Mono- and disubstitutions of (hepta-2,5-diyne-1,7-diol) bis(dicobalt) derivatives — Selectivity in Nicholas reactions[1]

Richard Guo, Romelo Gibe, and James R. Green

Abstract: Bis(hexacarbonyldicobalt) complexes of benzyl ether – methyl ether or benzyl ether – acetate derivatives of hepta-2,5-diyne-1,7-diols undergo selective Lewis-acid-mediated Nicholas reactions with enol silanes, silyl ketene acetals, and allylstannanes, preferentially replacing the methyl ether or acetate function. Hydride nucleophiles are similarly incorporated selectively using a benzyl ether – alcohol derivative. Subsequent Nicholas reaction at the benzyloxy-bearing site may be accomplished with an identical or a different nucleophile, affording skipped 1,4-diyne-$Co_4(CO)_{12}$ complexes. In instances of lower selectivity for monosubstitution reactions with benzyl ethers, reverting to the use of a menthyl ether – methyl ether complex gives much improved selectivity for methyl ether substitution.

Key words: cobalt alkyne complexes, Nicholas reaction, Lewis acids, 1,4-diynes.

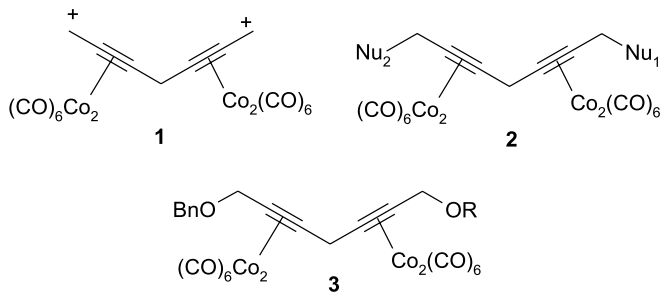
Résumé : Le bis(hexacarbonyldicobalt) forme des complexes avec des dérivés de l'hepta-2,5-diyne-1,7-diol portant un éther benzylique à une extrémité et un éther méthylique ou un acétate à l'autre extrémité qui donnent des réactions de Nicholas, catalysées par un acide de Lewis, avec des silanes énoliques, des acétals de cétènes silylés et des allylstannanes au cours desquelles il se produit un remplacement sélectif de l'éther méthylique ou de la fonction acétate. Les hydrures nucléophiles sont aussi incorporés d'une façon sélective en utilisant un dérivé portant à chaque extrémité un éther benzylique et un alcool. Une réaction de Nicholas subséquente au niveau du site portant le groupe benzyloxy-, réalisée avec un nucléophile identique ou différent, conduit des complexes 1,4-diyne-$Co_4(CO)_{12}$. Dans les cas où la sélectivité est plus faible lors des réactions de monosubstitution avec les éthers benzyliques, l'utilisation d'un complexe avec un dérivé portant un éther menthylique et un éther méthylique à chaque extrémité donne lieu à une sélectivité améliorée pour la substitution de l'éther méthylique.

Mots clés : complexes d'alcynes avec le cobalt, réaction de Nicholas, acides de Lewis, 1,4-diynes.

[Traduit par la Rédaction]

The chemistry of propargylhexacarbonyldicobalt cations, or the Nicholas reaction, has seen extensive use in organic synthesis (1). This interest stems from the predictable regiochemical and stereochemical aspects of the Nicholas reaction, and from the ability of cobalt alkyne complexes to protect the alkyne unit (2), to allow nonconventional alkyne geometries, to participate in synthetically useful cycloaddition reactions (3–5), and to alter the steric size of the formal alkyne function (6).

We have been interested in the use of tandem Nicholas reactions, both of derivatives of butyne-1,4-diol cobalt complexes, and of derivatives of bis(propargyl alcohol) complexes, for a number of synthetic purposes (7). The matter of selectivity where two sites for Nicholas reaction chemistry exist is an important issue, but this has been addressed only on rare occasion in butyne-1,4-diol-$Co_2(CO)_6$ derivatives (7*b*, 8), and not at all in the case of bis(propargyl alcohol)-$Co_4(CO)_{12}$ derivatives (9). Furthermore, substrates that would serve as synthons for skipped bis(propargyl) cations **1** selectively would give rise to 1,4-diyne complexes **2**, which are promising intermediates in the synthesis of compounds with skipped diene, diyne, or enyne functions, such as petrocortynes, petroformynes, and petrosiacetylenes (10), eicosanoids and oxoeicosanoids (11), including several of the leukotrienes (12). Consequently, we deemed the study of the selectivity in Nicholas reactions of **3** to be of importance; we have reported in preliminary form the substitution reactions of **3** and wish to more fully describe our efforts in this area (13).



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Dedicated to Professor Ed Piers for his many contributions to terpene chemistry and the application of organometallic chemistry to organic synthesis.

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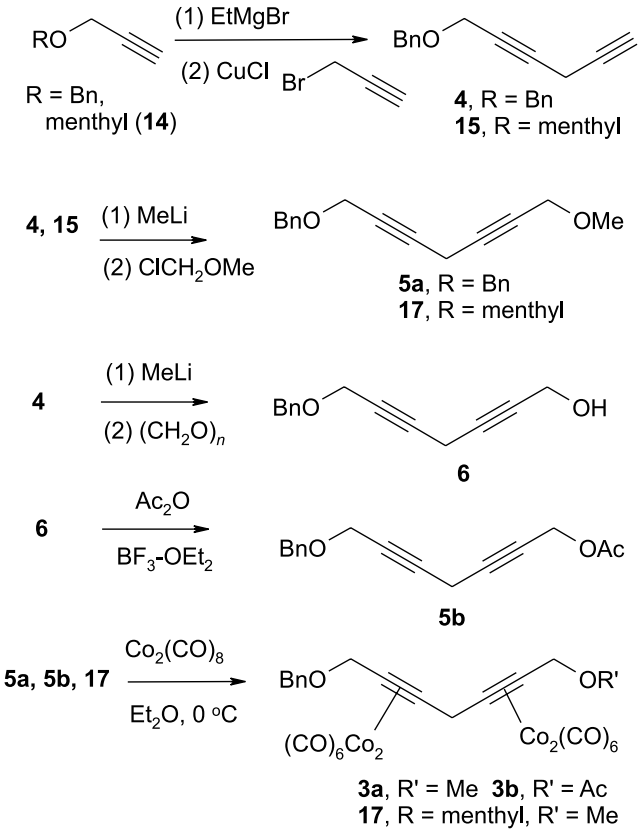
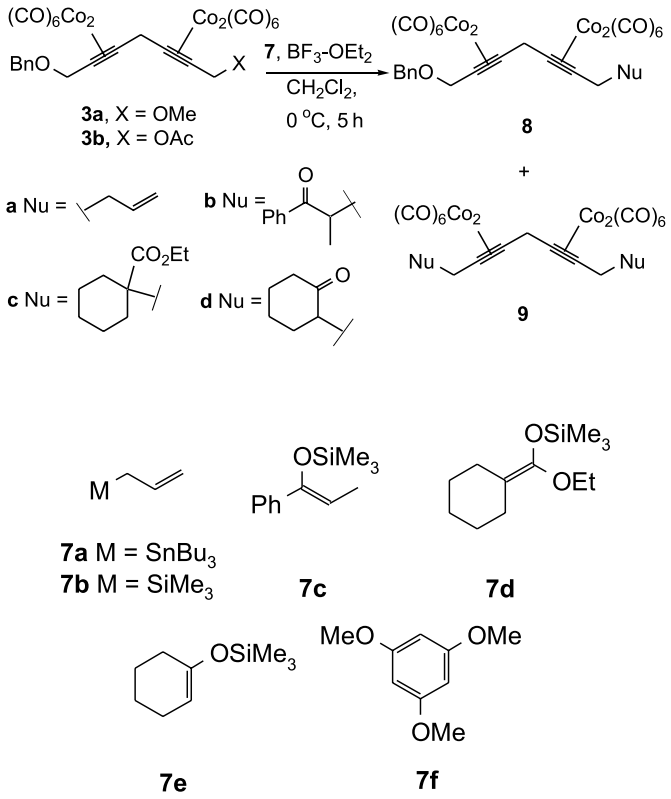
Scheme 1.



