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Stereoselective Synthesis of *meso*-1,5-Cyclodecadiynes

Gagik G. Melikyan,* Ryan Spencer, and Edwin Abedi

Department of Chemistry and Biochemistry, California State University Northridge, Northridge, California 91330-8262

gagik.melikyan@csun.edu

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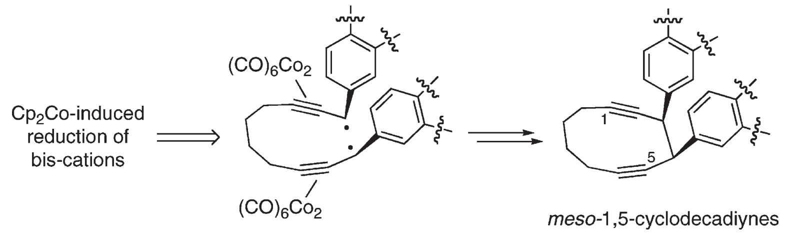

Reduction of $Co_2(CO)_6$-stabilized bis-propargyl cations with cobaltocene occurs with high *meso*-diastereoselectivity (up to 97%), affording, upon decomplexation, *meso*-1,5-cyclodecadiynes, otherwise hardly accessible.

Introduction

Synthesis of cyclic acetylenic compounds, in particular 1,5-cycloalkadiynes, has long been a synthetic challenge.[1] Existing methods suffer from a low step economy, inherent structural limitations, inability to control the stereoselectivity of cyclization, and low overall yields.[1,2] 1,5-Cyclodecadiynes occupy a unique niche in synthetic chemistry given their structural relationship to the cyclic enediynes, known anticancer agents.[3] They can act as the substrates for Cope rearrangement[4a] and trans-annular C−C bond forming reactions,[4b,c] serve as models for probing the through-space electronic interaction of the alkyne moieties,[5] and also provide an entry to a variety of classes of organic compounds (1,5-cyclodecadienes, 1,4-/1,5-cyclodecanediones, cyclodecynones). Parent 1,5-cyclodecadiyne was synthesized in 8 steps in a 1.9% overall yield.[2a] It is also accessible via cobalt-complexed propargyl cations that benefit from a bent geometry of the coordinated carbon−carbon triple bonds.[6] The same methodology, via the respective bis-cationic species, afforded 3,4-diphenyl-1,5-cyclodecadiyne in a 51% yield, as a mixture of *d*,*l*- and *meso*-diastereomers (90:10).[6] Recently, we reported on the diastereoselectivity of $Co_2(CO)_6$-mediated, Zn-induced intramolecular cyclizations of topologically diverse (0-, 4-, 3,4-, 3,4,5-)propargyl cations, affording 1,5-cyclodecadiynes.[7] The *d*,*l*:*meso* ratios in cyclized products varied in a wide range, from 80:20 to 54:46, with *d*,*l*-diastereomers being the dominant isomers. In the case of smaller rings, 1,5-cyclononadiyne[8a] and 1,5-cyclooctadiyne,[8b] *d*,*l*-configuration is still highly preferred (>98%). Analogously, trans-cyclized products were isolated from the cationic bis(1,3-pentadienyl)irontricarbonyl complexes when treated with zinc, a reducing agent.[9] Overall, thermodynamically more stable *d*,*l*-stereoisomers of 1,5-cyclodecadiynes appear to be formed predominantly, while *meso*-counterparts, more crowded and less stable, remain elusive synthetic targets. Herein we present the *first stereoselective synthesis of meso-1,5-cyclodecadiynes*.

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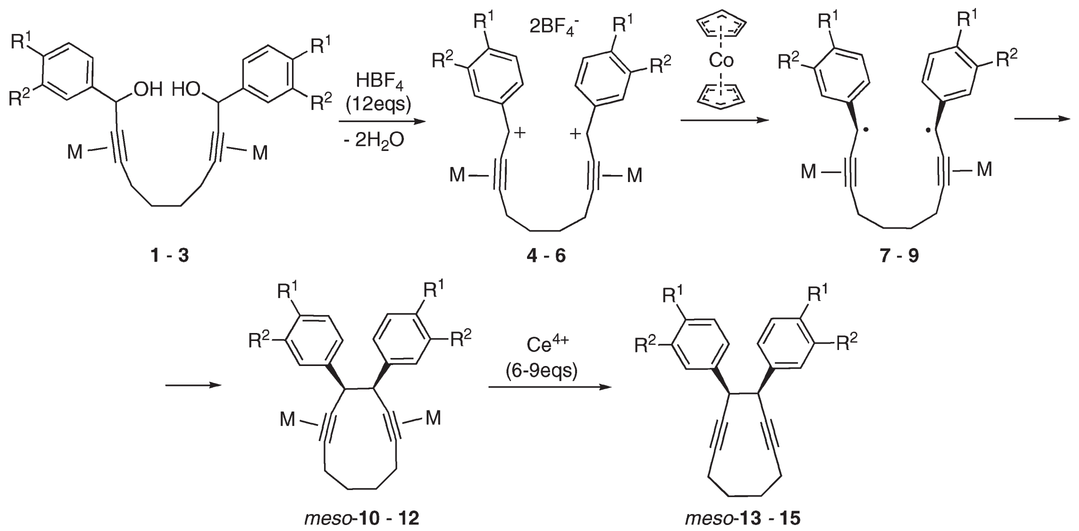
SCHEME 1. Cp_2Co-Mediated Intramolecular Cyclization Affording *meso*-1,5-Cyclodecadiynes



