Intramolecular Cyclizations of $Co_2(CO)_6$-Complexed Propargyl Radicals: Synthesis of *d*,*l*- and *meso*-1,5-Cyclodecadiynes

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Intramolecular radical cyclizations of $Co_2(CO)_6$-complexed bis-propargyl alcohols **1**−**5** provide an easy, two-step access to the otherwise hardly accessible *d*,*l*- and *meso*-3,4-diaryl-1,5-cyclodecadiynes **21**−**25**. The acid-induced generation of bis-cations **6**−**10** is followed by reduction with a 100-fold excess of zinc, generating key reactive intermediates, i.e. the cobalt-complexed bis-propargyl radicals **11**−**15**. The substitution pattern (0-, 4-, 3,4-, 3,4,5-) and the nature of aromatic substituents (H, i-Pr, OMe) are found essential both to the diastereoselectivity of the process—with *d*,*l*:*meso* ratios varying from 54:46 to 80:20—and the isolability of individual stereoisomers. In particular, an accumulation of methoxy groups on the periphery of the aromatic rings facilitates separation in both intra- and intermolecular reactions. The observed disparity in the level of diastereoselection in intra- and intermolecular reactions is accounted for on the basis of conformational analysis, calculation data for cobalt-complexed propargyl radicals, and the concept of a CH/π coordination. The new knowledge thus acquired has a predicting power, allowing future substrates to be designed, both topologically and stereoelectronically, in a manner favoring either *d*,*l* or *meso* diastereomers.

Introduction

Over the last two decades, the area of *ligand-based organometallic radical chemistry* has risen from relative obscurity to be a recognized research field, ripe for major contributions to the arsenal of organic and organometallic chemistry.[1] Complexation of organic molecules allows the moderation of radical species due to the relative bulkiness of the metal core and also the alteration of their electronic nature by interaction, through space or via bonds, with an orbital system of the transition metal.[1,2] Most importantly, the presence of the clusters allows for generation of radicals which cannot be accessed under conventional "organic" settings[3] and also for control of the chemo-, regio-, and stereoselectivity of radical transformations. To date, the synthetic potential uncovered so far is truly remarkable: a variety of novel methods for inter- and intramolecular radical C−C bond formation readily occurring in a diverse polyfunctional environment have been developed, in a highly selective manner.[1,2,4] Among *radical coupling reactions*, *intermolecular dimerizations* constutite the bulk of the experimental material available so far.[1,2,4,5] Our contribution to this field[6] is best represented by novel methods for generation and coupling of $Co_2(CO)_6$-coordinated propargyl radicals, including the spontaneous conversion[6g,i] of diamagnetic cobalt-complexed propargyl cations to respective radical species, and mediation

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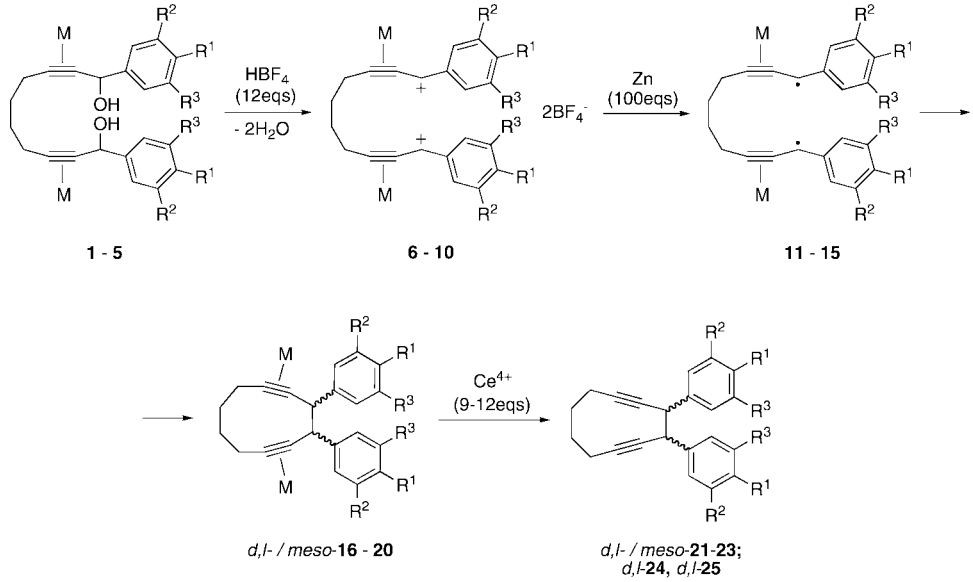
Scheme 1



M = $Co_2(CO)_6$; **1**, **6**, **11**, **16**, **21** $R^1=R^2=R^3=H$; **2**, **7**, **12**, **17**, **22** R^1=i-Pr, $R^2=R^3=H$;
3, **8**, **13**, **18**, **23** R^1=OMe, $R^2=R^3=H$; **4**, **9**, **14**, **19**, **24** $R^1=R^2$=OMe, $R^3=H$; **5**, **10**, **15**, **20**, **25** $R^1=R^2=R^3$=OMe.

with THF which has a remarkable accelerating effect.[6c,e,f,h,i] In *homo-coupling* and *cross-coupling* reactions, the level of stereocontrol achieved (up to 97% *d*,*l*) remains unprecedented for intermolecular organometallic radical dimerizations.[1,2,4] In contrast, *intramolecular radical coupling reactions* mediated by the transition metals remain an uncharted territory.[1,2] Sporadic reports on bis(1,3-pentadienyl)irontricarbonyl complexes[4a,b] describe the exclusive formation of trans-cyclized products, although given the description of the experimental protocol and the nature of analytical methods employed, these claims need to be further validated. In the *cobalt-alkyne series*, formation of the parent 3,4-diphenyl-1,5-cyclodecadiyne, via respective bis-cationic species, was reported in a 51% yield, as a mixture of *d*,*l* and *meso* diastereomers (90:10).[6b] Smaller rings, such as 1,5-cyclononadiyne[6e] and 1,5-cyclooctadiynes,[7] can also be assembled with high *d*,*l* diastereoselectivity (>98%), although isolation of organic products, given their instability, proved to be problematic.[7] Herewith we present the *first systematic account on the diastereoselectivity of the intramolecular coupling of cobalt-complexed bis-propargyl radicals leading to the formation of 10-membered cycloalkadiynes with 1,5-disposed acetylenic bonds.* The current study was undertaken to identify the steric, electronic, and conformational parameters governing the cyclization process and to better understand the impact of aromatic substituents and their topology and electronic nature.

Results and Discussion

The requisite bis-propargyl alcohols **1**−**5** were synthesized by the metalation of 1,7-octadiyne with BuLi and subsequent in situ condensation of the bis-lithium derivative with respective benzaldehydes,[8] followed by the complexation of triple bonds[9] with $Co_2(CO)_8$ (Scheme 1). Treatment with tetrafluoroboric acid[5,10] generates the bis-propargyl cations **6**−**10**, which can be precipitated from ethereal solutions at low temperatures. Given the very nature of intramolecular cyclizations, the radical centers in **11**−**15** have to be generated at a high rate to avoid intermolecular interactions, thermal decomposition, and side reactions, such as H-atom abstraction from the solvent. The bent geometry of cobalt−alkyne units (140–145°), proven by X-ray crystallography studies of the respective alcohols[5,10,11] and doubly stabilized cation,[6d] may also be retained in the requisite radicals, thus bringing propargyl radical centers in closer proximity to each other and facilitating a cyclization step. Empirically, the optimal molar ratio of substrates **1**−**5** and Zn, acting as a reducing agent, was found to be 1:100, a 50-fold excess per propargyl unit. Utilization of lesser quantities of Zn resulted in trace amounts of cyclized products **16**−**20**. Careful experimentation also revealed that the mode of addition of a large (100-fold) excess of zinc can itself affect the diastereoselectivity of the process. An optimized procedure—adding zinc at −50 °C, in one portion, and raising the reaction temperature to 20 °C—allows us to avoid local overheating and provides for reproducible results.

The stereoselectivity data on the cyclization reactions, both in crude mixtures and upon isolation, are summarized in Table 1. By NMR, the highest level of diastereoselection (*d*,*l*-**17**:*meso*-**17** = 80:20) is observed for the bis-cluster **2**, containing an isopropyl group in the para position of the aromatic ring (R^1 = i-Pr; $R^2=R^3=H$). Removal of the aromatic substituent results in a substantial decrease in stereoselectivity: derived from parent substrate **1**, the bis-cluster **16** ($R^1=R^2=R^3=H$), consists of *d*,*l* and *meso* diastereomers in the ratio of 67:33. Not only the topology but also the electronic nature of the substituents appears to be a contributing factor in the cyclization reaction. In substrate **3** (R^1 = OMe, $R^2=R^3=H$), an incorporation of a 4-OMe

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Table 1. Diastereoselectivity of Radical Reactions

substrate	substitution pattern	product	*d*,*l*:*meso*[a]	rel chromatographic mobility	*d*,*l*:*meso*[b]	decomplexed product	*d*,*l*:*meso*
1	0	**16**	67:33	inseparable	68:32	**21**	84:16[e]
2	4	**17**	80:20	inseparable	80:20	**22**	80:20
3	4	**18**	67:33	inseparable	66:34	**23**	73:27
4	3,4	**19**	67:33	separable	*c*	**24**	100:0[d]
5	3,4,5	**20**	54:46	separable	*c*	**25**	100:0[d]
26	3,4,5	**29**	80:20	separable	*c*	**30**	100:0[d]

[a] Diastereomeric ratios of the crude products. [b] Diastereomeric ratios of the isolated cobalt complexes. [c] Pure *d*,*l* and *meso* diastereomers were isolated by chromatographic means. [d] Only individual *d*,*l* diastereomers were decomplexed with ceric ammonium nitrate. [e] *d*,*l*-**16**:*meso*-**16** was equal to 80:20.

group at the aromatic nuclei "failed" to restore the level of *d*,*l* diastereoselectivity (*d*,*l*-**18**:*meso*-**18** = 67:33) observed for 4-isopropyl derivative **17**. The stereoselectivity seems to be indifferent toward the presence of an additional methoxy group ($R^1 = R^2 =$ OMe, $R^3 =$ H; *d*,*l*-**19**:*meso*-**19** = 67:33) but drops sharply with incorporation of the third group ($R^1 = R^2 = R^3 =$ OMe; *d*,*l*-**20**:*meso*-**20** = 54:46). The separability of diastereomeric pairs **16**−**20** is dependent upon the substitution pattern around aromatic nuclei (Table 1). The parent bis-cluster **16**, as well as its 4-substituted derivatives **17** and **18**, exhibited a comparable mobility on inorganic sorbents and could not be fully separated by means of either column or thin-layer chromatography. As Table 1 testifies (columns 4 and 6), the isolation procedures developed were such that the selective decomposition of diastereomers was completely avoided and isomeric compositions in the isolated material were fully representative of the genuine diastereoselectivity determined in crude mixtures. The 3,4-dimethoxy and 3,4,5-trimethoxy derivatives **19** and **20** can be readily separated on Florisil, affording respective *d*,*l* and *meso* diastereomers in homogeneous forms.

The overview of cyclization data (Table 1) allows us to conclude that a level of diastereoselection is dependent upon substituents located on the periphery of the molecule, at the aromatic nuclei. A priori, such an effect was difficult to predict on the basis of either chemical logic or existing literature precedence.[1–5,10] In bis-radicals **11**−**15**, aromatic substituents seem to be quite remote from the reaction site where two propargyl radicals couple and form a new carbon−carbon bond. It is worth mentioning that the common feature for all cyclization reactions studied is the preponderant formation of *d*,*l* diastereomers **16**−**20**. The relative configuration of *d*,*l*-**20** was determined by X-ray crystallography[12] (Figure 1, Tables 2 and 3). The disposition of substituents around the central C21−C22 bond confirms the stereochemical assignment and allows us to assess the amount of strain in the ring system bearing the bulky $Co_2(CO)_6$ cores. The dihedral angle between propargyl H atoms is equal to 127.0° (H21−C21−C22−H22), representing a significant deviation from the typical anti-disposed H atoms in *acyclic d*,*l* isomers (171–180°).[6b,e,f] In contrast to expectations, a smaller—nine-membered—ring of analogous structure[6e] exhibited a lesser degree of distortion (150.8°). All three pairs of substituents around the internal C21−C22 bond are, in fact, nearly eclipsed. The dihedral angle between aromatic rings—C23−C21−C22−C32—is only 0.2°, instead of the anticipated staggered gauche arrangement. In 1,5-