Scheme 2.



The requisite heptyne-1,7-diol derivatives were prepared from benzyl propargyl ether (Scheme 1). Copper(I)-catalyzed coupling of the corresponding bromomagnesium acetylide with propargyl bromide afforded diyne **4** (78% yield), which was functionalized in two ways. Deprotonation of **4** with MeLi and exposure of the resultant acetylide to chloromethyl methyl ether gave benzyl methyl diether **5a** (59% yield). Alternatively, treatment of the same lithium acetylide with paraformaldehyde gave ether alcohol **6** (55% yield), and subsequent acetylation with acetic anhydride – BF_3-OEt_2 afforded the benzyl ether acetate **5b** (69% yield). The bis(hexacarbonyldicobalt) complexes of the diynediol derivatives were then prepared in a straightforward manner by subjecting **5a** and **5b** to excess $Co_2(CO)_8$, to give **3a** (77% yield) and **3b** (78% yield), respectively.

With two related substrates in hand, we investigated reactions of **3a** and **3b** with a series of representative nucleophiles, including the allylmetals allyltributylstannane (**7a**) and allyltrimethylsilane (**7b**), propiophenone trimethylsilyl enol ether (**7c**), ethyl cyclohexanecarboxylate trimethylsilyl ketene acetal (**7d**), and cyclohexanone trimethylsilyl enol ether (**7e**), all mediated by BF_3-OEt_2 (Scheme 2).

Allylation of **3a** or **3b** could be accomplished by either allyltributylstannane or allyltrimethylsilane; allyltributyltin, however, proved to be the significantly superior nucleophile for monosubstitution reactions. In the case of methyl ether **3a**, for example, reaction of 1.0 equiv. of BF_3-OEt_2 at 0 °C with 2.0 equiv. allyltrimethylsilane gave **8a** in a 39% yield (80% yield based on recovered starting material), and considerable recovered **3a**. Additional amounts of BF_3-OEt_2 caused greater conversion, but afforded significant amounts of diallylated **9a**. Conversely, allyltributyltin afforded a 63% yield of **8a** (82% based on recovered starting material (brsm) **3a**) in the presence of 2.0 equiv. of BF_3-OEt_2 (0 °C, 2 equiv. allyltributyltin) with more manageable amounts of unreacted **3a** (24%) and **9a** (7.5% yield). With acetate **3b**, reasonable results could be obtained with 1.5 equiv. BF_3-OEt_2 (0 °C, 1.5 equiv. allyltributyltin), giving **8a** (62% yield, 75% yield based on recovered starting **3b**), with 17% recovered **3b** (Table 1).

This necessity to optimize nucleophile – electrophile – Lewis acid stoichiometries in each case proved to be a general requirement with **3a** and **3b** and all nucleophiles, but allowed for satisfactory amounts of monosubstitution products in most cases, normally by stopping at the 80%–90% conversion range. The substitution of silyl enol ether **7c** with **3b** was found to be able to give **8b** in a 64% yield (70% brsm), while silyl ketene acetal **7d** with **3b** gave a 63% yield (70% brsm) of **8c**. Silyl enol ether **7e** proved somewhat less selective, and reactions were terminated at lower conversion levels (60%–70%) to minimize disubstitution. Under these circumstances, acetate **3b** afforded **8d** in 41% (70% brsm), while with methyl ether **3a**, **8d** could be obtained in 43% yield (76% brsm).

Intentional disubstitution reactions were attempted in two cases, using excess BF_3-OEt_2–nucleophile combinations (4 equiv. each). In the case of diallylation of **3a**, allyltributylstannane proved satisfactory, giving **9a** (73% yield) along with 12% of **8a**. Nevertheless, allyltrimethylsilane was superior in this regard, as complete consumption of **3a** occurred to give **9a** in 90% yield. Propiophenone trimethylsilyl enol ether **7c** also was amenable to giving disubstitution,

Table 1. BF_3-Et_2O mediated substitution of benzyl ether complexes.

Entry	Substrate	Nucleophile	Stoichiometry[a]	Product, yield (%)[b]	
1	**3b**	**7b**	1.0/1.5/1.5	**8a**, 62 (75)	
2	**3a**	**7b**	1.0/2.0/2.0	**8a,** 63 (82)	**9a**, 8
3	**3b**	**7c**	1.0/2.0/1.0	**8b**, 64 (70)	**9b**, 6
4	**3b**	**7d**	1.0/2.0/1.0	**8c,** 63 (70)	
5	**3b**	**7e**	1.0/1.2/1.5	**8d,** 41 (56)	
6	**3a**	**7e**	1.0/1.2/1.0	**8d**, 42 (76)	**9d**, 6
7	**3a**	**7a**	1.0/4.0/4.0		**9a**, 90
8	**3a**	**7b**	1.0/4.0/4.0	**8a**, 12	**9a**, 73
9	**3b**	**7c**	1.0/4.0/4.0		**9b**, 70
10	**8a**	**7f**	1.0/2.0/2.0		**10a**, 95
11	**8c**	**7a**	1.0/2.0/2.0		**10b**, 76
12	**11**	Ph_3SnH	1.0/1.5/1.0	**13**, 84	

[a]Ratio of diyne substrate/nucleophile/BF_3-OEt_2.
[b]Yields in parentheses are based on recovered starting material (brsm).

transforming **3b** to **9b** as a 1:1 diastereomeric mixture (70% yield).

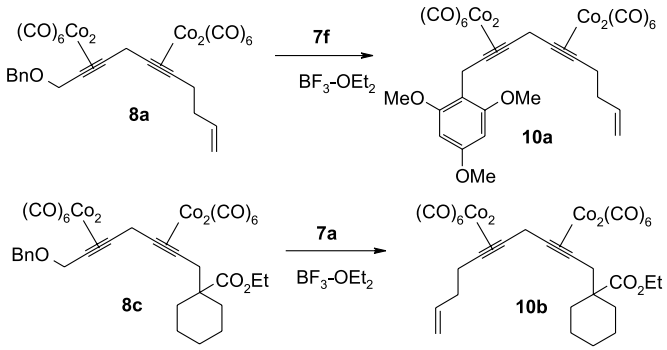
In addition to the persubstitution reactions described above, we wished to determine whether this framework possessed the ability to incorporate two different nucleophiles in disubstitution reactions. For this purpose, we chose allylation product **8a**, by virtue of the low reactivity of the isolated alkene function to many Lewis acid – nucleophile combinations. In the event, **8a** was subjected to reaction with BF_3-OEt_2 and 1,3,5-trimethoxybenzene (**7f**) (2 equiv. each, 0 °C). The benzyloxy function was replaced cleanly, and **10a** could be isolated in 95% yield. Ester-substituted **8c** also was successful in substitution by a second nucleophile, as allyltrimethylsilane and BF_3-OEt_2 (2.0 equiv. each, 0 °C) gave **10b** in 76% yield (Scheme 3).