M = $Co_2(CO)_6$; **1**, **4**, **7**, **10**, **13** R^1=R^2=H; **2**, **5**, **8**, **11**, **14** R^1=i-Pr, R^2=H; **3**, **6**, **9**, **12**, **15** R^1=R^2=OMe.

TABLE 1. Diastereoselectivity vs. Reducing Agent

entry	bis-propargyl alcohol	substitution pattern	bis-cluster	diastereoselectivity		decomplexation product	diastereoselectivity			
				Cp_2Co			Cp_2Co		Zn[7]	
				meso:*d*,*l*	de[a]		*meso*:*d*,*l*	de[a]	*meso*:*d*,*l*	de[b]
1	**1**	0	**10**	95:5	90	**13**	95:5	90	33:67	34
2	**2**	4-	**11**	90:10	80	**14**	95:5	90	20:80	60
3	**3**	3,4-	**12**	97:3	94	**15**	97:3	94	33:67	34

[a] Major diastereomer is *meso*. [b] Major diastereomer is *d*,*l*.

Results and Discussion

Bis-propargyl alcohols **1**−**3** were synthesized in two steps by the condensation of the respective benzaldehydes with bis-lithio derivatives of 1,7-octadiyne,[10] followed by the treatment of organic bis-propargyl alcohols with a 2-fold excess of dicobaltoctacarbonyl.[11] Tetrafluoroboric acid[7,12] was then used in a 12-fold excess to effect an elimination reaction and precipitation of the requisite bis-cations **4**−**6** (Scheme 1). Reduction with cobaltocene was carried out with an optimized molar ratio of propargyl diol:Cp_2Co, 1:4,[13] in dichloromethane, at −78 °C. The transfer of a single electron from cobaltocene, a 19e$^-$ reducing agent,[14] toward cationic centers, occurs rapidly even at low temperatures (−78 °C, 15 min), generating transient bis-radicals **7**−**9**. Nearly concurrent generation of radical centers, at a high dilution, promotes an intramolecular process while minimizing the impact of intermolecular interaction, formation of high-molecular assemblies, and H-atom abstraction from the solvent. In the purely organic setting, the formation of carbocycles is most complicated by the conformational freedom of the carbon chain, putting the reacting termini far apart from each other. The presence of the bulky $Co_2(CO)_6$-cores reduces the carbon chain flexibility and brings radical centers into a closer proximity due to the bent structure of the complexed triple bond.[15,16] Intramolecular cyclization afforded bis-complexes **10**−**12** with meso-diastereomers being the dominant components. The quantitative data on diastereoselectivity are summarized in Table 1. The highest stereoselectivity was observed in the case of 3,4-dimethoxy derivative **12** (*meso*:*d*,*l*, 97:3);[17] the presence of the 4-isopropyl group somewhat lowered the stereoselectivity (**11**, *meso*:*d*,*l*, 90:10) with the parent molecule **10** exhibiting an intermediate level of stereocontrol (*meso*:*d*,*l*, 95:5). Decomplexation of the crude bis-complexes **10**−**12** with ceric ammonium nitrate (6−9 equiv; −78 °C, acetone) afforded the organic counterparts, *meso*-1,5-cyclodecadiynes **13**−**15**. The stereochemical composition remained nearly unchanged in the

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(13) Larger excess of cobaltocene, up to 100 equiv, resulted in a rapid decomposition of the cyclized products, allegedly because of the overreduction of metal cores.