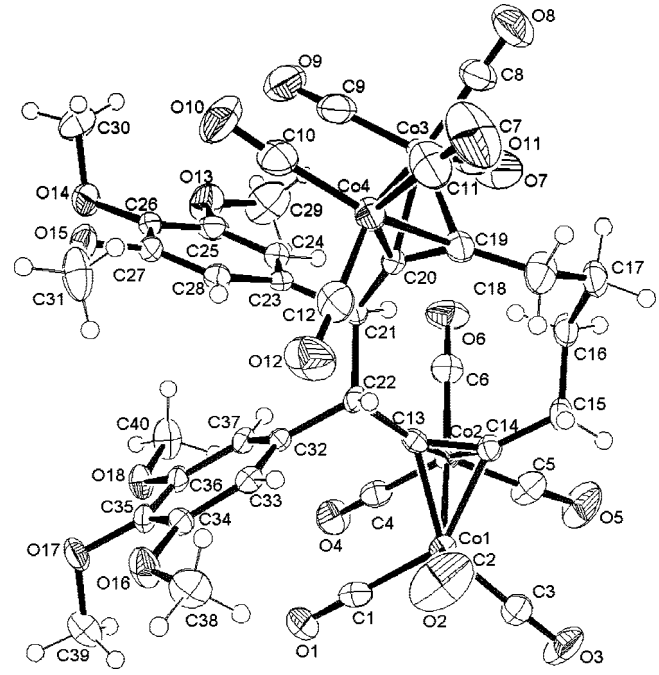

Figure 1. ORTEP diagram of the molecular structure of *d*,*l*-**20** with 30% probability ellipsoids.

cyclononadiyne,[6e] the value of the same dihedral angle is much higher (28.5°), indicating that, unexpectedly, a larger—10-membered—ring is sterically more distorted. For comparison, in *acyclic 1,5-alkadiynes* bearing phenyl[6b,f] or methyl[6e] groups, the observed deviation from an ideal gauche orientation is less significant (44–46°). Analogously, both propargyl bonds are nearly eclipsed with respective C−H bonds (C13−C22−C21−H21 = 12.6°, C20−C21−C22−H22 = 12.6°) further contributing to the torsional strain of the molecule. Perhaps the latter is best manifested by the severely stretched internal bond C21−C22 reaching a high value of 1.597 Å! Metal cores—Co_2C_2—represent the tetrahedrons with a skew geometry where the angles between Co−Co and C−C triple bonds noticeably deviate from the perpendicular arrangement (73.1, 73.4°).[5,10] Other noteworthy structural features of *d*,*l*-**20** include (a) a distorted planarity of alkyne moieties (C22−C13−C14−C15 = 10.4°, C18−C19−C20−C21 = 12.4°) which is less emphasized in *acyclic d,l-1,5-alkadiynes* (0.6–7.7°)[6e,f,i] and even in a smaller—9-membered—ring (3.6, 6.3°),[6e] (b) a lengthened coordinated C−C triple bond (1.33–1.34 Å vs 1.21 Å for the free ligand) reflective of the nature of the bonding between the unsaturated ligand and the transition metal,[5,10] (c) a bent geometry for coordinated alkyne units (140–149°) attendant with coordination to the transition metal and consequent decrease in bond order, (d) inequivalency of alkyne units, with one of them being significantly flatter than the other (C14−C13−C22 = 140.4°, C13−C14−C15=141.0°;C19−C20−C21=145.1°,C20−C19−C18

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Table 2. Summary of the Crystal Structure Data for *d,l*-20

formula	$C_{41}H_{34}Cl_2Co_4O_{18}$
fw	1121.30
temp, K	173(2)
cryst color	dark red
cryst size	0.27 × 0.26 × 0.08 mm^3
wavelength	0.71073 Å
cryst syst	monoclinic
unit cell dimens	
a	22.2291(5) Å
b	19.5356(5) Å
c	21.5056(5) Å
α	90°
β	92.0230(10)°
γ	90°
V	9333.2(4) Å^3
space group	$P2_1/c$
Z	8
D(calcd)	1.596 Mg/m^3
abs coeff	1.583 mm^{-1}
F(000)	4528
θ range for data collecn	1.66−26.37°
index ranges	$-27 \le h \le 27$, $-23 \le k \le 24$, $-26 \le l \le 26$
no. of rflns collected	75 555
no. of indep rflns	19 061 (R(int) = 0.0674)
completeness to $\theta = 26.37°$	99.9%
abs cor	semiempirical from equivalents
max, min transmission	0.8838, 0.6744
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	19 061/0/1183
goodness of fit on F^2	1.031
final R indices ($I > 2\sigma(I)$)	R1 = 0.0699, wR2 = 0.1725
R indices (all data)	R1 = 0.1201, wR2 = 0.2011
largest diff peak, hole	3.215, −1.761 e Å^{-3}

Table 3. Selected Bond Lengths (Å) and Bond and Torsion Angles (deg) for *d,l*-20

Bond Lengths

Co1−Co2	2.464(10)	Co3−Co4	2.464(12)
Co1−C13	1.967(5)	Co3−C19	1.967(6)
Co1−C14	1.961(5)	Co3−C20	1.973(5)
C13−C14	1.341(7)	C19−C20	1.332(8)
Co2−C13	1.991(5)	Co4−C19	1.972(6)
Co2−C14	1.964(5)	Co4−C20	1.988(6)
C13−C22	1.498(7)	C20−C21	1.504(7)
C14−C15	1.492(7)	C18−C19	1.495(8)
C21−C22	1.597(7)		

Bond Angles

C14−C13−C22	140.4(5)	C19−C20−C21	145.1(5)
C13−C14−C15	141.0(5)	C20−C19−C18	148.6(6)

Dihedral Angles

C22−C13−C14−C15	10.4
C23−C21−C22−C32	0.2
C13−C22−C21−H21	12.6
C21−C22−C32−C37	57.9
C22−C21−C23−C28	61.8
Co1−Co2−C13−C14	73.1
C20−C21−C22−C13	101.8
C20−C21−C22−C32	130.1
C18−C19−C20−C21	12.4
H21−C21−C22−H22	127.0
C20−C21−C22−H22	12.6
C21−C22−C32−C33	125.7
C22−C21−C23−C24	118.8
Co3−Co4−C19−C20	73.4
C23−C21−C22−C13	128.4

= 148.6°). Overall, *d,l*-**20**, containing a 10-membered ring with 1,5-disposed metal−alkyne units, appears to be severely distorted, revealing substantial deviations from standard bond lengths and bond and torsional angles.

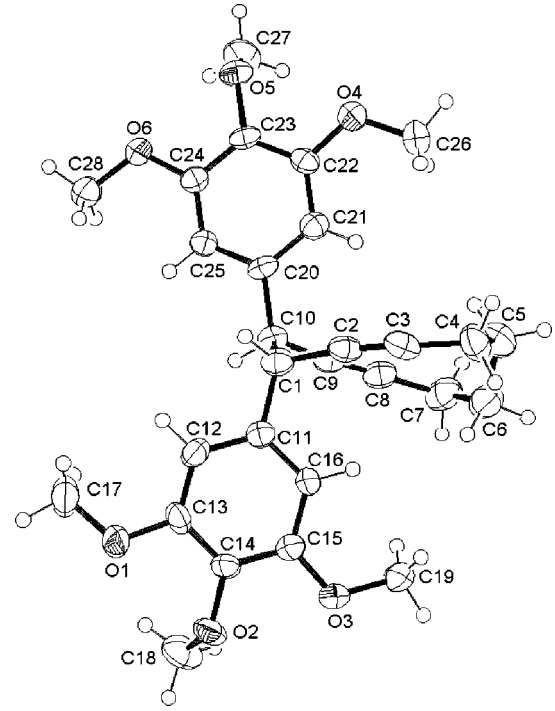


Figure 2. ORTEP diagram of the molecular structure of *d,l*-**25** with 30% probability ellipsoids.

Decomplexation reactions were carried out under oxidative conditions with ceric ammonium nitrate.[5,11] 1,5-Cyclodecadiynes **21**−**25** were isolated and characterized either as an inseparable mixture of *d,l* and *meso* diastereomers (**21**−**23**), or as individual stereoisomers (**24**, **25**). Given the structural delicacy of the requisite bis-clusters **16**−**20** and the sensitivity of organic products **21**−**25**, the experimental protocols were developed under which decomplexation was effected at low temperatures (−78 °C) with an excess of an oxidizing agent (9–12 equiv), followed by workup and isolation under anaerobic conditions (degassed water, NaCl; Florisil, organic solvents). No stereochemical mutations were observed in the course of oxidative removal of the metal cores. Stereochemical assignments were based on the configurations of requisite bis-clusters and also on the NMR signatures of the methyne protons. For diastereomeric mixtures (**21**−**23**), the stereochemical makeup of organic products was either the same as that of the requisite bis-clusters (**22**) or contained lesser concentrations of *meso* diastereomers, by 4–7%, because of the relative instability of the latter compared to that of the *d,l* counterparts (Table 1). To obtain independent proof for the configuration of individual *d,l* diastereomers, the relative configuration of *d,l*-**25** was determined by X-ray crystallography[12] (Figure 2, Tables 4 and 5). The lesser ring strain—due to the removal of bulky $Co_2(CO)_6$ cores—transpires in the staggered arrangement of substituents around the central C1−C10 bond, as opposed to a nearly eclipsed conformation in *d,l*-**20** (Figure 1). The dihedral angle between propargyl H atoms is equal to 79.9° (H1−C1−C10−H10), while endocyclic C−C bonds are disposed at 43.9° (C2−C1−C10−C9). The striking difference between X-ray structures of the bis-cluster *d,l*-**20** and its organic counterpart, *d,l*-**25**, is the disposition of aromatic rings. In the former, the presence of bulky metal cores forces aromatic rings into a nearly eclipsed spatial arrangement (Figure 1; C23−C21−C22−C32 = 0.2°), while in the latter, partially relieved from a steric burden due to the removal of metal cores, the aromatic rings move into an anti arrangement toward each other (Figure 2; C11−C1−

Table 4. Summary of the Crystal Structure Data for *d,l*-25

formula	$C_{28}H_{32}O_6$
fw	464.54
temp	173(2) K
cryst color	pale yellow
cryst size	0.14 × 0.12 × 0.07 mm^3
wavelength	0.710 73 Å
cryst syst	monoclinic
unit cell dimens	
a	6.9725(13) Å
b	9.5826(17) Å
c	36.815(7) Å
α	90°
β	91.424(8)°
γ	90°
V	2459.0(8) $Å^3$
space group	$P2_1/n$
Z	4
D (calcd)	1.255 Mg/m^3
abs coeff	0.087 mm^{-1}
F(000)	992
θ range for data collecn	2.20−26.47°
index ranges	$-8 \le h \le 8$, $-11 \le k \le 11$, $-46 \le l \le 25$
no. of rflns collected	19 450
no. of indep rflns	5017 (R(int) = 0.1737)
completeness to $\theta = 26.47°$	98.9%
abs cor	semiempirical from equivalents
max, min transmissn	0.9939, 0.9879
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	5017/0/313
goodness of fit on F^2	1.017
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0870, wR2 = 0.1380
R indices (all data)	R1 = 0.2470, wR2 = 0.1817
largest diff peak, hole	0.238, −0.244 e $Å^{-3}$

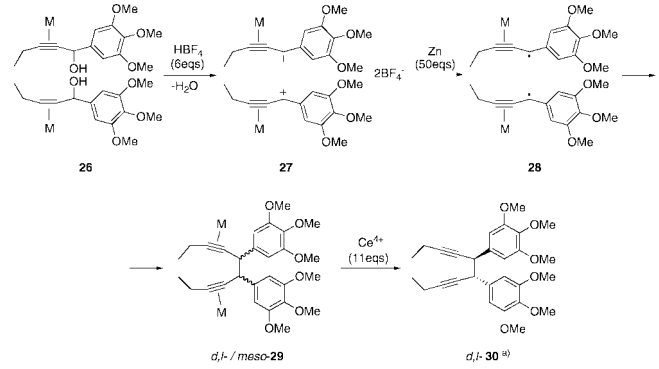
Table 5. Selected Bond Lengths (Å) and Bond and Torsion Angles (deg) for *d,l*-25

Bond Lengths			
C1−C10	1.576(6)	C5−C6	1.538(6)
C2−C3	1.173(6)	C8−C9	1.189(6)
Bond Angles			
C3−C2−C1	167.5(5)	C2−C3−C4	170.9(5)
C8−C9−C10	167.3(5)	C9−C8−C7	172.7(6)
Dihedral Angles			
C1−C2−C3−C4		23.0	
C2−C1−C10−C9		43.9	
C11−C1−C10−C9		77.5	
C11−C1−C10−C20		158.3	
C7−C8−C9−C10		22.0	
H1−C1−C10−H10		79.9	
C2−C1−C10−C20		80.2	
C11−C1−C10−H10		39.6	

C10−C20 = 158.3°). Other noteworthy structural features of *d,l*-**25** include (a) a significant deviation from planarity in alkyne moieties (C1−C2−C3−C4 = 23.0°, C7−C8−C9−C10 = 22.0°), even more enhanced than in the bis-cluster *d,l*-**20** (10.4, 12.4°), and (b) inequivalency of bond angles in alkyne units, with those closer to the four-carbon tether having a higher value (C3−C2−C1 = 167.5°, C8−C9−C10 = 167.3°; C2−C3−C4 = 170.9°, C9−C8−C7 = 172.7°).