As a final choice of nucleophile for Nicholas substitution reactions, we also chose to look at a stannane to induce an overall reduction. In this case, we selected substrate **11**, due to the *n*-pentyl group often being present as a (*Z*)-alkene substituent in leukotriene systems, and due to the fact that an alcohol function should be ionizable without destruction of the stannane nucleophile. This compound was prepared from **4**, by trapping of the lithium acetylide with pentanal, and reaction of unpurified alcohol **12** with $Co_2(CO)_8$ to form **11** (44% yield from **4**) (Scheme 4).

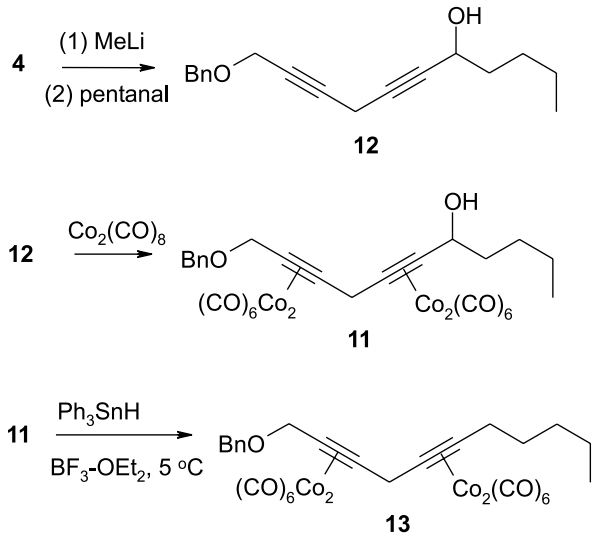
Reduction of **11** with BF_3-OEt_2 and a reactive stannane such as Bu_3SnH and Me_3SnH tended to be unselective, tending to give complete reduction of the alcohol and ether functions. Using the less reactive Ph_3SnH and BF_3-OEt_2 under carefully controlled conditions gave greater selectivity, however. At 5 °C, with 1.5 equiv. Ph_3SnH with 1.0 equiv. BF_3-OEt_2, total selectivity for reduction of the alcohol could be realized, and **13** (84% yield) was isolated as the sole product.

The results in Table 1 demonstrate that, in most cases, the benzyloxy function served as an acceptable potential leaving group which would be retained in monosubstitution reactions in deference to alcohol, methyl ether, or acetate functions. In the cases of allyltrimethylsilane (**7a**) and cyclohexanone silyl enol ether (**7e**) as the nucleophile, the reactions had to be terminated at relatively low levels of conversion and as a result the isolated yields of monosubstitution products **8a** and **8d** were limited. We deemed the selectivity in these cases insufficient, and chose to investigate alternatives that would give greater discrimination between oxygen functions, and hence, greater monosubstitution selectivity. We have observed selectivity in Nicholas reaction-based 4 + 3 cycloaddition chemistry by employing an isopropyl ether as the more slowly ionizing oxygen func-

Scheme 3.



Scheme 4.



tion (7*b*). Due to its straightforward preparation relative to isopropyl propargyl ether (14), we chose instead menthyloxy containing **14** (15) as a starting point. The bromomagnesium acetylide of this propargylic ether was coupled with propargyl bromide to afford diyne **15** (75% yield), which in turn was converted to the menthyl methyl diynyl diether bis(dicobalt) complex **16** by deprotonation and subsequent trapping with chloromethyl methyl ether, and exposure of unpurified intermediate **17** to $Co_2(CO)_8$ (72% yield overall from **15**) (Scheme 1).

With complex **16** in hand, we investigated its reactivity towards allyltrimethylsilane (**7a**) and cyclohexanone trimethylsilyl enol ether (**7e**). With allyltrimethylsilane, the use of near stoichiometric amounts of Lewis acid BF_3-OEt_2 resulted in the recovery of substantial amounts of starting **16**. For example, with even 2 equiv. of BF_3-OEt_2, allyltrimethylsilane (1.5 equiv., 12 h, –10 °C), 31% recovery of **16** was found in addition to **18a** (31%, 54% based on recovered **16**). The amount of conversion increased with further excess amounts of BF_3-OEt_2, and at 4 equiv., **16** was consumed completely and a 71% yield of **18a** was obtained (Scheme 5). Further increased amounts of Lewis acid gave a gradual degradation of product yield.

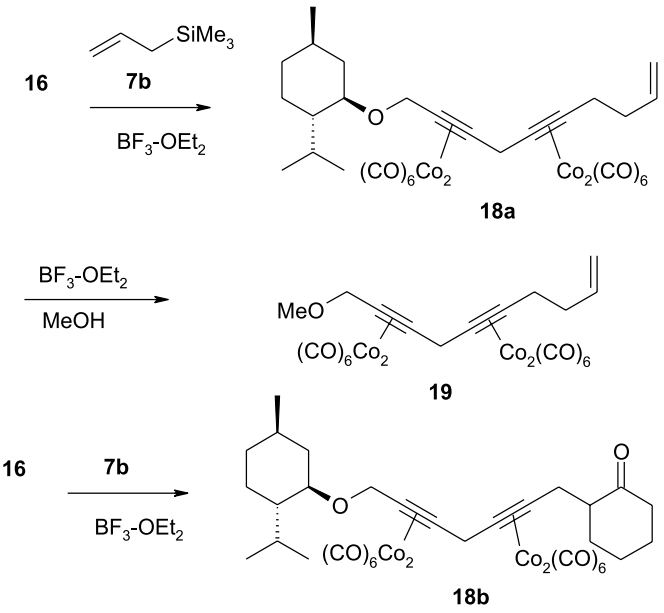
In the case of cyclohexanone trimethylsilyl enol ether (**7e**), an analogous trend was found with increasing amounts of BF_3-OEt_2, but modest amounts of starting material remained even at 4 equiv. (6% **16** recovery, 52% yield of **18b**, 60% yield brsm). In this case, switching the Lewis acid to Bu_2BOTf (1.2 equiv.), in addition to an excess (3 equiv.) of nucleophile gave an improved yield (71%) of **18b**, while greater excesses of this Lewis acid gave near-complete destruction of the product. In the case of **18b**, a new chiral centre was generated. An apparent doubling of the several of signals was apparent in both the ^1H and ^{13}C NMR spectra of **18b**, and integration of the signals showed that **18b** existed as a 1:1 diastereomeric mixture. This was most clearly apparent for ^1H NMR resonances for the diastereotopic propargyl methylene group α- to the ether oxygen, which resonated at 4.851 and 4.847 ppm, and 4.53 and 4.52 ppm for the two diastereomers. Due to the distance between the reacting centre and the nearest centre of chirality, this lack of asymmetric induction was not surprising.

We chose **18a** for study to determine whether the removal of the menthyloxy group was facile. Again, the substrate proved to be relatively sluggish in terms of reaction, but in the presence of 3 equiv. each of BF_3-OEt_2 and MeOH (0 °C, CH_2Cl_2), methoxy-substitution product **19** could be obtained in 65% yield (75% brsm).

A combination of these results with those of ref. 7*b* suggests the following approximate order in the kinetic ionization of oxygen-based functions in Nicholas reactions: OH > OMe, OAc > OBn > O-*i*-Pr, O-menthyl, OTBDMS. The dominant factor in this ordering is most likely steric accessibility to the oxygen atom, although it is likely that inductive effects in the benzyl ether plays some role in reducing its basicity. A lower basicity of the acetate function is also known (16, 17), but is offset by its innately better leaving group ability.