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(17) Complex [μ-η^2-1,10-bis(3′,4′-dimethoxyphenyl)-2,8-decadiyne]bis(dicobalthexacarbonyl) (**16**) was formed as a side product, supposedly by the H-atom abstraction from methylene chloride. Its structure was confirmed by independent synthesis by quenching bis-cation **6** with tributyltinhydride.

course of decomplexation—isolation (PTLC; silica gel) with the concentration of meso-diastereomers varying in the narrow range of 95−97% (Table 1). The methodology thus developed allows one to circumvent an isolation of bis-clusters **10**−**12**, proceeding directly to decomplexation without any additional purification.

The relative configuration of *meso*-**12** was determined by X-ray crystallography (Figure 1).[18] The disposition of substituents around the central C_9-C_{10} bond confirms the stereochemical assignment and illustrates how strained the ring system is adopting *meso*-configuration with bulky $Co_2(CO)_6$ cores present. The dihedral angle between propargyl H-atoms is equal to 82.6° ($H_{9A}-C_9-C_{10}-H_{10A}$), shedding light on a long observed, unusual NMR signature of these hydrogens: each of them is represented by a singlet, some 0.2 ppm apart from each other (4.57−4.67 and 4.76−4.86 ppm).[7] Another two pairs of substituents around the internal C_9-C_{10} bond—alkyne moieties and phenyl groups—are positioned under nearly right angles ($C_8-C_9-C_{10}-C_1$ 86.7°; $C_{19}-C_9-C_{10}-C_{11}$ 86.7°, respectively). For comparison, in the *d,l*-diastereomer[7] all three pairs of substituents around the internal bond were found to be nearly eclipsed (0.2°; 12.6°; 12.6°). The metal cores, Co_2C_2, represent distorted tetrahedrons wherein the angles between Co−Co and C−C triple bonds deviate, to a different degree, from the expected perpendicular arrangement (78.4°; 85.6°).[12,16,19] Curiously enough, in the case of *d,l*-diastereomer[7] the level of distortion was significantly higher and nearly identical for both cluster moieties (73.1°; 73.4°). Other noteworthy structural features of *meso*-**12** include the following: (a) a distorted planarity of alkyne moieties ($C_3-C_2-C_1-C_{10}$ 6.4°, $C_6-C_7-C_8-C_9$ 11.3°) that is less emphasized than that in the *d,l*-diastereomer (10.4°, 12.4°);[7] (b) a lengthened coordinated C−C triple bond (1.304−1.317 Å vs. 1.21 Å for the free ligand) and bent geometry for coordinated alkyne units (144−149°), both indicative of the nature of bonding between transition metal and π-bonded unsaturated ligand;[12,16,19] and (c) inequivalency of alkyne units attested by the bond angles around the coordinated triple bonds ($C_1-C_2-C_3$ 141.0°; $C_2-C_1-C_{10}$ 144.7°; $C_6-C_7-C_8$ 147.3°; $C_7-C_8-C_9$ 149.1°); the angles are somewhat higher, but still comparable with those reported for *d,l*-diastereomer (140.4°; 141.0°; 145.1°; 148.6°).[7]

The *meso*-configuration of diyne **15** was independently established by means of X-ray crystallography (Figure 2).[18] The removal of the bulky metal clusters was accompanied by the significant structural and conformational changes. Thus, hydrogen atoms around the central C_1-C_2 bond are positioned under 46.3° ($H_1-C_1-C_2-H_2$), as opposed to a nearly perpendicular arrangement (82.6°) in bis-cluster **12**. Analogously, phenyl groups are arranged nearly gauche to each other ($C_{11}-C_1-C_2-C_{19}$ 49.2°), as well as the alkyne moieties are ($C_{10}-C_1-C_2-C_3$ 44.8°). Bond angles around the triple bond lie within the expected range of 168−170°; planarity of alkyne moieties is also improved due to breaking away from the metal bondage (*meso*-**15** $C_2-C_3-C_4-C_5$ 2.4°; $C_8-C_9-C_{10}-C_1$ 9.6°; *meso*-**12** $C_3-C_2-C_1-C_{10}$ 6.4°, $C_6-C_7-C_8-C_9$ 11.3°). Dispositions of phenyl groups and vicinal H-atoms are best defined as *gauche*- and *anti*-spatial arrangements ($C_{11}-C_1-C_2-H_2$ 69.9°; $C_{19}-C_2-C_1-H_1$ 165.4°). In bis-cluster **12**, due to the presence of the bulky metal cores, one of those angles undergoes a significant change ($C_{19}-C_9-C_{10}-H_{10}$ 28.5°), while the other remains nearly