To gain more insight into the stereoelectronic and conformational parameters governing the stereoselectivity of intramolecular cyclizations, an *intermolecular radical coupling* was studied with the Co-complexed propargyl alcohol **26**, an *acyclic* and *isocarbon analogue* of the 3,4,5-trimethoxy derivative **5**. The specific aim was to *determine the impact of the tether* by comparing the diastereoselectivity of the intermolecular reaction with that of the intramolecular cyclization. In other words, to

Scheme 2



what extent could the conformational rigidity—attendant with the tethering of reacting propargyl termini—influence the level of stereocontrol in radical cyclizations. Propargyl alcohol **26** was treated with HBF_4 (6-fold excess, −20 °C), and upon isolation, the bis-cation **27** was reduced, at −50 °C, with a 50-fold excess of zinc, thus mimicking conditions of the intramolecular cyclization reaction (Scheme 2). From NMR data, radicals **28** dimerized with an enhanced stereoselectivity, affording *d,l*- and *meso*-**29** in the ratio of 80:20 (Table 1). Both stereoisomers were readily isolated in a homogeneous form with the major one being decomplexed, under oxidative conditions, to yield *d,l*-**30**.

The very fact that an intermolecular radical reaction could exhibit better stereoselectivity than its intramolecular variant is counterintuitive and is not consistent with literature precedents.[3,13] The incorporation of a carbon tether between two reactive sites restricts conformational freedom and brings reacting termini into a closer proximity to each other, thus positively impacting the stereochemical outcome of the reaction. Among representative examples are pinacol coupling, affording acyclic *threo- and erythro*-diols with low diastereoselectivity in intermolecular reactions (de 0–40%), and cyclic *threo*-diols with an excellent stereoselectivity (de 82–100%) in intramolecular cyclizations.[13a] The trend is further corroborated with [4 + 2] cycloadditions of nitroalkenes to olefins[13b] and electrooxidative alkylation of ethers.[13c] Shortening the tether is also proven to be a valuable tool in affecting the diastereoselectivity of cyclization reactions (de 90% vs 40%).[13d]

Conformational analysis of the bis-propargyl radicals **11**−**15** identifies three alternative orientations for the converging propargyl moieties (Figures 3 and 4). The *d,l* diastereomers **16**−**20** can be best formed from structure **A** (Figure 3), having eclipsed cobalt−alkyne units and a pair of H atom/Ar ring overlaps. Given the length of a four-carbon tether and bent geometry of propargyl moieties complexed to the metal core, the conformational flexibilities in structure **A** are severely limited. Consequently, the alternative orientations **B** and **C**, also leading to *d,l* diastereomers **16**−**20**, cannot materialize, a notion corroborated by molecular modeling studies. The conformational profile is analogous for *meso* diastereomers **16**−**20** (Figure 4): three alternative conformations can be envisioned—**D**, **E**, and **F**—with the former being the least constrained. Having identified

(13) (a) Yamamoto, Y.; Hattori, R.; Miwa, T.; Nakagai, Y.; Kubota, T.; Yamamoto, C.; Okamoto, Y.; Itoh, K. *J. Org. Chem.* **2001**, *66*, 3865. (b) Denmark, S. E.; Kesler, B. S.; Moon, Y. C. *J. Org. Chem.* **1992**, *57*, 4912. (c) Yoshida, J.; Sugawara, M.; Tatsumi, M.; Kise, N. *J. Org. Chem.* **1998**, *63*, 5950. (d) Spino, C.; Rezaei, H.; Dupont-Gaudet, K.; Belanger, F. *J. Am. Chem. Soc.* **2004**, *126*, 9926. See also: (e) Jung, M. E.; Rayle, H. L. *J. Org. Chem.* **1997**, *62*, 4601.

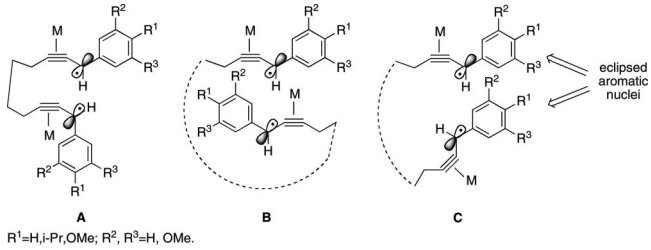


Figure 3. Eclipsed conformations forming *d*,*l* diastereomers **16**–**20**.

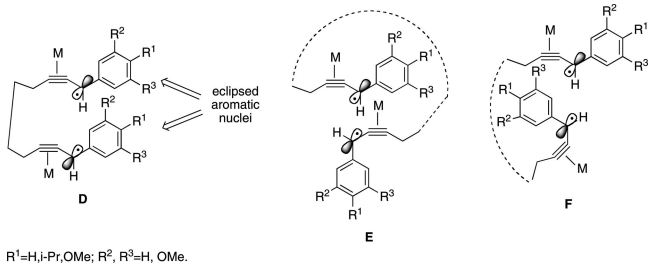


Figure 4. Eclipsed conformations forming *meso* diastereomers **16**–**20**.

two most favorable conformations for tethered propargyl radicals—**A** and **D**—it can be postulated that the diastereoselectivity observed for the unsubstituted 1,5-cyclodecadiyne **16** (*d*,*l*:*meso* = 67:33; Table 1) is reflective of the relative stabilities of converging radical species, with conformation **A** being energetically more preferred. The most noticeable feature of conformation **D** is the presence of *eclipsing aromatic rings* that can be a factor in determining its conformational stability. Its destabilizing effect may be caused by through-space repulsion between bulky aromatic substituents (R^1, R^2, R^3) or the same polarity, negative electronic clouds ("*face-to-face*" *stacking*).[14a–c] To the contrary, the stabilization may occur due to the *CH/π coordination* ("*slipped parallel*" *stacking*)[14b–d] between partially positive H atoms and the electron density over the aromatic nuclei. To establish if the repulsion between aromatic rings can affect the diastereoselectivity of the process—by decreasing the concentration of the respective *meso* diastereomers—semiempirical studies[15] were carried out for cobalt-complexed propargyl radicals **G**−**K** (Figure 5). The charges over the carbon atoms and radical centers allow us to assess the impact of the substituents upon electronic distribution and also provide the total charges over the aromatic nuclei. As numerical data suggest, an incorporation of an isopropyl group into the para position somewhat decreases the negative charge of the aromatic ring (**G**, −0.563 425; **H**, −0.526 483). Analogously, consecutive replacement of H atoms with methoxy groups in 4-, 3,4-, and 3,4,5-positions further lowers the negative charge, from −0.503 761 (**I**), via −0.279 558 (**J**), to −0.238 713 (**K**). Careful comparison of the cyclization and calculation data (Table 1, Figure 5) allows us to conclude that *there is no concurrent change in the level of diastereocontrol and negative charges*

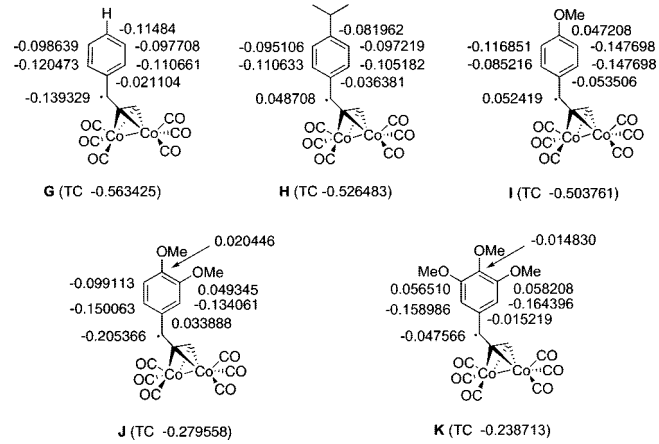


Figure 5. Charge distribution and total charges (TC) of the aromatic rings derived from PM3 calculations.

on the aromatic nuclei. For example, the stereoisomeric ratio remains the same for 4-methoxy and 3,4-dimethoxy derivatives **18** and **19** (*d*,*l*:*meso* = 67:33; Table 1), while the negative charge of the ring decreases significantly, from −0.503 761 (**I**) to −0.279 558 (**J**) (Figure 5). An increased amount of *meso* diastereomer in the 3,4,5-derivative **20**—*d*,*l*:*meso* = 54:46—can hardly be explained by an incremental decrease in the negative charge, from −0.279 558 (**J**) to −0.238 713 (**K**). Analogously, an improved diastereoselectivity in the 4-i-Pr derivative **17** (*d*,*l*:*meso* = 80:20) is hard to interpret by using the total charge as a main stereodirecting factor, since an aromatic ring in conformation **H** is less negative than that in parent species **G** (−0.526 483 vs −0.563 425).

The totality of these data indicate that while a negative charge of aromatic nuclei, and, attendant with it, the destabilizing repulsion between them (conformation **D**; Figure 4), can still be a contributing factor, the stereochemical outcome of intramolecular cyclizations is determined by other structural and electronic parameters. It is conceivable that a purely steric factor is the reason for an increased diastereoselectivity observed for 4-i-Pr derivative **17** (*d*,*l*:*meso* = 80:20; Table 1). When R^1 = i-Pr (Figure 4), an increased bulkiness of the substituents in the para positions of eclipsed aromatic rings by 71.5 Å^3 per isopropyl group (PCModel) could destabilize conformation **D**, leading to *meso* diastereomer **17**, and trigger a rotation around a propargyl bond, thus converting conformation **D** into **A**, leading to *d*,*l* diastereomer **17**.

Diastereoselectivity data for the 3,4,5-trimethoxy derivative **20** could be accounted for on the basis of CH/π-stacking coordination.[14a–d] It is a well established fact that a $C^{-\delta}-H^{+\delta}$ bond can coordinate to the face of the aromatic ring, which represents a negative end of the electric quadrupole moment.[14a–c] Although, in energetic terms, it is a weak inter or intramolecular interaction, it has a profound effect on molecular recognition, selectivity of organic reactions, stability of inclusion complexes, three-dimensional structure of proteins, and topology of protein–ligand complexes.[14b,c] The nature of the C−H bond, a soft acid, capable of coordinating with the centroid of the aromatic ring, a soft base, can be as diverse as that in methane,[14b] ethane,[14c] acetylene,[14b,c] benzene,[14a,b] methyl,[14b] methylene,[14b] or isopropyl[14c] groups. Most relevant to the current context are the reports in which OMe groups, acting as electrophiles, coordinate weakly polar C−H bonds with the aromatic moieties.[14d–f] By X-ray data, a more efficient interaction is observed in case of the aromatic ring bearing three MeO-groups of various topology (2,4,6-,[14d,e] 1,3,5-[14f]). Depicted in Figure 6

(14) (a) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593. (b) Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665 and references cited therein. (c) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem.* **2003**, *42*, 1210 and references cited therein. (d) van de Velde, C. M. L.; Chen, L. J.; Baeke, J. K.; Moens, M.; Dieltiens, P.; Geise, H. J.; Zeller, M.; Hunter, A. D.; Blockhuys, F. *Cryst. Growth Des.* **2004**, *4*, 823. (e) Wallet, J. C.; Molins, E.; Miravitlles, C. *Acta Crystallogr.* **2001**, *E57*, o1073. (f) Wolska, I.; Poplawski, J.; Lozowicka, B. *Pol. J. Chem.* **1998**, *72*, 2331. See also: (g) Gallivan, J. P.; Dougherty, D. A. *Org. Lett.* **1999**, *1*, 103.

(15) Titan; Wavefunction, Inc. All geometries were optimized at the PM3 level.

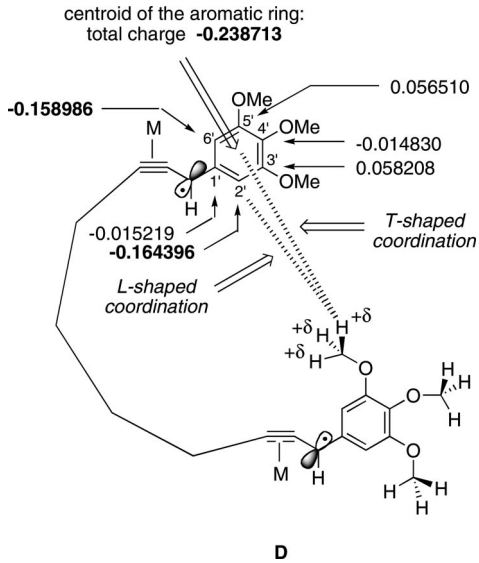


Figure 6. Incorporation of three methoxy groups stabilizing conformations **D** due to CH/π-coordination.