With respect to the nucleophiles concerned, no clear pattern of nucleophile reactivity vs. selectivity has emerged. For example, in the case of allylation, the more reactive allylstannane gives greater selectivity for monosubstitution; by contrast, a less reactive tin hydride (Ph_3SnH vs. Bu_3SnH or Me_3SnH) (18) is more productive in reductions. Nevertheless, by careful choice of conditions and nucleophile, synthetically useful amounts of selective monosubstitution products can be obtained in most cases using the benzyl substrates **3a** and **3b**. Disubstitution reactions of with either two identical or two different nucleophiles can also be accomplished in good to excellent yields. With the poorer cases for **3a** or **3b**, the menthyl ether complex **16** gives very good selectivity for monosubstitution; in fact, the menthoxy group is removed at all only sluggishly.

Scheme 5.



Experimental section

General methods

All solvents were used after distillation from the appropriate drying agent. Diethyl ether and THF were distilled from benzophenone ketyl immediately prior to use. Dichloromethane was distilled from CaH_2 immediately prior to use. Commercial BF_3-OEt_2 was distilled and stored under nitrogen. All reactions were performed under nitrogen unless otherwise noted. Flash chromatography was performed as described by Still et al. (19) using (230–240 mesh) silica gel 60.

NMR spectra were run at 500 MHz or 300 MHz for ^1H, and 125 MHz or 75 MHz for ^{13}C in $CDCl_3$; chemical shifts are given in ppm and coupling constants (*J*) are given in Hz. Mass spectra were run at the Chemistry and Biochemistry Mass Spectrometry Facility, University of Windsor, and the Mass Spectrometry Facility, Wayne State University.

6-Benzyloxy-1,4-hexadiyne (4)

To the freshly prepared EtMgBr (25 mmol) in dry THF (20 mL) was added 3-benzyloxy-1-propyne (3.000 g, 20.00 mmol) over 10 min. After several minutes, the THF began to reflux. When the exothermic reaction had subsided, the flask was warmed for 30 min at 55 °C. The solution was

then cooled to 30 °C and powdered CuCl (60 mg) was added. After 15 min, propargyl bromide (2.2 mL, 20 mmol) was added over 30 min. The mixture was warmed for 1 h to 60 °C. After cooling to room temperature, the reaction mixture was poured into a solution of NH_4Cl (3.0 g) and KCN (100 mg) in water (10 mL). After vigorous shaking, the reaction was subjected to a conventional workup. Flash chromatography (petroleum ether:diethyl ether, 10:1) followed by distillation afforded **4** (1.160 g, 78%); bp 116–120 °C/0.5 torr (1 torr = 133.322 Pa). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3292, 3030, 2856, 1496. ^{1}H NMR δ: 7.35 (m, 5H), 4.62 (s, 2H), 4.20 (t, *J* = 3.4, 2H), 3.26 (m, 2H), 2.13 (t, *J* = 4.5, 1 H). ^{13}C NMR δ: 137.9, 128.8, 128.5, 128.3, 80.4, 78.2, 77.9, 72.0, 69.5, 57.9, 10.1. MS *m/e*: 184 (M^+). HR-MS *m/e* for $C_{13}H_{12}O$ calcd. (M^+): 184.0888; found: 184.0886.

7-Benzyloxy-2,5-heptadiyn-1-ol (6)

To **4** (1.000 g, 5.4 mmol) in dry Et_2O (10 mL) was added MeLi (1.5 mol L^{-1} in Et_2O, 3.6 mL, 5.4 mmol) at –78 °C over 20 min. Thereafter, the solution was warmed to –30 °C and paraformaldehyde (300 mg) was added. After 45 min, the mixture was heated under reflux for 3 h. After cooling to room temperature, the mixture was poured into ice water (10 mL), and a conventional workup performed. Flash chromatography (petroleum ether – diethyl ether, 1:1) followed by distillation afforded **6** (640 mg, 55%); bp 125–129 °C/0.5 torr (1 torr = 133.322 Pa). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3402, 3030, 2914, 2282. ^{1}H NMR δ: 7.27–7.35 (m, 5H), 4.60 (s, 2H), 4.28 (s, 2H), 4.18 (t, *J* = 2.1, 2H), 3.29 (m, 2H), 1.62 (s, 1 H). ^{13}C NMR δ: 137.7, 128.8, 128.5, 128.3, 80.9, 79.8, 79.5, 77.1, 72.1, 57.9, 51.4, 10.4. MS *m/e*: 214 (M^+). HR-MS *m/e* for $C_{14}H_{14}O_2$ calcd. (M^+): 214.0994; found: 214.0990.

1-Acetoxy-7-benzyloxy-2,5-heptadiyne (5b)

To a mixture of compound **6** (1.200 g, 5.60 mmol) and Ac_2O (0.75 mL, 8.4 mmol) in THF (10 mL) was added an excess of BF_3-Et_2O at –78 °C over a period of 20 min. The reaction was warmed to 0 °C, and monitored by TLC. After 1.5 h, when the starting material had disappeared, the reaction mixture was poured into satd. $NaHCO_3$(aq). After a conventional workup, flash chromatography (petroleum ether:diethyl ether, 1:1) afforded product **5b** (985 mg, 69%); bp 108–110 °C/0.5 torr (1 torr = 133.322 Pa). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3030, 2929, 2280, 1722, 1604, 1495. ^{1}H NMR δ: 7.27–7.40 (m, 5H), 4.68 (t, *J* = 2.1, 2H), 4.59 (s, 2H), 4.17 (t, *J* = 2.1, 2H), 3.29 (pentet, *J* = 2.1, 2H), 2.09 (s, 3H). ^{13}C NMR δ:170.0, 137.3, 128.3, 128.0, 127.8, 80.6, 79.8, 76.8, 74.6, 71.6, 57.4, 52.3, 20.6, 9.9. MS *m/e*: 256 (M^+). HR-MS *m/e* for $C_{16}H_{16}O_3$ calcd. (M^+): 256.1099; found: 256.1100.

Dodecacarbonyl[μ^4-(η,η,η,η)(1-acetoxy-7-benzyloxy-2,5-heptadiyne)]tetracobalt (2 Co-Co) (3b)

General procedure for complexation

To a solution of **5b** (1.000 g, 3.90 mmol) in anhyd. Et_2O (20 mL) at 0 °C was added an excess of dicobalt octacarbonyl. After 4 h, the reaction mixture was allowed to warm to room temperature. The resulting mixture was filtered through Celite® and the solvent was removed in vacuo. Flash chromatography (petroleum ether:diethyl ether, 15:1) afforded product **3b** (2.580 g, 78%). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3031, 2922, 2860, 2087, 2034, 1742, 1626. ^{1}H NMR δ: 7.27–7.39 (m, 5H), 5.30 (s, 2H), 4.69 (s 2H), 4.66 (s, 2H), 4.61 (s, 2H), 2.09 (s, 3H). ^{13}C NMR δ: 199.4, 170.5, 137.7, 128.4, 127.7, 127.6, 92.8, 91.5, 91.1, 90.3, 73.1, 69.9, 64.3, 41.0, 20.3. MS (LSI-MS) *m/e*: 827 (M – 1)$^+$, 744 (M – 3CO)$^+$, 688 (M – 5CO)$^+$, 660 (M – 6CO)$^+$. Anal. calcd. for $C_{28}H_{16}Co_4O_{15}$ (%): C 40.61, H 1.95; found: C 40.49, H 1.88.

