, 2H), 7.60 (d, J = 7.4, 1H), 7.47 (m, 2H), 4.20 (q, J = 7.1, 2H), 2.83 (m, 2H), 2.69 (m, 2H), 1.28 (t, J = 7.1, 3H); ^{13}C NMR 177.9, 171.1, 136.7, 133.9, 129.5, 128.4, 94.0, 79.7, 60.9, 32.4, 15.0, 14.1; MS *m/e* 230 (M^+). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.43, H, 6.11.

Ethyl 7-Methyl-6-oxo-4-octynoate (15g). Reaction of **11g** (0.1684 g) with CAN according to the general procedure gave **15g** (0.0650 g, 95%) after distillation: bp 105−110 °C (0.39 torr); IR (neat, NaCl) ν_{max} 2214, 1739, 1674 cm^{-1}; ^1H NMR δ 4.18 (q, J = 7.1, 2H), 2.71 (m, 2H), 2.61 (m, 2H), 2.59 (m, obscured, 1H), 1.28 (t, J = 7.1, 3H), 1.17 (d, J = 6.8, 6H); ^{13}C NMR 191.9, 171.0, 92.4, 79.7, 60.8, 42.8, 32.4, 17.7, 14.7, 14.0; MS *m/e* 196 (M^+). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.12, H, 8.22.

Methyl 5-(Ethoxycarbonyl)-4-methyl-2-pentynoate (15j). Reaction of **11j** (0.1733 g) with CAN according to the general procedure gave **15j** (0.0565 g, 99%) after distillation: bp 90−95 °C (0.8 torr); IR (neat, NaCl) ν_{max} 2237, 1732, 1715 cm^{-1}; ^1H NMR δ 4.15 (q, J = 7.1, 2H), 3.74 (s, 3H), 3.08 (m, 1H), 2.59 (dd, J = 7.0, 15.9, 1H), 2.42 (dd, J = 7.5, 15.9, 1H), 1.27 (d, J = 6.9, 3H), 1.25 (t, J = 7.1, 3H); ^{13}C NMR 170.6, 154.0, 91.2, 73.0, 60.8, 52.5, 40.2, 22.5, 19.4, 14.1; MS *m/e* 198 (M+); HRMS for $C_{10}H_{14}O_4$ calcd (M^+) 198.0892, found 198.0896.

4,5-*syn*-4,5-Dimethyl-1,6-diphenyl-2-hexyne-1,6-dione (15l). Reaction of **11l** (0.1786 g) with CAN according to the general procedure sequentially gave ***anti*-15l** (0.0090 g, 16%) and ***syn*-15l** (0.0403 g, 73%) after preparative TLC (petroleum ether:Et_2O, 2:1):

***anti*-15l:** bp 130 °C (0.74 torr); IR (neat, NaCl) ν_{max} 2211, 1681, 1645 cm^{-1}; ^1H NMR δ 8.16 (d, J = 7.0, 2H), 7.99 (d, J = 7.2, 2H), 7.55−7.7 (m, 2H), 7.45−7.55 (m, 4H), 3.64 (dq, J = 8.8, 6.9, 1H), 3.33 (dq, J = 8.8, 6.7, 1H), 1.45 (d, J = 6.9, 3H), 1.33 (d, J = 6.7, 3H); ^{13}C NMR 201.8, 178.1, 136.8, 136.2, 134.0, 133.5, 129.6, 128.9, 128.6, 128.3, 98.1, 81.4, 45.5, 29.7, 19.1, 17.1; MS *m/e* 290 (M^+); HRMS *m/e* for $C_{20}H_{18}O_2$ calcd (M^+) 290.1307, found 290.1300.

***syn*-15l:** bp 130 °C (0.74 torr); IR (neat, NaCl) ν_{max} 2216, 1683, 1645 cm^{-1}; ^1H NMR δ 7.95−8.10 (m, 4H), 7.45−7.70 (m, 4H), 7.36 (apparent t, J = 7.7, 2H), 3.77 (dq, J = 7.4, 7.0, 1H), 3.24 (dq, J = 7.4, 6.9, 1H), 1.37 (d, J = 7.0, 3H), 1.34 (d, J = 6.9, 3H); ^{13}C NMR 201.9, 178.0, 136.8, 136.1, 133.8, 133.3, 129.4, 128.8, 128.4 (2 resonances, incidental overlap), 98.4, 80.1, 45.0, 28.7, 16.5, 14.7; MS *m/e* 290 (M^+); HRMS *m/e* for $C_{20}H_{18}O_2$ calcd (M^+) 290.1307, found 290.1316.

6,1′-*syn*- and 6,1′-*anti*-6-(2-Oxocyclohexyl)-2-methyl-4-heptyn-3-one (15m). Reaction of **11m** (0.1267 g) with CAN according to the general procedure gave **15m** (0.0509 g, 92%) after preparative TLC (petroleum ether:Et_2O, 2:1): bp 100−105 °C (0.19 torr); IR (neat, NaCl) ν_{max} 2208, 1712, 1673 cm^{-1}; ^1H NMR δ 3.18 and 3.14 (m, 1H), 2.5−2.65 (m, 1H), 2.1−2.5 (m, 4H), 2.07 (m, 1H), 1.93 (m, 1H), 1.5−1.85 (m, 3H), 1.21 (d, J = 6.9) and 1.18 (d, J = 7.1)(3H), 1.13 (two doublets, obscured, 6H); ^{13}C NMR 210.0 and 209.4, 192.3 and 192.2, 97.9 and 96.7, 81.0 and 79.7, 54.6 and 53.9, 43.0, 42.2 and 42.0, 31.1 and 29.1, 27.8 and 27.3, 25.4 and 25.1, 24.9, 18.6 and 15.9, 17.9; MS *m/e* 220 (M^+); HRMS *m/e* for $C_{14}H_{20}O_2$ calcd (M^+) 220.1463, found 220.1462.

4,5-*syn*-Methyl 4-Ethyl-5-methyl-6-oxo-6-phenyl-2-hexynoate (15p). To a solution of **11p** (0.1208 g) in acetone (25 mL) was added Me_3NO (0.3 g). The solution was stirred 5 h at ambient temperature, and 3 M $HCl_{(aq)}$ was added. The mixture was partitioned between water and Et_2O and extracted several times with Et_2O. The combined ethereal layers were extracted once with saturated $NH_4Cl_{(aq)}$, dried over $MgSO_4$, and concentrated under reduced pressure. Preparative TLC (petroleum ether:Et_2O) gave **15p** (0.0507 g, 88%): bp 85−90 °C (0.58 torr); IR (neat, NaCl) ν_{max} 2231, 1715, 1683 cm^{-1}; ^1H NMR δ 7.92 (d, J = 6.6, 2H), 7.59 (t, J = 6.6, 1H), 7.48 (m, 2H), 3.72 (m, obscured, 1H), 3.71 (s, 3 H), 2.91 (m, 1H), 1.47−1.74 (m, 2H), 1.27 (d, J = 7.1, 3H), 1.05 (t, J = 7.3, 3H); ^{13}C NMR 201.6, 154.0, 136.2, 133.2, 128.7, 128.3, 90.6, 74.7, 52.4, 43.6, 35.7, 23.0, 14.4, 11.7; MS *m/e* 258 (M^+); HRMS *m/e* for $C_{16}H_{18}O_3$ calcd (M^+) 258.1256, found 258.1255.

Supporting Information Available: ^{13}C NMR spectra of **6d**, **6f**, **6g**, **15a**, **15j**, ***syn*-15l**, ***anti*-15l**, **15m**, **15p** and ORTEP diagram of **11i** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead for ordering information.

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