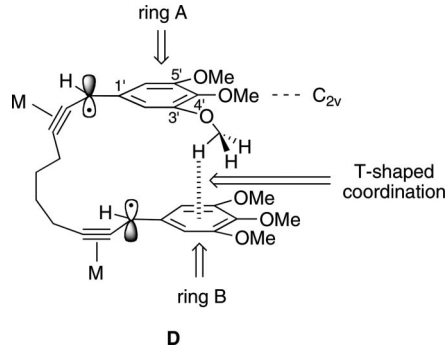


Figure 7. The CH/π-coordination stabilizing conformation **D** and leading to *meso* diastereomer **20**.

is the conformation **D** (Figure 4), leading to *meso* diastereomer **20**, wherein the atom charges over the aromatic ring, as well as the total charge are shown. In the presence of three methoxy groups, the 3′-, 4′-, and 5′-carbon atoms appear to be nearly neutral (C3′, 0.058 208; C4′, −0.014 830; C5′, 0.056 510), while C2′ and C6′ atoms gather significant electron density (−0.164 396, −0.158 986) (Figures 5 and 6). Thus, the coordination with H atoms of the methoxy groups, in a CH/π mode, could occur either with C2′/C6′ carbon atoms (*L-shaped coordination*[14b]) or with the centroid of the benzene ring (*T-shaped coordination*[14b]), the negative end of the electric quadrupole moment (TC, −0.238 713; Figure 5). An alternative way to depict a CH/π coordination that stabilizes conformation **D** is shown in Figure 7. The 3′-methoxy group of ring A, an electrophile, can coordinate in a T-shaped mode[14b,d] with the center of ring B, a nucleophile, with both aromatic rings being shifted away from each other in order to avoid a destabilizing face-to-face repulsion. It is conceivable that the stabilizing CH/π-coordination leading to *meso* diastereomers is the most effective in the 3,4,5-trimethoxy bis-radical **15** (Scheme 1) because of its substitution pattern. The presence of a C_{2v} symmetry axis allows for coordination to occur in any of two conformations around the benzylic bond (Figure 7). In contrast, in the 3′,4′-dimethoxy derivative **14** (Scheme 1) the rotation around the benzylic bond can disrupt the coordination in question, thus lowering the concentration of the respective *meso* diastereomer (Table 1: **19**, *d*,*l*:*meso* = 67:33; **20**, *d*,*l*:*meso* = 54:46). Conformational analysis and the concept of CH/π coordination also allow us to interpret the diastereoselectivity observed in *intermolecular* radical coupling, leading to the acyclic 1,5-alkadiyne **29** (Scheme 2, Table 1: *d*,*l*:*meso* = 80:20). A pair of converging propargyl radicals (**L**, Figure 8), in comparison to its tethered analogue **A** (Figure 3), will be inferior in its stability due to the repulsion between terminal methyl groups. Rotation around a benzylic bond will allow the radicals to facilitate reapproachment by distancing methyl groups, and metal cores, from each other. Upon rotation, the converging radical pair **M** will preserve a slipped parallel stacking between aromatic rings and give rise to the *d*,*l* diastereomer **29** (Figure 8).

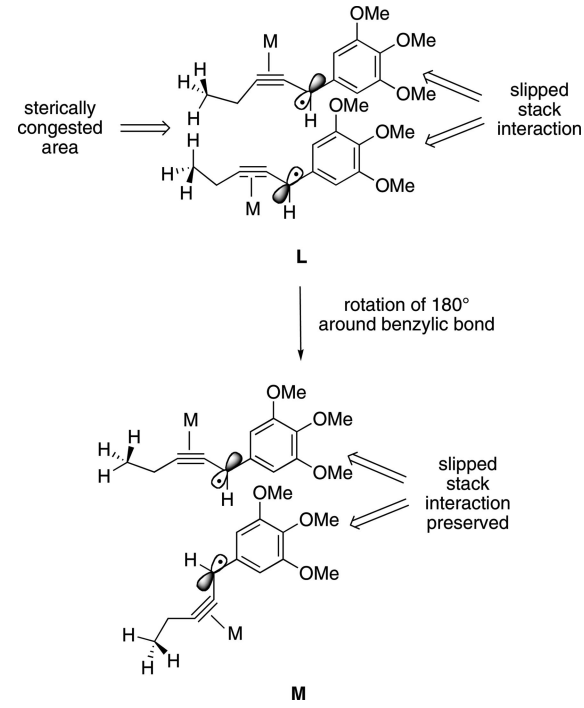


Figure 8. Eclipsed conformations forming *meso* and *d*,*l* diastereomers **29**.

Medium-sized ring closures of diacetylenes are synthetically challenging; therefore, only a few examples of *symmetrical* 1,5-cyclodecadiynes have been reported.[16] The *parent* 1,5-cyclodecadiyne was prepared via thermolysis of selenadiazoles[16a] and lithium-initiated ring closure of α,ω-dichlorides[16b] in low yields (1.9%, eight steps;[16a] ~4.6%, three steps[16b]). The 3,4-dihydroxy derivative of 1,5-cyclodecadiyne was synthesized by different methods,[16c–g] varying in their efficiency and stereochemical outcome (two to seven steps; 0.9–40%). Most importantly, the methodologies developed for 3,4-dihydroxy-1,5-cyclodecadiyne are inherently limited in scope by utilizing unstable propargyl dialdehydes as substrates.[16e,f] To the best of our knowledge, there are no alternative methods for the preparation of the reported 3,4-diaryl-1,5-cyclodecadiynes **21**−**25**, or their structural analogues. This class of compounds is synthetically and medicinally relevant because the aromatic nuclei allow for the introduction of a multitude of substituents with a variety of

(16) (a) Gleiter, R.; Kratz, D.; Schafer, W.; Schehlmann, V. *J. Am. Chem. Soc.* **1991**, *113*, 9258. (b) Haberhauer, G.; Roers, R.; Gleiter, R. *Tetrahedron Lett.* **1997**, *38*, 8679. (c) Semmelhack, M. F.; Gallagher, J. *Tetrahedron Lett.* **1993**, 4121. (d) Boss, C.; Keese, R. *Tetrahedron* **1997**, *53*, 3111. (e) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1992**, *114*, 5859. (f) Klein, M.; Zabel, M.; Bernhardt, G.; König, B. *J. Org. Chem.* **2003**, *68*, 9379. (g) Pitsch, W.; Klein, M.; Zabel, M.; König, B. *J. Org. Chem.* **2002**, *67*, 6805.

substitution patterns, thus generating 1,5-cyclodecadiynes which may serve as precursors to their respective enediynes, potential anticancer agents.[17]

Conclusion

The intramolecular cyclization of cobalt-complexed propargyl radicals represents a viable synthetic approach to otherwise hardly accessible *d*,*l*- and *meso*-3,4-diaryl-1,5-cyclodecadiynes. Diastereoselectivity—*d*,*l*:*meso* ratio—varies in the range of 54:46 to 80:20, with the separability of individial stereoisomers being dependent upon the nature of substituents and their substitution pattern. In particular, an accumulation of methoxy groups on the periphery of the aromatic rings facilitates the separation in both intra- and intermolecular reactions. Calculation data indicate that a negative charge over the aromatic ring and, attendant with it, an electrostatic repulsion between nuclei are not the main determinants of stereochemical outcome of the cyclization reactions. The concept of CH/π coordination is invoked to interpret diastereoselectivity data for 3,4,5-trimethoxy derivatives, which favors the *meso* stereoisomer in *intra*molecular cyclizations and, in contrast, facilitates the formation of the *d*,*l* counterpart in *inter*molecular coupling reactions. The knowledge thus acquired has a predicting power, allowing future substrates to be designed, both topologically and stereoelectronically, in a manner favoring either *d*,*l* or *meso* diastereomers.

Experimental Section

All manipulations of air-sensitive materials were carried out in flame-dried Schlenk-type glassware on a dual-manifold Schlenk line interfaced to a vacuum line. Argon and nitrogen (Airgas, ultrahigh purity) were dried by passing through a Drierite tube (Hammond). All solvents were distilled before use under dry nitrogen over appropriate drying agents (ether, THF, from sodium benzophenone ketyl; CH_2Cl_2, from CaH_2; benzene, from sodium). All reagents were purchased from Sigma-Aldrich and Acros and used as received. $Co_2(CO)_8$ and $Ce(NH_4)_2(NO_3)_4$ were purchased from Strem. NMR solvents were supplied by Cambridge Isotope Laboratories. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 (^{1}H, 400 MHz) spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported relative to tetramethylsilane. Spin–spin coupling constants (*J*) are given in hertz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Melting temperatures (uncorrected) were measured on a Mel-Temp II (Laboratory Devices) apparatus and Optimelt Automated Meltemp. Silica Gel S735-1 (60–100 mesh; Fisher) was used for flash column chromatography. Analytical and preparative TLC analysis (PTLC) were conducted on silica gel 60 F_{254} (EM Science; aluminum sheets) and silica gel 60 PF_{254} (EM Science; w/gypsum; 20 × 20 cm), respectively. Eluents used were ether (E), petroleum ether (PE), pentane (P), and benzene (B). Mass spectra were run at the Regional Center on Mass-Spectroscopy, UC Riverside, Riverside, CA (FAB, ZAB-SE; CI-NH_3, 7070EHF; Micromass; TOF Agilent 6210 LCTOF instrument with a Multimode source).

(μ-η^2-1,10-Diphenyl-2,8-decadiyne-1,10-diol)bis(dicobalt hexacarbonyl) (1). Under an atmosphere of nitrogen, a solution of n-BuLi in hexane (21 mmol, 13 mL/1.6 M) was added dropwise (20 min) to a solution of 1,7-octadiyne (1.06 g, 10 mmol) in dry THF (100 mL) at −20 °C. Upon addition, the reaction mixture was stirred at −20 °C for 1 h. The temperature was gradually increased to 0 °C (15 min), and the reaction mixture was stirred for an additional 45 min. A solution of LiBr (1.91 g, 22 mmol; dried at 180 °C for 2 h) in dry THF (50 mL) was added dropwise (15 min) at −40 °C, and the reaction mixture was stirred for 1 h. A solution of benzaldehyde (2.31 g, 22 mmol) in dry THF (10 mL) was added dropwise (15 min) at −40 °C; the reaction mixture was stirred overnight at room temperature, cooled to 0 °C, and then quenched with H_2O (100 mL) and saturated NH_4Cl (100 mL). Ether (100 mL) was added to the reaction mixture, and the organic product was salted out. The aqueous layer was extracted with ether (2 × 50 mL), and the combined ethereal fractions were dried (Na_2SO_4). Upon concentration under reduced pressure ($^1/_2$ of the initial volume), under an atmosphere of nitrogen, the crude diol (3.18 g, 10 mmol; assuming 100% yield) was added to a solution of dicobalt octacarbonyl (7.18 g, 21 mmol) in dry ether (150 mL). The reaction mixture was stirred at room temperature overnight, concentrated under reduced pressure, and fractionated on silica gel (400 g, 5:1 PE:E) to give complex **1** (5.72 g, 64.3%) as dark red crystals. T_{dec} = 110–130 °C (without melting; sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (3:1 P:E): R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (4H, m, $2CH_2$), *d*,*l*-**1**/*meso*-**1** 2.346, 2.348 (2H, d, 2OH, J = 3.6, J = 3.6), 2.75 (4H, m, $2CH_2$), 5.93 (2H, d, 2CH, J = 3.2), 7.29−7.50 (10H, m, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.1, 33.8 (C4, C5), 74.8 (C1), 98.6, 102.1 (C2, C3), 125.8, 128.6, 129.0, 144.2 (aromatic C), 199.8, 200.1 (CO). MS FAB$^+$: *m*/*z* 873 (M^+ − OH), 806 (M^+ − 3CO), 761 (M^+ − 4CO − OH), 722 (M^+ − 6CO), 666 (M^+ − 8CO), 638 (M^+ − 9CO), 610 (M^+ − 10CO), 564 (M^+ − 11CO − H_2O), 554 (M^+ − 12CO), 536 (M^+ − 12CO − H_2O), 477 (M^+ − 12CO − H_2O − Co), 419 (M^+ − 12CO − OH − 2Co). Anal. Found: C, 45.86; H, 2.40. Calcd for $C_{34}H_{22}O_{14}Co_4$: C, 45.84; H, 2.47.

***d*,*l*- and *meso*-(μ-η^2-3,4-Diphenyl-1,5-cyclodecadiyne)bis(dicobalt hexacarbonyl) (16).** Under an atmosphere of nitrogen, a solution of the bis-alcohol **1** (89 mg, 0.10 mmol) in dry ether (10 mL) was added dropwise (10 min) to a solution of $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol) in dry ether (20 mL) at +5 °C. The reaction mixture was stirred at +5 °C for 10 min, the temperature was decreased to 0 °C, an ethereal layer was removed, and the biscation **6** was washed with dry ether (2 × 15 mL). The residual amount of ether was removed under reduced pressure at −30 °C, and the cation **6** was partially dissolved in dry CH_2Cl_2 (20 mL) at −10 °C and treated with Zn (650 mg, 10.00 mmol) at +5 °C. The reaction mixture was stirred for 90 min at 20 °C (TLC control), filtered through a short bed of Florisil (1 cm), concentrated under reduced pressure, and fractionated on a PTLC plate (7:1 pentane:CH_2Cl_2; 2 plates) to give **16** (35 mg, 41.2%; by NMR, 80:20 *d*,*l*-**16**:*meso*-**16**) as a dark red solid. T_{dec} = 90–146 °C (with partial melting; sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (7:1 pentane:CH_2Cl_2): R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$): *d*,*l*-**16** + *meso*-**16** δ *meso* 1.66 (1H, m, CH), *d*,*l* 1.85 (2H, m, 2CH), *meso* 1.89 (1H, m, CH), *d*,*l* + *meso* 2.14 (2H + 1H, m, CH), *meso* 2.35 (1H, m, CH), *d*,*l* 3.18 (2H, m, 2CH), *meso* 3.25 (2H, m, 2CH), *meso* 3.38 (1H, m, CH), *d*,*l* 3.47 (2H, m, 2CH), *meso* 3.79 (1H, 7 lines, CH), *d*,*l* 4.60 (2H, s, H3, H4), *meso* 4.66 (1H, s, H3), *meso* 4.86 (1H, s, H4), *d*,*l* 6.57 (2H, d, aromatic H, J = 7.6), *d*,*l* 6.86 (2H, t, aromatic H, J = 7.6), *d*,*l* 7.07 (4H, m, aromatic H), *d*,*l* (2H) + *meso* 7.18–7.41 (m, aromatic H). MS FAB$^+$: *m*/*z* 828 (M^+ − CO), 800 (M^+ − 2CO), 772 (M^+ − 3CO), 744 (M^+ − 4CO), 716 (M^+ − 5CO), 688 (M^+ − 6CO), 660 (M^+ − 7CO), 632 (M^+ − 8CO), 604 (M^+ − 9CO), 601 (M^+ − Co − 7CO), 576 (M^+ − 10CO), 548 (M^+ − 11CO), 520 (M^+ − 12CO), 517 (M^+ − Co − 10CO). HR MS-FAB: calcd for $C_{31}H_{20}O_9Co_4$ (M^+ − 3CO), 771.843 524; found, 771.842 200.