1-Benzyloxy-7-methoxy-2,5-heptadiyne (5a)

To a solution of compound **4** (480 mg, 2.60 mmol) in dry Et_2O (10 mL) was added MeLi (1.48 mol L^{-1} in Et_2O, 2.2 mL, 3.3 mmol) at –78 °C over 20 min. The mixture was stirred for 30 min at –78 °C. Chloromethyl methyl ether (0.20 mL, 2.60 mmol) was added dropwise over 20 min, and the temperature was then allowed to rise to room temperature. The reaction was kept at room temperature for 2 h. Thereafter, cold water was added and the mixture subjected to a conventional workup. Flash chromatography (petroleum ether:diethyl ether, 10:1) afforded product **5a** (330 mg, 59%); bp: 112–114 °C/0.5 torr (1 torr = 133.322 Pa). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3031, 2929, 2280, 1604, 1495. ^{1}H NMR δ: 7.27–7.37 (m, 5H), 4.60 (s 2H), 4.18 (t, *J* = 2.0, 2H), 4.10 (t, *J* = 2.0, 2H), 3.38 (s, 3H), 3.30 (t, *J* = 2.0, 2H). ^{13}C NMR δ: 137.2, 128.1, 127.7, 127.5, 80.1, 80.0, 76.4, 76.3, 71.2, 59.6, 57.2, 57.1, 9.6. MS *m/e*: 228 (M^+). HR-MS *m/e* for $C_{15}H_{16}O$ calcd. (M^+): 228.1150; found: 228.1155.

Dodecacarbonyl[μ^4-(η,η,η,η)(1-benzyloxy-7-methoxy-2,5-heptadiyne)]tetracobalt (2 Co-Co) (3a)

Compound **5a** (300 mg, 1.32 mmol) was subjected to reaction with $Co_2(CO)_8$ via the general procedure. Flash chromatography (petroleum ether:diethyl ether, 20:1) afforded product **3a** (810 mg, 77%). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3033, 2926, 2087, 2049, 2021. ^{1}H NMR δ: 7.27–7.39 (m, 5H), 4.73 (s, 2H), 4.69 (s, 2H), 4.65 (s, 2H), 4.57 (s, 2H), 3.44 (s, 3H). ^{13}C NMR δ: 199.6, 137.9, 128.4, 127.7, 127.5, 93.1, 92.7, 91.5, 91.2, 73.1, 72.6, 69.8, 58.8, 41.1. MS (EI) *m/e*: 744 (M – 2CO)$^+$, 716 (M – 3CO)$^+$. (LSI-MS) *m/e*: 799 (M – 1)$^+$, 716 (M – 3CO)$^+$, 632 (M – 6CO)$^+$.

Dodecacarbonyl[μ^4-(η,η,η,η)(1-benzyloxy-9-ene-2,5-decadiyne)]tetracobalt (2 Co-Co) (8a)

General procedure for substitution reactions

To a solution of compound **3b** (300 mg, 0.36 mmol) and nucleophile **7b** (179 mg, 0.54 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added freshly distilled BF_3-Et_2O (77 mg, 0.54 mmol) dissolved in CH_2Cl_2 (5 mL) over 30 min. After 5 h, $NaHCO_3$(aq) was added. After a conventional workup, flash chromatography (petroleum ether:diethyl ether, 20:1) afforded product **8a** (183 mg, 62%); a subsequent fraction contained **3b** (50 mg, 16.7%). **8a**: IR (neat, NaCl) (cm^{-1}) ν_{max}: 3033, 2928, 2087, 2040, 1642. ^{1}H NMR δ: 7.27–7.39 (m, 5H), 5.89 (m, 1H), 5.14 (dd, *J* = 1.5, 15.6, 1H), 5.08 (dd, *J* = 1.5, 10.2, 1H), 4.72 (s, 2H), 4.68 (s, 2H), 4.64 (s, 2H), 2.95 (t, *J* = 8.0, 2H), 2.40 (m, 2H). ^{13}C NMR δ: 199.6, 137.8, 136.8, 128.4, 127.8, 127.5, 116.0, 93.8, 93.6, 93.5, 92.6, 73.1, 69.8, 41.2, 35.6, 32.8. MS (EI) *m/e*: 726 (M –

3CO)$^+$, 586 (M – 8CO)$^+$. MS (LSI-MS) *m/e*: 726 (M – 3CO)$^+$, 642 (M – 6CO)$^+$.

From **3a**: To a solution of complex **3a** (200 mg, 0.25 mmol) in CH_2C1_2 (15 mL) was condensed with nucleophile **7b** (166 mg, 0.50 mmol) in the presence of BF_3-Et_2O (71 mg, 0.50 mmol, 2 equiv.) according to the general procedure. After flash chromatography (petroleum ether:diethyl ether, 20:1), **8a** (127 mg, 63%) was obtained, followed by **3a** (47 mg, 23.5%).

From **3a** and **7a**: The reaction of the complex **3a** (200 mg, 0.25 mmol) with **7a** (79 µL, 57 mg, 0.50 mmol) in the presence of BF_3-Et_2O (36 mg, 0.25 mmol, 1 equiv.) according to the general procedure. After flash chromatography (petroleum ether:diethyl ether, 20:1), **8a** (79 mg, 39%) was obtained, followed by **3a** (102 mg, 51%).

Dodecacarbonyl[μ^4-(η,η,η,η)(1-benzyloxy-8-methyl-9-oxo-9-phenyl-2,5-nonadiyne)]tetracobalt (2 Co-Co) (8b)

Complex **3b** (300 mg, 0.36 mmol) was reacted with the nucleophile **7c** (150 mg, 0.72 mmol) in the presence of BF_3-Et_2O (51 mg, 0.36 mmol) via the general procedure. Flash chromatography (petroleum ether:diethyl ether, 10:1) afforded **8b** (208 mg, 64%). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3033, 2934, 2085, 2063, 1990, 1683. ^{1}H NMR δ: 8.04 (d, *J* = 7.7, 2H), 7.27–7.59 (m, 8H), 4.76 (s, 2H), 4.75 (s, 2H), 4.58 (d, *J* = 4.8, 2H), 3.74 (m, 1H), 3.71 (1/2AB, *J* = 11.7, 1H), 2.93 (1/2AB, *J* = 11.7, 1H), 1.37 (d, *J* = 6.7, 3H). ^{13}C NMR δ: 201.7, 199.6, 137.9, 135.5, 133.3, 128.7, 128.3, 127.6, 127.5, 127.4, 97.3, 93.9, 93.0, 91.0, 73.0, 69.8, 43.1, 41.0, 36.1, 19.4. MS (EI) *m/e*: 818 (M – 3CO)$^+$, 762 (M –5CO)$^+$. (LSI-MS) *m/e*: 819 (M + 1 – 3CO)$^+$, 763 (M + 1 – 5CO)$^+$, 735 (M + 1 – 6CO)$^+$. A subsequent fraction contained **3b** (27 mg, 9%).

Dodecacarbonyl[μ^4-(η,η,η,η)(1-benzyloxy-7-(1-ethoxycarbonylcyclohexyl)-2,5-heptadiyne)]tetracobalt (2 Co-Co) (8c)

Compound **3b** was (300 mg, 0.36 mmol) reacted with nucleophile **7d** (150 mg, 0.72 mmol) in the presence of BF_3-Et_2O (51 mg, 0.36 mmol) according to the general procedure. Flash chromatography (petroleum ether:diethyl ether, 15:1) afforded product **8c** (210 mg, 63%). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3033, 2935, 2094, 2086, 2022, 1730. ^{1}H NMR δ: 7.27–7.39 (m, 5H), 4.73 (s, 2H), 4.70 (s, 2H), 4.60 (s, 2H), 4.20 (q, *J* = 7.0, 2H), 3.23 (s, 2H), 1.25–2.17 (m, 13H). ^{13}C NMR δ: 199.7, 175.4, 137.8, 128.4, 127.7, 127.5, 95.2, 93.0, 92.9, 90.9, 73.0, 69.7, 60.6, 48.1, 41.0, 34.6, 25.5, 22.8, 14.0. MS (EI) *m/e*: 840 (M – 3CO)$^+$, 700 (M – 7CO)$^+$. (LSI-MS) *m/e*: 840 (M – 3CO)$^+$, 728 (M – 6CO)$^+$. A subsequent fraction contained **3b** (28 mg, 9%).