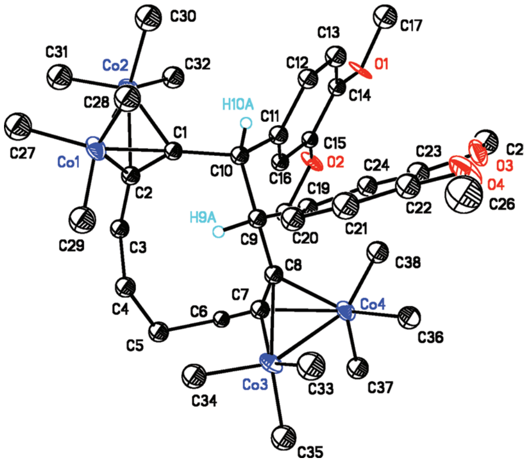

FIGURE 1. ORTEP diagram of molecular structure of *meso*-**12** with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): C(1)−C(2) 1.317; C(7)−C(8) 1.304; C(9)−C(10) 1.568; C(2)−C(1)−C(10) 144.7; C(7)−C(8)−C(9) 149.1; C(1)−C(2)−C(3) 141.0; C(6)−C(7)−C(8) 147.3; C(3)−C(2)−C(1)−C(10) 6.4; C(6)−C(7)−C(8)−C(9) 11.3; C(3)−C(4)−C(5)−C(6) 66.6; H(9A)−C(9)−C(10)−H(10A) 82.6; C(1)−C(10)−C(9)−H(9A) 30.4; C(8)−C(9)−C(10)−H(10A) 160.2; C(8)−C(9)−C(10)−C(1) 86.7; C(8)−C(9)−C(10)−C(11) 45.0; C(19)−C(9)−C(10)−C(11) 86.7.

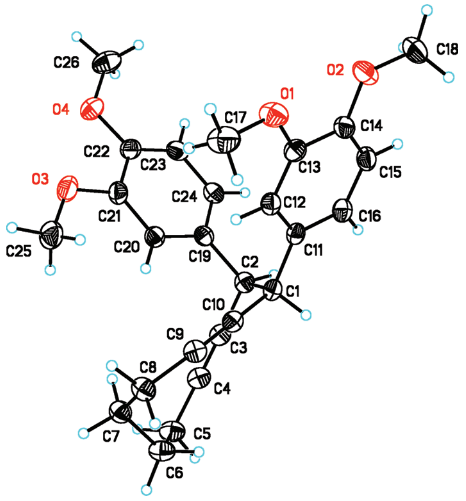

FIGURE 2. ORTEP diagram of molecular structure of *meso*-**15** with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): C(3)−C(4) 1.196; C(9)−C(10) 1.198; C(1)−C(2) 1.587; C(9)−C(10)−C(1) 168.6; C(2)−C(3)−C(4) 168.9; C(3)−C(4)−C(5) 170.0; C(8)−C(9)−C(10) 168.6; C(2)−C(3)−C(4)−C(5) 2.4; C(8)−C(9)−C(10)−C(1) 9.6; C(5)−C(6)−C(7)−C(8) 127.5; H(1)−C(1)−C(2)−H(2) 46.3; C(10)−C(1)−C(2)−H(2) 160.9; C(3)−C(2)−C(1)−H(1) 69.8; C(10)−C(1)−C(2)−C(3) 44.8; C(11)−C(1)−C(2)−C(3) 174; C(11)−C(1)−C(2)−C(19) 49.2.

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(18) (a) *APEX II*, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison, WI 53711-5373, 2005. (b) *SAINT*, Version 6.45A, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison, WI 53711-5373, 2003. (c) A short history of SHELX: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122. (d) Wilson, A. J. C., Ed. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1992; Vol. C, Tables 6.1.1.4 (pp 500−502) and 4.2.6.8 (pp 219−222).

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unaltered ($C_{11}-C_{10}-C_9-H_9$ 162.2°). Overall, in the course of the decomplexation, the meso-stereoisomer mostly retains its spatial arrangement with *cis*-phenyl groups occupying the axial and equatorial positions of the 10-membered ring (**12** $C_{19}-C_9-C_{10}-C_{11}$ 86.7°; **15** $C_{11}-C_1-C_2-C_{19}$ 49.2°). For comparison, the respective *d,l*-diastereomer[7] underwent a drastic change when released from a metal bondage: phenyl groups being nearly eclipsed in the bis-cluster (0.2°) sprang up into diaxial positions in the organic molecule (158.3°).[7]