At −50 °C, under analogous conditions, the ratio of *d*,*l*-**16** and *meso*-**16** in the crude mixture was equal to 67:33 (Table 1). Upon isolation on a PTLC plate, the ratio of inseparable diastereomers remains practically the same (68:32 *d*,*l*-**16**:*meso*-**16**).

(17) (a) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang, D. *Tetrahedron* **1996**, *52*, 6453. (b) Smith, A. L.; Nicolaou, K. C. *J. Med. Chem.* **1996**, *39*, 2103. (c) Basak, A.; Mandal, S.; Bag, S. S. *Chem. Rev.* **2003**, *103*, 4077.

***d,l*- and *meso*-3,4-Diphenyl-1,5-cyclodecadiyne (21).** Under an atmosphere of nitrogen, $Ce(NH_4)_2(NO_3)_6$ (406 mg, 0.74 mmol) was degassed and dissolved in acetone (11 mL, degassed). The solution was cooled to −78 °C and added dropwise (10 min) at −78 °C to a degassed solution of **16** (57 mg, 0.067 mmol, 80:20 *d*,*l*:*meso*) dissolved in acetone (10 mL, degassed). The reaction mixture was stirred for 2 h at −78 °C (TLC control), treated (−78 °C, N_2) with a degassed saturated aqueous solution of NaCl (10 mL), and extracted with pentane (3 × 15 mL). The combined organic layers were dried (4 Å); the solvent, upon filtration of the solution through a short bed of Florisil (5 cm), was stripped away under reduced pressure. Diyne **21** was obtained (18 mg, 95.1%; by NMR, 84:16 *d*,*l*-**21**:*meso*-**21**) as a yellowish wax. The compound crystallized, as a yellowish solid, in 90 days at −20 °C. Mp: 67.9–83.2 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (5:1 PE:E): $R_f = 0.53$. ^{1}H NMR (400 MHz, $CDCl_3$): *d*,*l*-**21** + *meso*-**21** δ 1.93 (4H, m, $2CH_2$), 2.32 (4H, m, $2CH_2$), *d*,*l* 3.78 (2H, s, 2CH), *meso* 4.21 (2H, s, 2CH), 6.94–6.99, 7.05–7.10, 7.20–7.30 (10H, m, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ *d*,*l*-**21** 20.9, 28.0 (C7−C10), 48.9 (C3, C4), 82.1, 89.7 (C1, C2, C5, C6), 127.2, 127.9, 128.3, 141.0 (aromatic C); *meso*-**21** 20.9, 27.9 (C7−C10), 46.0 (C3, C4), 82.8, 89.1 (C1, C2, C5, C6), 126.7, 127.5, 128.8, 137.9 (aromatic C). MS FAB$^+$: *m*/*z* 284 (M^+), 254, 241, 228, 205, 193, 178, 165, 128, 91. HR MS-FAB: calcd for $C_{22}H_{21}$ ($M^+ + H$), 285.1643; found, 285.1641.

[μ-η^2-1,10-Bis(4′-isopropylphenyl)-2,8-decadiyne-1,10-diol]-bis(dicobalt hexacarbonyl) (2). Under an atmosphere of nitrogen, a solution of n-BuLi in hexane (42 mmol, 26.25 mL/1.6 M) was added dropwise to a solution of 1,7-octadiyne (2.12 g, 20 mmol) in dry THF (65 mL) at −20 °C (20 min). Upon addition, the reaction mixture was stirred at −20 °C for 1 h. The temperature was gradually increased to 0 °C (15 min), and the reaction mixture was stirred for an additional 45 min. A solution of LiBr (3.92 g, 45 mmol) in dry THF (35 mL) was added dropwise (15 min) to the reaction mixture at −40 °C and the mixture stirred for 1 h. A solution of 4-isopropylbenzaldehyde (6.51 g, 44 mmol) in dry THF (20 mL) was added dropwise (15 min) to the reaction mixture at −40 °C. The reaction mixture was stirred overnight at room temperature, cooled to 0 °C, and then quenched with H_2O (50 mL) and saturated NH_4Cl (50 mL). An aqueous layer was extracted with ether (2 × 25 mL), and combined ethereal fractions were dried over Na_2SO_4. Upon concentration under reduced pressure (half of the initial volume), under an atmosphere of nitrogen, the crude diol (8.04 g, 20 mmol; assuming 100% yield) was added to a solution of dicobalt octacarbonyl (15.05 g, 44 mmol) in dry ether (150 mL). The reaction mixture was stirred at room temperature overnight, concentrated under reduced pressure, and fractionated on a silica gel column (420 g; 7:1, 3:1, 1:1 PE:E) to give **2** (6.93 g, 35.6%) as dark red crystals. Mp: 120–124 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (5:1 E:A): $R_f = 0.38$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.22 (12H, d, $4CH_3$, $J = 6.9$), 1.56 (4H, s, $2CH_2$), 2.32 (2H, d, 2OH, $J = 3.2$), 2.79 (4H, br s, $2CH_2$), 2.90 (2H, sep, 2CH), 5.90 (2H, d, 2CH), 7.29 (8H, AB spectrum, aromatic H, $J = 8.0$). MS FAB$^+$: *m*/*z* M^+ 974, 956 ($M^+ - H_2O$), 890 ($M^+ - 3CO$), 845 ($M^+ - H_2O - 4CO + H^+$), 806 ($M^+ - 6CO$), 750 ($M^+ - 8CO$), 722 ($M^+ - 9CO$), 705 ($M^+ - H_2O - 9CO + H^+$), 694 ($M^+ - 10CO$), 677 ($M^+ - H_2O - 10CO + H^+$), 648 ($M^+ - H_2O - 11CO$), 620 ($M^+ - H_2O - 12CO$), 561 ($M^+ - H_2O - 12CO - Co$), 503 ($M^+ - H_2O - 12CO - 2Co + H^+$). Anal. Found: C, 49.61; H, 3.66. Calcd for $C_{40}H_{33}O_{14}Co_4$: C, 49.28; H, 3.42.

***d,l*- and *meso*-[μ-η^2-3,4-Bis(4-isopropylphenyl)-1,5-cyclodecadiyne]bis(dicobalt hexacarbonyl) (17).** Under an atmosphere of nitrogen, a solution of bis-alcohol **2** (97 mg, 0.10 mmol) in dry ether (10 mL) was added dropwise (10 min) to a solution of $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol) in dry ether (20 mL) at +5 °C. The reaction mixture was stirred at +5 °C for 10 min, the temperature was decreased to −30 °C, an ethereal layer was removed, and the bis-cation **7** was washed with dry ether (2 × 15 mL). The residual amount of ether was removed under reduced pressure, and the cation **7** was dissolved in dry CH_2Cl_2 (20 mL), cooled to −50 °C, and stirred for 15 min. The solution was treated with Zn (650 mg, 10.00 mmol) at −50 °C and stirred for 5 min. The cooling bath was replaced with a water bath, and the reaction mixture was stirred for 16 h at 20 °C (TLC control). The crude mixture was filtered through a short bed of Florisil (1 cm), concentrated under reduced pressure (by NMR, 80:20 *d*,*l*-**17**:*meso*-**17**), and fractionated on a PTLC plate (20:1 pentane:benzene; 2 plates activated at 150 °C for 2 h) to give **17** (40 mg, 42.8%; by NMR, 80:20 *d*,*l*-**17**:*meso*-**17**) as a dark red solid. T_{dec} = 130–150 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL, monitored by TLC). TLC (20:1 PE:E): $R_f = 0.49$. ^{1}H NMR (400 MHz, $CDCl_3$): *d*,*l*-**17** + meso-**17** δ *d*,*l* 1.09 (6H, d, $2CH_3$, $J = 6.8$), 1.10 (6H, d, $2CH_3$, $J = 6.8$), *meso* 1.175 (3H, d, CH_3, $J = 7.2$), 1.178 (3H, d, CH_3, $J = 6.8$), 1.229 (3H, d, CH_3, $J = 6.8$), 1.233 (3H, d, CH_3, $J = 7.2$), 1.64 (1H, m, CH), *d*,*l* 1.83 (2H, m, CH_2), *meso* 1.88 (1H, m, CH), *d*,*l* 2.11 (2H, m, CH_2), *meso* 2.11 (1H, m, CH), 2.31 (1H, m, CH), *d*,*l* 2.75 (2H, sept, 2CH), *meso* 2.84 (1H, sept, CH, $J = 6.8$), 2.91 (1H, sept, CH, $J = 6.8$), *d*,*l* 3.16 (2H, m, CH_2), *meso* 3.22 (2H, m, CH_2), 3.35 (1H, m, CH), *d*,*l* 3.45 (2H, m, CH_2), *meso* 3.77 (1H, m 7 lines, CH), *d*,*l* 4.54 (2H, s, H3, H4), *meso* 4.67 (1H, s, H3(4)), 4.79 (1H, s, H4(3)-), *d*,*l* 6.45 (2H, d, aromatic H, $J = 7.2$), 6.68 (2H, d, aromatic H), 7.00 (4H, AB spectrum, aromatic H, $J_{av} = 7.4$), *meso* 7.16–7.24 (8H, m, aromatic H). MS FAB$^+$: *m*/*z* M^+ 940, 856 ($M^+ - 3CO$), 828 ($M^+ - 4CO$), 800 ($M^+ - 5CO$), 772 ($M^+ - 6CO$), 744 ($M^+ - 7CO$), 716 ($M^+ - 8CO$), 688 ($M^+ - 9CO$), 660 ($M^+ - 10CO$), 632 ($M^+ - 11CO$), 514 ($M^+ - 11CO - 2Co$), 486 ($M^+ - 12CO - 2Co$), 427 ($M^+ - 12CO - 3Co$), 369 ($M^+ - 12CO - 4Co + H^+$). HR MS FAB: calcd for $C_{37}H_{32}O_9Co_4$ ($M^+ - 3CO$), 855.937 424; found, 855.933 500.

***d,l*- and *meso*-3,4-Bis(4′-isopropylphenyl)-1,5-cyclodecadiyne (22).** Under an atmosphere of nitrogen, $Ce(NH_4)_2(NO_3)_6$ (114 mg, 0.208 mmol) was degassed and dissolved in acetone (8 mL, degassed). The solution was cooled to −78 °C and added dropwise (10 min) to a degassed solution of **17** (24 mg, 0.026 mmol, 80:20 *d*,*l*:*meso*) dissolved in acetone (10 mL, degassed) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C, and an additional amount of CAN (14 mg, 0.026 mmol), dissolved in acetone (1 mL, degassed), was cooled to −78 °C and added dropwise (1 min) to the reaction mixture. The temperature was increased to −50 °C (15 min), and the reaction mixture was stirred for an additional 45 min (TLC control). The reaction mixture was treated (−78 °C, N_2) with a degassed saturated aqueous solution of NaCl (20 mL). The mixture was then transferred to a separatory funnel charged with a saturated aqueous solution of NaCl (20 mL) and extracted with dry ether (2 × 15 mL). The combined organic layers were dried (Na_2SO_4), and the solvent, upon filtration, was stripped away under reduced pressure. By PTLC (pentane), **22**, a yellow wax, was obtained (6.2 mg, 64.6%) as an inseparable mixture of diastereomers (by NMR, 80:20 *d*,*l*-**22**:*meso*-**22**). TLC (10:1 PE:E): $R_f = 0.58$. ^{1}H NMR (400 MHz, $CDCl_3$): *d*,*l*-**22** + *meso*-**22** δ *meso* 1.15 (12H, d, $4CH_3$, $J = 6.8$), *d*,*l* 1.24 (6H, d, $2CH_3$, $J = 7.0$), 1.25 (6H, d, $2CH_3$, $J = 6.8$), *d*,*l* + *meso* 1.95 (4H, m, $2CH_2$), 2.31 (4H, m, $2CH_2$), *meso* 2.78 (2H, sept, 2CH), *d*,*l* 2.89 (2H, sept, 2CH), 3.74 (2H, s, 2CH), *meso* 4.13 (2H, s, 2CH), 6.86 (8H, AB spectrum, aromatic H, $J = 8.4$), *d*,*l* 7.21 (8H, AB spectrum, aromatic H, $J = 8.0$). ^{13}C NMR (100 MHz, $CDCl_3$): *d*,*l*-**22** + *meso*-**22** δ *d*,*l* + *meso* 21.0 (C7, C10), 24.0 (4C, i-Pr), *meso* 27.9 (C8, C9), *d*,*l* 28.0 (C8, C9), *meso* 33.6 (C3, C4), *d*,*l* 33.7 (C3, C4), *meso* 45.8 (2C, i-Pr), *dl* 48.3 (2C, i-Pr), *d*,*l* 82.6, 89.2 (C1, C2, C5, C6), *meso* 83.1, 88.5 (C1, C2, C5, C6), *d*,*l* 126.4, 127.6, 138.5, 147.6 (aromatic C), *meso* 125.4, 128.5, 135.0, 147.6 (aromatic C). MS TOF: *m*/*z* calcd for MH^+, 369.2582; found, 369.2578.