Dodecacarbonyl[μ^4-(η,η,η,η)(1-benzyloxy-7-(2-oxocyclohexyl)-2,5-heptadiyne)]tetracobalt (2 Co-Co) (8d)

Complex **3b** (200 mg, 0.24 mmol) was condensed with the nucleophile **7e** (86 mg, 0.29 mmol) in the presence of BF_3-Et_2O (51 mg, 0.36 mmol) via the general procedure. Flash chromatography (petroleum ether:diethyl ether, 10:1) afforded **8d** (85 mg, 41%). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3033, 2933, 2085, 2022, 1716. ^{1}H NMR δ: 7.27–7.39 (m, 5H), 4.75 (s, 2H), 4.72 (s, 2H), 4.64 (s, 2H), 3.58 (m, 1 H), 1.49–2.60 (m, 10H). ^{13}C NMR δ: 210.9, 199.6, 137.9, 128.3, 127.6, 127.5, 98.1, 93.6, 92.9, 91.1, 73.0, 69.8, 53.4, 42.0, 41.2, 35.4, 32.8, 28.2, 25.3. MS (EI) *m/e*: 782 (M – 3CO)$^+$, 642 (M – 8CO)$^+$. (LSI-MS) *m/e*: 782 (M – 3CO)$^+$, 698 (M – 6CO)$^+$. A subsequent fraction contained **3b** (54 mg, 27%).

From **3a**: The complex **3a** (300 mg, 0.37 mmol) also reacted with the nucleophile **7e** (78 mg, 0.44 mmol) in the presence of BF_3-Et_2O (54 mg, 0.38 mmol) via the general procedure. Flash chromatography afforded **8d** (141 mg, 43%), followed by **3a** (130 mg, 43%).

Dodecacarbonyl[μ^4-(η,η,η,η)(trideca-1,12-diene-5,8-diyne)]tetracobalt (2 Co-Co) (9a)

Complex **3a** (200 mg, 0.25 mmol) was condensed with nucleophile **7b** (331 mg, 1.00 mmol) in the presence of BF_3-Et_2O (142 mg, 1.00 mmol) via the general procedure. Flash chromatography (petroleum ether:diethyl ether, 10:1) afforded **9a** (127 mg, 73%). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3085, 2941, 2093, 2022, 1643. ^{1}H NMR δ: 5.94 (m, 2H), 5.17 (dd, *J* = 1.4 Hz, 17.2, 2H), 5.10 (dd, *J* = 1.4, 10.0, 2H), 4.65 (s, 4H), 2.99 (t, *J* = 7.9, 4H), 2.40 (m, 2H). ^{13}C NMR δ: 199.9, 136.8, 116.0, 98.5, 92.6, 41.4, 35.6, 32.8. MS (EI): 716 (M – 1CO)$^+$, 688 (M – 2CO)$^+$. (LSI-MS) *m/e*: 716 (M – 1CO)$^+$, 604 (M – 5CO)$^+$. A subsequent fraction contained **8b** (27.0 mg, 12%)

Under directly analogous conditions, the reaction of complex **3a** (200 mg, 0.25 mmol) with **7a** (0.16 mL, 1.0 mmol) and BF_3-OEt_2 (142 mg, 1.00 mmol) afforded product **9a** (170 mg, 90%).

Dodecacarbonyl[μ^4-(η,η,η,η)(2,10-dimethyl-1,11-diphenylundeca-4,7-diyne-1,11-dione)]tetracobalt (2 Co-Co) (9b)

Complex **3b** (75.1mg, 0.0907 mmol) was condensed with **7c** (74.9mg, 0.363 mmol) in the presence of BF_3-OEt_2 (46 µL, 0.36 mmol) via the general procedure. Flash chromatography (petroleum ether:diethyl ether, 10:1) gave **9b** (59.0 mg, 70%) as a 1:1 diastereomeric mixture. IR (neat, NaCl) (cm^{-1}) ν_{max}: 2093, 2084, 2051, 2017, 1683. ^{1}H NMR δ: 8.03 (d, *J* = 8.0, 4H), 7.57 (t, *J* = 7.6, 2H), 7.48 (apparent t, *J* = 7.7, 4H), 4.56 + 4.46 (AB, *J* = 18.1) and 4.52 (s) (2H), 3.73–3.81 (m, 4H), 2.91–3.03 (m, 2H), 1.41 (d, *J* = 6.5) and 1.39 (d, *J* = 6.5) (6H). ^{13}C NMR δ: 201.7, 199.9 and 199.5, 135.5, 133.29 and 133.28, 128.8, 128.4, 97.4 and 97.3, 93.9 and 93.8, 43.1, 41.0 and 40.9 36.0, 19.6 and 19.4. MS (EI) *m/e*: 844 (M – 3CO)$^+$, 648 (M – 10CO)$^+$. (LSI-MS) *m/e*: 929 (M + 1)$^+$, 844 (M – 3CO)$^+$.

Dodecacarbonyl[μ^4-(η,η,η,η)(1-(2,4,6-trimethoxyphenyl)dec-9-ene-2,5-diyne)]tetracobalt (2 Co-Co) (10a)

Compound **8a** (240 mg, 0.30 mmol) was condensed with 1,3,5-trimethoxybenzene (**7f**) (101 mg, 0.60 mmol) in the presence of BF_3-Et_2O (85 mg, 0.60 mmol) via the general procedure. Flash chromatography (petroleum ether:diethyl ether, 20:1) afforded **10a** (245 mg, 95%). IR (neat, NaCl) (cm^{-1}) ν_{max}: 3007, 2942, 2082, 2045, 2022, 1615. ^{1}H NMR δ: 6.14 (s, 2H), 5.95 (m, 1H), 5.18 (dd, *J* = 1.5, 17.0, 1H), 5.08 (dd, *J* = 1.5, 10.0, 1H), 4.59 (s, 2H), 4.17 (s, 2H), 3.81 (s, 3H), 3.77 (s, 6H), 3.06 (t, *J* = 8.1, 2H), 2.45 (m, 2H). ^{13}C NMR δ: 199.9, 160.5, 158.7, 136.9, 115.8, 108.2, 100.2, 98.4, 93.5, 92.8, 89.9, 55.3, 54.7, 41.2, 35.6, 32.8, 26.0. MS

(EI): 842 (M – 1CO)$^+$, 786 (M – 3CO)$^+$. (LSI-MS) *m/e* 767 (M – 3CO)$^+$, 730 (M – 5CO)$^+$.