[μ-η^2-1,10-Bis(4′-methoxyphenyl)-2,8-decadiyne-1,10-diol]bis-(dicobalt hexacarbonyl) (3). Under an atmosphere of nitrogen, a solution of n-BuLi in hexane (84 mmol, 52.5 mL/1.6 M) was added dropwise (20 min) to a solution of 1,7-octadiyne (4.24 g, 40 mmol) in dry THF (130 mL) at −20 °C. Upon addition, the reaction mixture was stirred at −20 °C for 1 h. The temperature was gradually increased to 0 °C (15 min), and the reaction mixture was stirred for an additional 45 min. A solution of LiBr (7.83 g, 90 mmol; dried at 180 °C for 2 h) in dry THF (70 mL) was added dropwise (15 min) to the reaction mixture at −40 °C and stirred for 1 h. A solution of anisaldehyde (11.97 g, 88 mmol) in dry THF (40 mL) was added to the reaction mixture dropwise (15 min) at −40 °C. The reaction mixture was stirred overnight at room temperature, cooled to 0 °C, and then quenched with H_2O (50 mL) and saturated NH_4Cl (50 mL). An aqueous layer was extracted with ether (2 × 25 mL), and combined ethereal fractions were dried over Na_2SO_4. Upon concentration under reduced pressure (half of the initial volume), under an atmosphere of nitrogen, the crude diol (15.12 g, 40 mmol; assuming 100% yield) was added to a solution of dicobalt octacarbonyl (30.10 g, 88 mmol) in dry ether (300 mL). The reaction mixture was stirred at room temperature overnight, concentrated under reduced pressure, and fractionated on a silica gel column (500 g, 1:1 PE:E; 1:1 E:A) to give complex **3** (19.8 g, 52.1%) as dark red crystals. Mp: 86–109 °C (with decomposition; sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (1:1 PE:E): $R_f = 0.49$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.75 (4H, br s, $2CH_2$), 2.35 (2H, d, 2OH, $J = 3.0$), 2.76 (4H, s, 2 CH_2), 3.80 (6H, s, $2CH_3$), 5.88 (2H, d, 2CH), 6.91 (4H, d, aromatic H, $J = 6.0$), 7.36 (4H, d, aromatic H). MS FAB+: *m*/*z* 933 ($M^+ - OH$), 866 ($M^+ - 3CO$), 849 ($M^+ - OH - 3CO$), 782 ($M^+ - 6CO$), 726 ($M^+ - 8CO$), 698 ($M^+ - 9CO$), 670 ($M^+ - 10CO$), 624 ($M^+ - H_2O - 11CO$), 596 ($M^+ - H_2O - 12CO$), 537 ($M^+ - H_2O - 12CO - Co$), 479 ($M^+ - H_2O - 12CO - 2Co + H^+$). Anal. Found: C, 45.70; H, 2.93. Calcd for $C_{36}H_{26}O_{16}Co_4$: C, 45.47; H, 2.74.

***d*,*l*- and *meso*-[μ-η^2-3,4-Bis(4′-methoxyphenyl)-1,5-cyclodeca-diyne]bis(dicobalt hexacarbonyl) (18).** Under an atmosphere of nitrogen, a solution of the bis-alcohol **3** (95 mg, 0.10 mmol) in dry ether (5 mL) was added dropwise (5 min) to a solution of $HBF_4 \cdot Me_2O$ (161 mg, 1.2 mmol) in dry ether (20 mL) at +5 °C. The reaction mixture was stirred at +5 °C for 10 min, the temperature was decreased to 0 °C, an ethereal layer was removed, and the bis-cation **8** was washed with dry ether (2 × 15 mL). The temperature was decreased to −20 °C, the residual amount of ether was removed under reduced pressure, and the bis-cation **8** was dissolved in dry CH_2Cl_2 (20 mL). The solution was cooled to −50 °C, stirred for 15 min, and treated with Zn (650 mg, 10.00 mmol). The reaction mixture was stirred for 5 min, the cold bath was replaced with a water bath (20 °C), and the reaction mixture was stirred for an additional 15 min (TLC control). The crude mixture was filtered through a short bed of Florisil (1 cm), concentrated under reduced pressure (NMR: 67:33 *d*,*l*-**18**:*meso*-**18**), and isolated by PTLC (10:1 PE:E; 2 plates) to give **18** (38 mg, 41.5%; 66:34 *d*,*l*:*meso*) as a dark red solid. $T_{dec} = 59.7-69.5$ °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (2:1 PE:E): $R_f = 0.57$. ^{1}H NMR (400 MHz, $CDCl_3$): *d*,*l*-**18** + *meso*-**18** δ *meso* 1.63 (1H, m, CH), *d*,*l* 1.83 (2H, m, 2CH), *meso* 1.88 (1H, m, CH), *d*,*l* + *meso* 2.12 (2H + 1H, m, 2CH + CH), *meso* 2.32 (1H, m, CH), *d*,*l* + *meso* 3.08−3.28 (2H + 2H, m, 2CH + 2CH), *d*,*l* + *meso* 3.30–3.53 (2H + 2H, m, 2CH + 2CH), *d*,*l* 3.70 (6H, s, 2OMe), *meso* 3.77 (3H, s, OMe), 3.82 (3H, s, OMe), *d*,*l* 4.52 (2H, s, 2CH), *meso* 4.59 (1H, s, CH), 4.79 (1H, s, CH), *d*,*l* 6.47 (4H, br s, aromatic H), *d*,*l* + *meso* 6.63–7.22 (4H + 8H, m, aromatic H). MS FAB$^+$: *m*/*z* 832 ($M^+ - 3CO$), 804 ($M^+ - 4CO$), 776 ($M^+ - 5CO$), 747 ($M^+ - 6CO - H$), 719 ($M^+ - 7CO - H$), 691 ($M^+ - 8CO - H$), 663 ($M^+ - 9CO - H$), 635 ($M^+ - 10CO - H$), 607 ($M^+ - 11CO - H$), 576 ($M^+ - 10CO - Co - H$), 548 ($M^+ - 11CO - Co - H$), 520 ($M^+ - 12CO - Co - H^+$), 461 ($M^+ - 12CO - 2Co - H^+$). HR MS FAB: calcd for $C_{33}H_{24}O_{11}Co_4$ ($M^+ - 3CO$), 831.864 653; found, 831.863 500.

***d*,*l*- and *meso*-3,4-Bis(4′-methoxyphenyl)-1,5-cyclodecadiyne (23).** Under an atmosphere of nitrogen, $Ce(NH_4)_2(NO_3)_6$ (175 mg, 0.32 mmol) was degassed and dissolved in acetone (8 mL, degassed). The solution was cooled to −78 °C and added dropwise (10 min) to a degassed solution of **18** (38 mg, 0.04 mmol, 69:31 *d*,*l*:*meso*; repurified sample) dissolved in acetone (15 mL, degassed) at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, an additional amount of $Ce(NH_4)_2(NO_3)_6$ (22 mg, 0.04 mmol) in acetone (1 mL, degassed, precooled to −78 °C) was added dropwise (1 min), and this mixture was stirred for an additional 30 min. To bring the reaction to completion, 3 equiv more of $Ce(NH_4)_2(NO_3)_6$ (3 × 22 mg, 0.04 mmol) were added under analogous conditions (1 equiv, −78 °C, 1.5 h; 1 equiv, −78 °C, 30 min; 1 equiv, −50 °C, 15 min). The temperature was then increased to −30 °C (5 min), and the mixture was stirred for 1 h (TLC control) and treated (−78 °C, N_2) with a degassed saturated aqueous solution of NaCl (20 mL). The mixture was then transferred to a separatory funnel charged with a saturated aqueous solution of NaCl (20 mL) and extracted with dry ether (3 × 15 mL). The combined organic layers were dried (Na_2SO_4), and the solvent, upon filtration, was stripped away under reduced pressure. Diyne **23** was obtained (6 mg, 43.5%; by NMR, 73:27 *d*,*l*-**23**:*meso*-**23**), as a pale yellow oil, by column chromatography using Florisil (8 g, degassed, 5:1 P:E, degassed). TLC (3:1 PE:E): $R_f = 0.35$. ^{1}H NMR (400 MHz, C_6D_6): *d*,*l*-**23** + *meso*-**23** δ *d*,*l* + *meso* 1.68 – 1.89 (4H + 4H, m, $2CH_2 + 2CH_2$), 2.08–2.35 (4H + 4H, m, $2CH_2 + 2CH_2$), *meso* 3.24 (6H, s, 2OMe), *d*,*l* 3.36 (6H, s, 2OMe), *d*,*l* 4.00 (2H, s, 2CH), *meso* 4.27 (2H, s, 2CH), *meso* 6.70 (4H, d, aromatic H, $J = 8.6$), *d*,*l* 6.81 (4H, d, aromatic H, $J = 8.6$), *meso* 7.10 (4H, d, aromatic H), *d*,*l* 7.28 (4H, d, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): *d*,*l*-**23** + *meso*-**23** δ *d*,*l* + *meso* 20.9 (C7, C10), *meso* 27.8 (C8, C9), *d*,*l* 27.9 (C8, C9), *meso* 45.5 (C3, C4), *d*,*l* 48.2 (C3, C4), *meso* 55.15 (OMe), *d*,*l* 55.24 (OMe), *d*,*l* 82.9 (C1, C6), *meso* 83.3 (C1, C6), *meso* 88.6 (C2, C5), *d*,*l* 88.8 (C2, C5), *meso* 113.0, 129.7, 129.9, 158.4 (aromatic C); *d*,*l* 113.6, 128.9, 132.7, 158.6 (aromatic C). MS TOF: *m*/*z* calcd for MH^+, 345.1855; found, 345.1851.

[μ-η^2-1,10-Bis(3′,4′-dimethoxyphenyl)-2,8-decadiyne-1,10-diol]bis(dicobalt hexacarbonyl) (4). Under an atmosphere of nitrogen, a solution of n-BuLi in hexane (42 mmol, 26.25 mL/1.6 M) was added dropwise (30 min) to a solution of 1,7-octadiyne (2.12 g, 20 mmol) in dry ether (65 mL) at −20 °C. Upon addition, the reaction mixture was stirred at 20 °C for 4.5 h. The temperature was decreased to 0 °C, and ground solid 3,4-dimethoxybenzaldehyde (6.97 g, 42 mmol) was added along with dry ether (100 mL). The reaction mixture was stirred for 18 h, cooled to 0 °C, and then quenched with saturated NH_4Cl (100 mL). An aqueous layer was extracted with ether (5 × 35 mL). An additional amount of ether (100 mL) and acetone (50 mL) was used to transfer the residual amount of the product onto the organic layer. The combined organic fractions were dried over Na_2SO_4. Upon concentration under reduced pressure (half of the initial volume), under an atmosphere of nitrogen, the crude diol (8.76 g, 20 mmol; assuming 100% yield) was added to a solution of dicobalt octacarbonyl (15.05 g, 44 mmol) in dry ether (150 mL). The reaction mixture was stirred at room temperature for 5 h, brought to dryness under reduced pressure, loaded with acetone (75 mL, flushed column for 30 min with N_2 to remove acetone), and fractionated on a silica gel column (520 g, 20:1 CH_2Cl_2:E) to give complex **4** (4.22 g, 20.9%) as dark red crystals. T_{dec} = 138.6–156.8 °C (sealed capillary; dried by co-evaporation with benzene, 3 × 1 mL). TLC (10:1 CH_2Cl_2:E): $R_f =$ 0.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75 (4H, m, $2CH_2$), 2.32 (2H, d, 2OH, $J = 3.2$), 2.78 (4H, m, $2CH_2$), 3.86 (6H, s, 2OMe), 3.89 (6H, s, 2OMe), 5.87 (2H, d, 2CH, $J = 2.8$), 6.85 (2H, d, aromatic H5, $J = 8.0$), 6.95 (2H, dd, aromatic H6, $J = 1.6$), 7.00

(2H, s, aromatic H2). MS FAB+: *m/z* 992 ($M^+ - H_2O$), 926 ($M^+ - 3CO$), 881 ($M^+ - 4CO - OH$), 842 ($M^+ - 6CO$), 786 ($M^+ - 8CO$), 758 ($M^+ - 9CO$), 730 ($M^+ - 10CO$), 684 ($M^+ - 11CO - H_2O$), 656 ($M^+ - 12CO - H_2O$), 597 ($M^+ - 12CO - Co - H_2O$), 539 ($M^+ - 12CO - 2Co - OH$). Anal. Found C, 45.32; H, 3.04. Calcd for $C_{38}H_{30}O_{18}Co_4$: C, 45.15; H, 2.97.

***d,l*- and *meso*-[μ-η^2-3,4-Bis(3′,4′-dimethoxyphenyl)-1,5-cyclodecadiyne]bis(dicobalt hexacarbonyl) (19).** Under an atmosphere of nitrogen, a solution of the bis-alcohol **4** (101 mg, 0.10 mmol) in dry ether (15 mL) was added dropwise (15 min) to a solution of $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol) in dry ether (20 mL) at 5 °C. The reaction mixture was stirred at 5 °C for 10 min, the temperature was decreased to 0 °C, an ethereal layer was removed, and the bis-cation **9** was washed with dry ether (2 × 15 mL). The residual amount of ether was removed under reduced pressure, and the cation **9** was dissolved in dry CH_2Cl_2 (20 mL). The solution was cooled to −50 °C, stirred for 15 min, and treated with Zn (650 mg, 10.00 mmol). The reaction mixture was stirred for 5 min, the cooling bath was replaced with a water bath (20 °C), and the reaction mixture was stirred for 18 h (unoptimized). The crude mixture was filtered through a short bed of Florisil (1 cm) and concentrated under reduced pressure (NMR: 67:33 *d,l*-**19**:*meso*-**19**). Fractionation on a Florisil column (25 g, degassed, −5 °C, degassed 50:1 CH_2Cl_2:E) gave *meso*-**19** (10.9 mg, 11.2%) and *d,l*-**19** that was further purified by PTLC (2:1 PE:E; 17.1 mg, 17.5%).

meso-**19**: dark red crystals upon coevaporation with pentane (3 × 1 mL). T_{dec} = 87.5 – 144.4 °C (without melting; sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (20:1 CH_2Cl_2:E): R_f = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (1H, m, CH), 1.90 (1H, m, CH), 2.15 (1H, m, CH), 2.33 (1H, m, CH), 3.17−3.42 (3H, m, CH_2, CH), 3.79 (3H, s, OMe), 3.80 (1H, m, CH), 3.83 (3H, s, OMe), 3.89 (6H, s, 2OMe), 4.57 (1H, br s, CH), 4.80 (1H, s, CH), 6.64–6.93 (6H, m, aromatic H). MS FAB+: *m/z* 892 ($M^+ - 3CO$), 864 ($M^+ - 4CO$), 752 ($M^+ - 8CO$), 724 ($M^+ - 9CO$), 696 ($M^+ - 10CO$), 668 ($M^+ - 11CO$), 640 ($M^+ - 12CO$), 606 ($M^+ - 9CO - 2Co$), 550 ($M^+ - 11CO - 2Co$), 522 ($M^+ - 12CO - 2Co$), 463 ($M^+ - 12CO - 3Co$), 432 ($M^+ - 11CO - 4Co$). HR MS/FAB: *m/z* calcd for $C_{35}H_{28}O_{13}Co_4$ ($M^+ - 3CO$), 891.885 783; found, 891.8850.

d,l-**19**: dark red crystals upon coevaporation with pentane (3 × 1 mL). T_{dec} = 130.2−154.0 °C (with partial melting, sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (20:1 CH_2Cl_2:E): R_f = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84 (2H, m, CH_2), 2.14 (2H, m, CH_2), 3.20 (2H, m, 2CH), 3.34 (3H, s, OMe), 3.46 (2H, m, 2CH), 3.75 (3H, br s, OMe), 3.79 (3H, s, OMe), 3.83 (3H, br s, OMe), 4.54 (2H, s, 2CH), 5.90−6.25 (2H, m, aromatic H), 6.38–6.85 (4H, m, aromatic H). MS FAB+: *m/z* 892 ($M^+ - 3CO$), 864 ($M^+ - 4CO$), 836 ($M^+ - 5CO$), 808 ($M^+ - 6CO$), 780 ($M^+ - 7\ CO$), 752 ($M^+ - 8CO$), 724 ($M^+ - 9CO$), 668 ($M^+ - 11CO$). HR MS/FAB: *m/z* calcd for $C_{35}H_{28}O_{13}Co_4$ ($M^+ - 3CO$), 891.885 783; found, 891.8880.

***d,l*-3,4-Bis(3′,4′-dimethoxyphenyl)-1,5-cyclodecadiyne (24).** Under an atmosphere of nitrogen, $Ce(NH_4)_2(NO_3)_6$ (49.32 mg, 0.09 mmol) was degassed and dissolved in acetone (8 mL, degassed). The solution was cooled to −78 °C and added dropwise (15 min) to a degassed solution of *d,l*-**19** (11 mg, 0.01 mmol) dissolved in acetone (5 mL, degassed) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C, and an additional amount of $Ce(NH_4)_2(NO_3)_6$ (5.48 mg, 0.01 mmol) in acetone (1 mL, degassed; precooled to −78 °C) was added dropwise (2 min). The temperature was increased to −50 °C (10 min), and the reaction mixture was stirred for 30 min. An additional amount of $Ce(NH_4)_2(NO_3)_6$ (5.48 mg, 0.01 mmol) in acetone (1 mL, degassed, precooled to −78 °C) was added dropwise (2 min) at −50 °C, and the reaction mixture was stirred for another 15 min. The temperature was increased to −30 °C (8 min), stirred for 30 min (TLC control), and treated (−78 °C, N_2) with a degassed saturated aqueous solution of NaCl (20 mL). The mixture was then transferred to a separatory funnel charged with a saturated aqueous solution of NaCl (20 mL) and extracted with dry ether (2 × 15 mL). The combined organic layers were dried (Na_2SO_4), and the solvents, upon filtration, were stripped away under reduced pressure. PTLC isolation (20:1 CH_2Cl_2:E) afforded *d,l*-**24** (3.3 mg, 82.5%) as a pale yellow solid. Mp: 93.0−94.6 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (20:1 CH_2Cl_2:E): R_f = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (4H, m, $2CH_2$), 2.31 (4H, m, $2CH_2$), 3.68 (2H, s, 2CH), 3.80 (6H, s, 2OMe), 3.85 (6H, s, 2OMe), 6.70–6.78 (6H, m, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0 (C7, C10), 27.9 (C8, C9), 48.6 (C3, C4), 55.8, 55.9 (4OMe), 83.0, 88.9 (C1, C2, C5, C6), 110.8, 111.1, 120.1, 132.9, 148.1, 148.6 (aromatic C). MS TOF: *m/z* calcd for $C_{26}H_{29}O_4$ (MH^+), 405.2066; found, 405.2068.

[μ-η^2-1,10-Bis(3′,4′,5′-trimethoxyphenyl)-2,8-decadiyne-1,10-diol]bis(dicobalt hexacarbonyl) (5). Under an atmosphere of nitrogen, a solution of n-BuLi in hexane (42 mmol, 26.25 mL/1.6 M) was added dropwise (15 min) to a solution of 1,7-octadiyne (2.12 g, 20 mmol) in dry THF (65 mL) at −20 °C. Upon addition, the reaction mixture was stirred at −20 °C for 30 min. The temperature was gradually increased to 0 °C (15 min), and the reaction mixture was stirred for an additional 45 min. A solution of LiBr (3.65 g, 42 mmol; dried at 180 °C for 2 h) in dry THF (35 mL) was added dropwise (15 min) to the reaction mixture at −40 °C and stirred for 1 h. A solution of 3,4,5-trimethoxybenzaldehyde (8.23 g, 42 mmol) in dry THF (30 mL) was added at −40 °C dropwise (15 min) and stirred overnight at ambient temperature. The reaction mixture was cooled to 0 °C and quenched with H_2O (50 mL) and saturated NH_4Cl (50 mL). An aqueous layer was extracted with ether (3 × 35 mL), and combined ethereal fractions were dried over Na_2SO_4. Upon concentration under reduced pressure (half of the initial volume), under an atmosphere of nitrogen, the crude diol (9.96 g, 20 mmol; assuming 100% yield) was added to a solution of dicobalt octacarbonyl (15.05 g, 44 mmol) in dry ether (150 mL). The reaction mixture was stirred at room temperature overnight, concentrated under reduced pressure, and fractionated on a silica gel column (400 g, ether) to give complex **5** (2.95 g, 13.8%) as dark red crystals. T_{dec} = 90–107 °C. TLC (ether): R_f = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80 (4H, m, $2CH_2$), 2.45 (2H, d, 2OH, J = 3.2), 2.85 (4H, m, $2CH_2$), 3.81 (6H, s, 2OMe), 3.87 (12H, s, 4OMe), 5.86 (2H, d, 2CH), 6.69 (4H, s, aromatic). MS FAB+: *m/z* 986 ($M^+ - 3CO$), 941 ($M^+ - 4CO - OH$), 902 ($M^+ - 6CO$), 846 ($M^+ - 8CO$), 819 ($M^+ - 9CO + H$), 791 ($M^+ - 10CO + H$), 774 ($M^+ - 10CO + H - OH$), 744 ($M^+ - 11CO - H_2O$), 734 ($M^+ - 12CO$), 731 ($M^+ - 10CO - Co$), 716 ($M^+ - 12CO - H_2O$). Anal. Found: C, 44.14; H, 3.00. Calcd for $C_{40}H_{34}O_{20}Co_4$: C, 44.36; H, 3.18.

***d,l*- and *meso*-[μ-η^2-3,4-Bis(3′,4′,5′-trimethoxyphenyl)-1,5-cyclodecadiyne]bis(dicobalt hexacarbonyl) (20).** Under an atmosphere of nitrogen, a solution of the bis-alcohol **5** (107 mg, 0.10 mmol) in dry ether (30 mL) was added dropwise (30 min) to a solution of $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol) in dry ether (20 mL) at +5 °C. The reaction mixture was stirred at +5 °C for 10 min, the temperature was decreased to −5 °C, the ethereal layer was removed, and the bis-cation **10** was washed with dry ether (2 × 15 mL). The residual amount of ether was removed under reduced pressure at −30 °C, and the cation **10** was suspended in dry CH_2Cl_2 (20 mL) at −15 °C. The reaction mixture was treated with Zn (650 mg, 10 mmol) at +5 °C and stirred for 1 h at 20 °C (TLC control). The crude mixture was filtered through a short bed of Florisil (1 cm), concentrated under reduced pressure (NMR: 54:46 *d,l*-**20**:*meso*-**20**), and fractionated on a Florisil column (15 g, degassed, −5 °C; degassed 1:1 PE:E; E). *d,l*-**20** (19.7 mg, 19.0%; after repurification on Florisil, 15 g, CH_2Cl_2:E, 10:1) and *meso*-**20** (25.2 mg, 24.3%) were obtained.

d,l-**20**: dark red solid. T_{dec} = 121.1−159.8 °C. TLC (1:1 PE:E): R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82 (2H, m, 2CH), 2.13 (2H, m, 2CH), 3.17 (2H, m, 2CH), 3.35 (6H, s, 2OMe), 3.45 (2H, m, 2CH), 3.71 (6H, s, 2OMe), 3.80 (6H, s, 2OMe), 4.47 (2H, s, 2CH), 5.80 (2H, d, aromatic H, J = 1.6), 6.41 (2H, d, aromatic H). MS FAB+: *m/z* 952 (M^+ − 3CO), 924 (M^+ − 4CO), 896 (M^+ − 5CO), 868 (M^+ − 6CO), 840 (M^+ − 7CO), 812 (M^+ − 8CO), 784 (M^+ − 9CO), 728 (M^+ −11CO), 700 (M^+ −12CO). HR-MS/FAB: calcd for $C_{40}H_{33}O_{18}Co_4$ (MH^+), 1036.899 481; found, 1036.9000. Single crystals suitable for X-ray structure analysis (Figure 1) were obtained by methanol vapor diffusion into a solution of *d,l*-**20** in CH_2Cl_2 (+5 °C, 3 days).

meso-**20**: dark red oil. TLC (1:1 PE:E): R_f = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (1H, m, CH), 1.91 (1H, m, CH), 2.17 (1H, m, CH), 2.35 (1H, m, CH), 3.19–3.39 (2H, m, 2CH), 3.74 (6H, s, 2OMe), 3.80 (6H, s, 2OMe), 3.82 (6H, s, 2OMe), 3.92 (2H, m, 2CH), 4.59 (1H, s, CH), 4.76 (1H, s, CH), 6.44 (1H, br s, aromatic H), 6.50 (2H, s, aromatic H), 6.51 (1H, br s, aromatic H). MS-FAB+: *m/z* M^+ 952 (M^+ − 3CO), 924 (M^+ − 4CO), 868 (M^+ − 6CO), 812 (M^+ − 8CO), 784 (M^+ − 9CO), 756 (M^+ − 10CO), 728 (M^+ − 11CO), 697 (M^+ − 10CO − Co), 666 (M^+ − 9CO − 2Co), 582 (M^+ − 12CO − 2Co). HR MS/FAB: calcd for $C_{37}H_{32}O_{15}Co_4$ (M^+ − 3CO), 951.906 912; found, 951.9088.