Dodecacarbonyl[μ^4-(η,η,η,η)(1-(1-carboethoxycyclohexyl)dec-9-ene-2,5-diyne)]tetracobalt (2 Co-Co) (10b)

Compound **8c** (109.8 mg, 0.119 mmol) was reacted with allyltrimethylsilane (38 μL, 0.24 mmol) and BF_3-OEt_2 (30 μL, 0.24 mmol) via the standard procedure. Flash chromatography (petroleum ether:diethyl ether, 25:1) afforded **10b** (77.6 mg, 76%), as a red-brown oil. IR (neat, KBr) (cm^{-1}) ν_{max}: 2094, 2084, 2048, 2014, 1728. ^{1}H NMR δ: 5.95 (m, 1H), 5.17 (d, *J* = 17.1, 1H), 5.10 (d, *J* = 10.3, 1H), 4.60 (s, 2H), 4.21 (q, *J* = 7.1, 2H), 3.27 (s, 2H), 2.95–3.05 (m, 2H), 2.38–2.50 (m, 2H), 2.12–2.30 (m, 2H), 1.20–1.75 (m, 8H), 1.28 (t, *J* = 7.1, 3H). ^{13}C NMR δ: 199.9, 199.8, 175.4, 136.8, 115.8, 98.5, 95.2, 92.8, 92.6, 60.6, 48.1, 43.8, 41.2, 35.6, 34.6, 32.5, 29.7, 25.6, 22.8, 14.0. MS (EI): 774 (M – 3CO)$^+$, 718 (M – 5CO)$^+$. (LSI-MS) *m/e*: 774 (M – 3CO)$^+$, 718 (M – 5CO)$^+$, 690 (M – 6CO)$^+$.

Synthesis of dodecacarbonyl[μ^4-(η,η,η,η)(1-benzyloxy-7-hydroxy-2,5-undecadiyne)]tetracobalt (2 Co-Co) (11)

To a solution of freshly prepared 6-benzyloxy-1,4-hexadiyne (**4**) (56.4 mg, 3.06 mmol) in THF at –78 °C was added methyllithium (3.06 mL, 1.5 mol L^{-1}, 4.59 mmol). The mixture was stirred for 20 min and freshly distilled pentanal (651 μL, 6.12 mmol) was added dropwise. After stirring for 3 h, the reaction mixture diluted with cold water at 0 °C. Following a conventional workup, the crude product was diluted with diethyl ether and placed in an ice bath. An excess amount of cobalt carbonyl was added and the mixture stirred for 3.5 h. Following removal of the volatiles under reduced pressure, flash chromatography (petroleum ether:diethyl ether, 20:1) gave (**11**) (90.2 mg, 44%) as a red-brown oil. IR (neat) (cm^{-1}) ν_{max}: 3386, 2919, 2012. ^{1}H NMR δ: 7.32 (m, 5H), 4.68 (m, 7H), 2.79 (d, *J* = 5.2, 1H), 1.64 (m, 3H), 1.36 (m, 3H), 0.92 (t, *J* = 7.1, 3H). ^{13}C NMR δ: 199.6, 199.3, 137.0, 128.5, 128.1, 128.0, 102.4, 92.0, 91.3, 91.0, 73.4, 71.5, 70.1, 41.2, 39.2, 28.5, 22.4, 13.9. MS (EI) *m/e*: 758 (M – 3CO)$^+$, 618 (M – 8CO)$^+$. (LSI-MS) *m/e*: 757 (M – 1 – 3CO)$^+$, 617 (M – 1 – 8CO)$^+$.

Dodecacarbonyl[μ^4-(η,η,η,η)(1-benzyloxy-2,5-undecadiyne)]tetracobalt (2 Co-Co) (13)

To a solution of (**11**) (353 mg, 0.41 mmol) and Ph_3SnH (220 mg, 0.62 mmol) in CH_2Cl_2 (10 mL) at 5 °C was added BF_3-Et_2O (53 μL, 0.41 mmol). After stirring for 20 h with regular monitoring by TLC, the reaction mixture was diluted with water and subjected to conventional workup. Flash chromatography (petroleum ether:diethyl ether, 100:1) afforded (**13**) as a red-brown oil (290 mg, 84%). IR (neat) (cm^{-1}) ν_{max}: 2933, 2099. ^{1}H NMR δ: 7.35 (m, 5H), 4.74 (s, 2H), 4.70 (s, 2H), 4.65 (s, 2H), 2.84 (t, *J* = 8.0, 2H), 1.66 (m, 2H), 1.41 (m, 4H), 0.95 (t, *J* = 7.0, 3H). ^{13}C NMR δ: 200.0, 199.5, 137.8, 128.3, 127.7, 127.4, 99.7, 93.0, 92.5, 91.1, 73.0, 69.7, 41.2, 33.3, 31.6, 31.5, 22.3, 13.8. MS (EI) *m/e*: 742 (M – 3CO)$^+$, 658 (M – 6CO)$^+$. MS (ES–) *m/e*: 768.5 (M – 2CO-H)$^-$, 740.5 (M – 3CO-H)$^-$.

(1′*R*, 2′*S*, 5′*R*)- 1-Menthoxy-2,5-heptadiyne (15)

To a freshly prepared solution of EtMgBr (15.0 mmol) in dry THF (20 mL) was added 3-menthyloxy-1-propyne (**14**) (1.464 g, 7.53 mmol) in a cannula under a stream of nitrogen. The solution was heated for 30 min at 60 °C and cooled to room temperature. CuCl was added (74 mg, 0.75 mmol), followed by propargyl bromide (1.67 mL, 18.0 mmol). The solution was heated to reflux for 1 h. A conventional workup and subsequent flash chromatography (100% hexane) afforded (**15**) (1.313 g, 75%) as a colorless oil. $[\alpha]_D^{25}$ –66.9 (*c* 1.17 acetone). IR (neat) (cm^{-1}) ν_{max}: 3312, 2954, 2869. ^{1}H NMR δ: 4.16 (t of 1/2AB, *J* = 2.0, 15.5, 1H), 4.11 (t of 1/2AB, *J* = 1.9, 15.5, 1H), 3.16 (m, 3H), 2.18 (m, 1H), 2.03 (m, 1H), 1.57 (m, 2H), 1.57 (m, 1H), 1.34 (m,1H), 0.70–1.00 (m, 4H), 0.87 (d, *J* = 6.6, 3H), 0.84 (d, *J* = 7.1, 3H), 0.74 (d, *J* = 6.9, 3H). ^{13}C NMR δ: 78.5, 77.78, 77.74, 77.72, 68.8, 55.4, 48.0, 39.7, 34.3, 31.3, 25.2, 23.1, 22.2, 20.9, 16.0, 9.5. MS (EI) *m/e*: 232 (M)$^+$. HR-MS calcd. for $C_{16}H_{24}O$: 232.1827; found: 232.1826.

(1′*R*, 2′*S*, 5′*R*)- Dodecacarbonyl[μ^4-(η,η,η,η)(1-menthoxy-7-methoxy-2,5-heptadiyne)]tetracobalt (2 Co-Co) (16)

To a solution of **15** (1.75 g, 7.50 mmol) in diethyl ether (20 mL) at –78 °C was added MeLi (8.0 mL, 1.40 mol L^{-1}, 11.2 mmol). The solution was then stirred for 20 min, and chloromethyl methyl ether (1.13 mL, 15.0 mmol) was added. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Following a conventional workup, the resulting crude product was dissolved in anhyd. Et_2O (20 mL) and cooled to 0 °C. An excess of cobalt carbonyl was added and the solution stirred for 3.5 h. The resulting crude product was filtered though Celite®, and the resulting filtrate was concentrated under reduced pressure. Flash chromatography (petroleum ether:diethyl ether, 50:1) gave **16** (3.946 g, 72%) as a red-brown oil. $[\alpha]_D^{22}$ +72 (*c* 0.036 acetone). IR (neat) (cm^{-1}) ν_{max}: 2923, 2052. ^{1}H NMR δ: 4.8 (d, *J* = 12.5, 1H), 4.6 (m, 4H), 4.51 (d, *J* = 12.5, 1H), 3.52 (s, 3H), 3.26 (apparent dt, *J* = 4.1, 10.5, 1H), 2.31 (m, 1H), 2.14 (d, *J* = 12.0, 1H), 1.67 (m, 2H), 1.41 (m, 1H), 1.31 (m, 1H), 0.88–1.10 (m, 3H), 0.96 (d, *J* = 6.0, 3H), 0.90 (d, *J* = 7.0, 3H), 0.80 (d, *J* = 6.9, 3H). ^{13}C NMR δ: 199.7, 94.7, 92.7, 91.6, 90.7, 79.3, 72.6, 67.8, 58.8, 48.2, 41.0, 40.3, 34.5, 31.6, 25.3, 23.1, 22.3, 20.8, 15.9. MS (EI) *m/e*: 820 (M – CO)$^+$, 596 (M – 9CO)$^+$. MS (ES+) *m/e*: 691 (M + K – 7CO)$^+$.

(1′*R*, 2′*S*, 5′*R*)- Dodecacarbonyl[μ^4-(η,η,η,η)(1-menthoxydec-9-ene-2,5-diyne)]tetracobalt (2 Co-Co) (18a)

To a solution of **16** (207 mg, 0.244 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added BF_3·Et_2O (144 μL, 1.14 mmol). The solution stirred for 10 min; thereafter, allyltrimethysilane (67 μL, 0.42 mmol) was added and the reaction was continued until none of the starting **16** was detected in TLC analysis (12 h). A conventional workup and subsequent flash chromatography (100% petroleum ether) afforded **18a** (148 mg, 71%) as a red-brown oil. $[\alpha]_D^{22}$ +52 (*c* 0.079 acetone). IR (neat) (cm^{-1}) ν_{max}: 2924, 2085, 2049. ^{1}H NMR δ: 5.94 (m, 1H), 5.17 (d, *J* = 17.0, 1H), 5.10 (d, *J* = 12.1, 1H), 4.82 (d, *J* = 12.4, 1H), 4.65 (s, 2H), 4.50 (d, *J* = 12.4, 1H), 3.24 (apparent dt, *J* = 4.0, 10.5, 1H), 2.99 (m, 2H), 2.42 (m, 2H), 2.29 (m, 1H), 2.11 (br d, *J* = 12.1 1H), 1.63 (m, 2H), 1.30 (m, 1H), 1.28 (m, 1H), 0.85–1.17 (m, 3H), 0.95 (d, *J* = 6.4, 3H), 0.89 (d, *J* = 7.0, 3H), 0.78 (d, *J* = 7.0, 3H). ^{13}C

NMR δ: 199.7, 136.8, 115.9, 98.5, 94.6, 92.9, 90.5, 79.3, 67.8, 48.2, 41.2, 40.2, 35.5, 34.5, 32.8, 31.6, 25.4, 23.1, 22.3, 20.8, 15.9. MS (EI) *m/e*: 802 $(M - 2CO)^+$, 774 $(M - 3CO)^+$. MS (ES+) *m/e*: 795 $(M - 3CO + Na - H_2)^+$, 688 $(M - 6CO + Na - H_2)^+$.

(1′*R*, 2′*S*, 5′*R*)- Dodecacarbonyl[μ⁴-(η,η,η,η)(1-menthoxy-7-(2-oxocyclohexyl)-2,5-heptadiyne)]tetracobalt (2 Co-Co) (18b)

To a solution of **16** (90 mg, 0.12 mmol) and the trimethylsilyl enol ether of cyclohexenone **7e** (62 mg, 0.36 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added Bu_2BOTf (73 μL, 1 mol L^{-1}). The solution was stirred for 3 h, and further Bu_2BOTf (74 μL, 1 mol L^{-1}) was added; stirring was continued until none of the starting **16** was detected in TLC analysis (12 h) (total amount of Bu_2BOTf used: 147 μL, 0.14 mmol). A conventional workup and subsequent flash chromatography (100% petroleum ether) afforded **18b** (70 mg, 71%, de = 0) as a red brown oil. IR (neat) (cm^{-1}) ν_{max}: 2929, 2869, 2085, 2053. ^1H NMR δ: 4.851 (d, *J* = 12.5) and 4.847 (d, *J* = 12.5) (1H), 4.61 (m, 2H), 4.53 (d, *J* = 12.5) and 4.52 (d, *J* = 12.5) (1H), 3.59 (dd, *J* = 6.5, 15.5, 1H), 3.24 (apparent dt, *J* = 4.1, 10.5, 1H), 2.59 (m, 2H), 2.45 (m, 1H), 2.38 (m, 1H), 2.27 (m, 2H), 2.12 (m, 2H), 1.92 (m, 1H), 1.65 (m, 6H), (m, 1H), 0.85–1.15 (m, 3H), 0.95 (d, *J* = 6.6, 3H), 0.88 (d, *J* = 6.9, 3H), 0.77 (d, *J* = 7.2, 3H). ^{13}C NMR δ: 211.0, 199.8, 98.0, 94.7, 94.6, 93.8, 90.4, 79.3, 79.2, 67.7,53.4, 48.2,42.1, 40.2, 35.6, 35.5, 34.5, 32.7, 31.6, 28.2, 25.4, 23.1, 22.3, 20.9, 15.9. MS (EI+) *m/e*: 830 $(M - 3CO)^+$, 718 $(M - 7\ CO)^+$. MS (ES+) *m/e*: 937 $(M + Na)^+$, 909 $(M + Na - CO)^+$.

Dodecacarbonyl[μ⁴-(η,η,η,η)(1-methoxydec-9-ene-2,5-diyne)]tetracobalt (2 Co-Co) (19)

To a solution of **18a** (122 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added BF_3-Et_2O (83 μL, 0.65 mmol). The solution was stirred for 10 min, and MeOH (20 μL, 0.49 mmol) was added. After stirring for 12 h, the crude reaction mixture was subjected to conventional workup. Flash chromatography (100% petroleum ether) afforded **19** (66 mg, 65%, 74% yield based on recovered **18a**) as a red brown oil. IR (neat) (cm^{-1}) ν_{max}: 2922, 2085, 2049. ^1H NMR δ: 5.90 (m, 1H), 5.16 (d, *J* = 17.1, 1H), 5.10 (d, *J* = 10.7, 1H), 4.6 (d, *J* = 11.7, 4H), 3.5 (s, 3H), 2.9 (m, 2H), 2.42 (m, 2H). ^{13}C NMR δ: 199.8, 199.6, 136.8, 115.9, 98.6, 92.7, 92.6, 91.3, 72.6, 58.9, 41.2, 35.5, 32.7. MS (EI) *m/e*: 678 $(M - 2CO)^+$, 650 $(M - 3CO)^+$; (ES–) 733 $(M - H)^-$, 705 $(M - H - CO)^-$, 677 $(M - H - 2CO)^-$, 649 $(M - H - 3CO)^-$. HR-MS (ES–) *m/e* calcd. for $C_{23}H_{14}Co_4O_{13}$: $(M^+ - H - 2CO)$ 676.7786; found: 676.7767. A subsequent fraction contained the starting **18a** (14.8 mg, 12%).

Material on deposit

The ^1H NMR spectra of **4** and **5a** and the ^{13}C NMR spectra of **3a**–**3b**, **5a**–**5b**, **6**, **8a**–**8d**, **9a**–**9b**, **10a**–**10b**, **11**, **12**, **15**, **16**, **18a**–**18b**, and **19** have been deposited as supplementary material.[3]

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[3] Copies of materials on deposit may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council of Canada, Ottawa, ON, K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).

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