At −50 °C, under analogous conditions, the ratio of *d,l*-**20** and *meso*-**20** in the crude mixture was equal to 54:46 (Table 1).

***d,l*-3,4-Bis(3′,4′,5′-trimethoxyphenyl)-1,5-cyclodecadiyne (25).** Under an atmosphere of nitrogen, $Ce(NH_4)_2(NO_3)_6$ (29.8 mg, 0.0544 mmol) was degassed and dissolved in acetone (8 mL, degassed). The solution was cooled to −78 °C and added dropwise (12 min) to a degassed solution of *d,l*-**20** (7 mg, 0.0068 mmol) in acetone (5 mL, degassed) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C. The temperature was increased to −50 °C (10 min), and the reaction mixture was stirred for an additional 1 h. The temperature was then decreased to −78 °C, and an additional amount of $Ce(NH_4)_2(NO_3)_6$ (3.7 mg, 0.0068 mmol) in acetone (1 mL, degassed, precooled to −78 °C) was added dropwise (1 min). The temperature was increased to −50 °C (10 min), and the reaction mixture was stirred for 30 min. Then an additional amount of $Ce(NH_4)_2(NO_3)_6$ (3.7 mg, 0.0068 mmol) in acetone (1 mL, degassed, precooled to −78 °C) was added dropwise (1 min) at −50 °C and stirred for 45 min. The final amount of $Ce(NH_4)_2(NO_3)_6$ (3.7 mg, 0.0068 mmol) in acetone (1 mL, degassed, precooled to −78 °C) was added dropwise (1 min) at −50 °C and stirred for 2 h. The temperature was increased to −40 °C (2 min), stirred for 30 min, warmed to −30 °C (1 min), and stirred for 15 min (TLC control). The reaction mixture was treated (−78 °C, N_2) with a degassed, saturated aqueous solution of NaCl (10 mL), transferred to a separatory funnel charged with a saturated aqueous solution of NaCl (10 mL), and extracted with dry ether (3 × 15 mL). The combined organic layers were dried (Na_2SO_4), and the solvents, upon filtration, were stripped away under reduced pressure. The crude product was chromatographed on Florisil (10 g, ether, acetone) to afford *d,l*-**25** (2.7 mg, 85.6%) as a pale yellow solid. An analytical sample was obtained by PTLC (20:1 CH_2Cl_2:E; 2.0 mg, 63.4%). Mp: 111.5–112.9 °C (sealed capillary, dried by coevaporation with benzene, 3 × 1 mL). TLC (ether): R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (4H, m, $2CH_2$), 2.31 (4H, m, $2CH_2$), 3.65 (2H, s, 2CH), 3.78 (12H, s, 4OMe), 3.80 (6H, s, 2OMe), 6.41 (4H, s, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0 (C7, C10), 27.7 (C8, C9), 49.1 (C3, C4), 56.1, 60.9 (6OMe), 82.6, 89.2 (C1, C2, C5, C6), 105.1, 135.7, 137.1, 152.9 (aromatic C). MS TOF: *m/z* calcd for $C_{28}H_{33}O_6$ (MH^+), 465.2277; found, 465.2261. Single crystals suitable for X-ray structure analysis (Figure 2) were obtained by methanol vapor diffusion into a solution of *d,l*-**25** in CH_2Cl_2 (+5 °C, 1 day).

X-ray Crystallography of *d,l*-20 and *d,l*-25.[12] Suitable crystals of *d,l*-**20** and *d,l*-**25** were coated with Paratone N oil, suspended in a small fiber loop, and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 APEX II CCD sealed-tube diffractometer with graphite-monochromated Mo Kα (0.710 73 Å) radiation. Data were measured using a series of combinations of ψ and ω scans with 10 s frame exposures and 0.5° frame widths. Data collection, indexing, and initial cell refinements were all carried out using APEX II[12a] software. Frame integration and final cell refinements were done using SAINT[12b] software. The final cell parameters were determined from least-squares refinement on 9860 and 556 reflections, respectively.

The structures were solved using direct methods and difference Fourier techniques (SHELXTL, V6.12).[12c] Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least-squares with isotropic U_{ij}'s related to the atom's ridden upon. All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from ref 12d. Structure solution, refinement, graphics, and generation of publication materials were performed by using SHELXTL V6.12 software. Additional details of data collection and structure refinement are given in Table 1.

[μ-η^2-1-(3′,4′,5′-Trimethoxyphenyl)-2-pentyn-1-ol]dicobalt Octacarbonyl (26). Under an atmosphere of nitrogen, 1-butyne (1.62 g, 30 mmol) was bubbled through a solution of n-BuLi/hexane (33 mmol, 21 mL/1.6 M) in dry THF (100 mL) at −10 °C and stirred for 5 h. A solution of 3,4,5-trimethoxybenzaldehyde (5.88 g, 30 mmol) in dry THF (25 mL) was added dropwise (20 min) at −10 °C. The reaction mixture was stirred overnight at 20 °C, cooled to 0 °C, and quenched with H_2O (50 mL) and a saturated aqueous solution of NH_4Cl (50 mL). The aqueous layer was extracted with ether (3 × 35 mL), and combined ethereal fractions were dried (Na_2SO_4). Upon concentration under reduced pressure (half of the initial volume), under an atmosphere of nitrogen, the crude alcohol (7.50 g, 30 mmol; assuming 100% yield) was added to a solution of dicobalt octacarbonyl (11.29 g, 33 mmol) in dry ether (150 mL) at 20 °C and stirred for 3 h. The crude mixture was concentrated under reduced pressure and fractionated on silica gel (240 g, 3:1 PE:E) to give complex **26** (7.63 g, 47.4%) as a brick red solid. Mp: 95.1–98.5 °C (sealed capillary, dried by coevaporation with benzene, 3 × 1 mL). TLC (1:2 PE:E): R_f = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (3H, t, CH_3, J = 7.2), 2.32 (1H, m, OH), 2.79 (2H, ABX_3, CH_2, J = 15.6), 3.79 (3H, s, OMe), 3.87 (6H, s, OMe), 5.84 (1H, d, CH, J = 3.2), 6.68 (2H, s, aromatic H). MS TOF: *m/z* calcd for $C_{20}H_{18}O_{10}Co_2Na$ (MNa^+), 558.9462; found, 558.9447.

***d,l*- and *meso*-[μ-η^2-5,6-Bis(3′,4′,5′-trimethoxyphenyl)-3,7-decadiyne]bis(dicobalt hexacarbonyl) (29).** Under an atmosphere of nitrogen, a solution of the alcohol **26** (107 mg, 0.2 mmol) in dry ether (5 mL) was added dropwise (8 min) to a solution of $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol) in dry ether (20 mL) at +5 °C. The reaction mixture was stirred at +5 °C for 10 min, the temperature was decreased to 0 °C, ether was removed, and the cation **27** was washed with dry ether (2 × 15 mL). The residual amount of ether was removed under reduced pressure at −30 °C. The cation **27** was dissolved in dry CH_2Cl_2 (20 mL), cooled to −50 °C, and stirred for 15 min. Zinc (650 mg, 10 mmol) was added at −50 °C, and the reaction mixture was stirred for 5 min. The cooling bath was replaced with a water bath (20 °C), and the suspension was stirred for an additional 15 min (TLC/NMR control) and filtered through a short bed of Florisil (1 cm). The crude mixture was concentrated under reduced pressure (NMR: 80:20 *d,l*-**29**:*meso*-**29**) and fractionated on a Florisil column (20 g, degassed, −5 °C, CH_2Cl_2) to give *d,l*-**29** (41.6 mg, 40.1%) and *meso*-**29** (14.7 mg, 14.2%).

d,l-**29**: dark red solid. T_{dec} = 149.5–156.6 °C (sealed capillary, dried by coevaporation with benzene, 3 × 1 mL). TLC (1:2 PE:E): R_f = 0.46. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (6H, t, $2CH_3$,

$J = 7.2$), 2.71 (4H, ABX_3, $2CH_2$, $J = 15.8$), 3.65 (12H, br s, 4OMe), 3.77 (6H, s, 2OMe), 4.68 (2H, s, 2CH), 6.15 (4H, broad signal, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8, 27.0 (C2, C9, C1, C10), 55.7 (C5, C6), 60.7 (2OMe), 60.9 (4OMe), 100.9, 101.1 (C3, C4, C7, C8), 108.3 (br signal, aromatic C), 136.9, 137.6, 152.2 (aromatic C), 199.4, 200.5 (CO). MS TOF: *m*/*z* calcd for $C_{40}H_{34}O_{18}Co_4Na$ (MNa^+), 1060.8971; found, 1060.8953.

meso-**29** (an analytical sample was obtained by decomplexation−recomplexation sequence, by using $Ce(NH_4)_2(NO_3)_6$ and $Co_2(CO)_8$, respectively): dark red solid. T_{dec} = 166.6–179.2 °C (sealed capillary, dried by coevaporation with benzene, 3 × 1 mL). TLC (CH_2Cl_2): $R_f = 0.43$. ^1H NMR (400 MHz, $CDCl_3$): δ 0.98 (6H, t, CH_3, $J = 7.2$), 1.74 (4H, ABX_3, $2CH_2$, $J = 16.0$), 3.81 (6H, s, 2OMe), 3.85 (6H, s, 2OMe), 3.95 (6H, s, 2OMe), 4.44 (2H, s, 2CH), 6.50 (2H, d, aromatic H, $J = 1.6$), 6.76 (2H, d, aromatic). MS TOF: *m*/*z* calcd for $C_{40}H_{34}O_{18}Co_4Na$ (MNa^+), 1060.8971; found, 1060.8968.

***d*,*l*-5,6-Bis(3′,4′,5′-trimethoxyphenyl)-3,7-decadiyne (30).** Under an atmosphere of nitrogen, $Ce(NH_4)_2(NO_3)_6$ (104 mg, 0.192 mmol) was degassed and dissolved in acetone (8 mL, degassed). The solution, precooled to −78 °C, was added dropwise (8 min) to a degassed solution of *d*,*l*-**29** (24.9 mg, 0.024 mmol) dissolved in acetone (10 mL, degassed) at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, and an additional amount of $Ce(NH_4)_2(NO_3)_6$ (13 mg, 0.024 mmol) dissolved in acetone (1 mL, degassed, precooled to −78 °C) was added dropwise (1 min). The reaction mixture was stirred at −78 °C for 15 min, an additional amount of $Ce(NH_4)_2(NO_3)_6$ (13 mg, 0.024 mmol) dissolved in acetone (1 mL, degassed, precooled to −78 °C) was added dropwise (1 min), and then stirring was continued for another 15 min. The temperature was increased to −50 °C (15 min), the reaction mixture was stirred for 15 min and then warmed to −30 °C (5 min) and stirred for an additional 30 min. The final amount of $Ce(NH_4)_2(NO_3)_6$ (13 mg, 0.024 mmol) was dissolved in acetone (1 mL, degassed), precooled to −78 °C, and added dropwise (1 min) to the reaction mixture and stirred for 30 min at −30 °C. The temperature was increased to −15 °C (5 min) and the mixture stirred for 15 min (TLC control). The reaction mixture was treated (−78 °C, N_2) with a degassed, saturated aqueous solution of NaCl (20 mL). The mixture was then transferred to a separatory funnel charged with a saturated aqueous solution of NaCl (20 mL) and extracted with dry ether (2 × 15 mL). The combined organic layers were dried (Na_2SO_4), and the solvents, upon filtration, were stripped away under reduced pressure. The crude product was filtered through a short bed of Florisil (1 cm) to afford *d*,*l*-**30** (10.9 mg, 97.3%) as a pale yellow solid. Mp: 100–101 °C (sealed capillary, dried by coevaporation with benzene, 3 × 1 mL). TLC (1:3 PE:E): $R_f = 0.31$. ^1H NMR (400 MHz, $CDCl_3$): δ 1.18 (6H, t, $2CH_3$, $J = 7.2$), 2.27 (4H, q, $2CH_2$), 3.75 (12H, s, 4OMe), 3.80 (6H, s, 2OMe), 3.83 (2H, s, 2CH), 6.41 (4H, s, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6 (C2, C9), 14.3 (C1, C10), 46.0 (C5, C6), 56.0 (4OMe), 60.8 (2OMe), 79.2 (C4, C7), 86.8 (C3, C8), 106.0, 134.8, 137.0, 152.5 (aromatic C). MS TOF: *m*/*z* calcd for $C_{28}H_{34}O_6Na$ (MNa^+), 489.2253; found, 489.2259.

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Supporting Information Available: CIF files and tables giving crystallographic details, bond distances and angles, atomic coordinates and equivalent isotropic displacement parameters, and torsion angles for *d*,*l*-**20** and *d*,*l*-**25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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