Stereoselective formation of *meso*-diastereomers **13**−**15** could not have been predicted based on the literature precedence.[20−22] In *intramolecular cyclization reactions*,[7−9] the respective *d,l*-diastereomers—8-, 9-, and 10-membered—are formed either exclusively, or with high stereoselectivity (*d,l* 95−100%). *In intermolecular coupling reactions*, systematic studies on cobalt-complexed propargyl radicals[21] revealed the stereochemical dominance of *d,l*-diastereomers with a variety of topologically and functionally diverse substrates. With zinc acting as a reducing agent,[7] the ratio of *meso*- and *d,l*-1,5-cyclodecadiynes varies from 33:67 to 20:80 (Table 1). Replacing zinc with Cp_2Co allowed us to *fully reverse the stereochemical preference for d,l-configuration and achieve a high level of meso-diastereoselectivity* (90−97%; Table 1). Thus, for 1,5-cyclodecadiyne **10** with unsubstituted aromatic rings, the 33:67 diastereomeric ratio of *meso*:*d,l* converts to 95:5 (Table 1; entry 1). The impact of the reducing agent is more pronounced for 4-isopropyl derivative **11**: the highest observed *d,l*-diastereoselectivity (*meso*:*d,l* 20:80)[7] completely reverses (*meso*:*d,l* 90:10) with preponderant formation of *meso*-diastereomer (Table 1; entry 2). It is notable that cyclization reactions occur under *kinetic control*, producing thermodynamically less favored stereoisomers. Thus, *meso*-diastereomer **10** is higher in energy—by 5.6 kcal/mol—than its *d,l*-counterpart (PCModel, v. 9.1). In a separate set of experiments, the coupling reaction was proven *irreversible*: no interconversion was detected under standard conditions with both *d,l*- and *meso*-**12** preserving their configurational integrity. Over the two steps (cation generation/cyclization, decomplexation), the total yields of *meso*-1,5-cyclodecadiynes **13**−**15** vary in the range of 28−36%. With zinc as a reducing agent, the yields of cyclization products—containing predominantly *d,l*-diastereomers—fell within the same range (24−39%).[7] In comparison, by using purely organic means, assembling a 10-membered ring with 1,5-disposed triple bonds can be done in 8 steps, with a low 1.9% overall yield.[2a]

The disparity in the stereochemical outcome of radical coupling reactions—with zinc and Cp_2Co as alternative reducing agents—was first observed by us[21f] in *intermolecular cross-coupling reactions*. In particular, replacing Zn with Cp_2Co decreased the level of *d,l*-diastereoselectivity in the case of both terminal and γ-substituted propargyl alcohols, by 5−18% and 4−15%, respectively.[21f] Apparently, the rise in the concentration of the respective *meso*-diastereomers points out that Cp_2Co does generally favor the *meso*-configuration. In intermolecular reactions the impact is incremental, while in intramolecular cyclizations it amounts to a full reversal of the stereochemical outcome.

The observed stereochemical switch might be derived from the combination of several factors, such as conformational equilibrium, reaction temperature, reduction rate, ion−radical interactions, as well as homogeneity of the reaction mixture. The requisite, preorganized bis-cations can be represented by two pseudocyclic conformations, **A** and **B**, around the propargylic bond (Figure 3). The reduction with Cp_2Co, a 19e$^-$ species,[14] rapidly occurs at −78 °C, generating bis-radicals **C** and **D**, respectively. To examine if the observed reversal of stereoselectivity is a *temperature effect*, the reduction reaction was carried out at various temperatures (−40, 0, +40 °C) and diastereomeric composition was determined for metal complex **10** and decomplexation product **13** (Table 2). As the experimental data indicate, diastereoselectivity is, in fact, dependent upon temperature, switching from *meso*:*d,l* 95:5 at −78 °C to 42:58 at +40 °C (entries 1 and 4). The intermediate data—87:13 and 58:42 at −40 and 0 °C, respectively—further attest to the trend observed (entries 2 and 3; Table 2). Most importantly, adding a powerful reducing agent at higher temperatures, up to +40 °C, did not compromise the total yield of the diastereomeric mixtures, further validating the assumption that the reversal of stereoselectivity does in fact take place. More studies are in progress to understand the intimate nature of the temperature effect observed, in particular the dependence of conformational equilibria and rotational freedoms in cations (**A**, **B**) and radicals (**C**, **D**) upon reaction temperature, as well as the potential impact of cobaltocene-derived counterion ($Cp_2Co^+BF_4^-$).

Conclusions

Reduction of cobalt-complexed bis-propargyl alcohols with cobaltocene provides an easy, two-step access to *meso*-1,5-cyclodecadiynes with an excellent stereoselectivity (90−97%). To the best of our knowledge, this method represents the first synthetically viable procedure for the synthesis of this class of organic compounds with *meso*-configuration. The method contributes to the synthetic repertoire of radical chemistry mediated by transition metals. Its use as a key step in total synthesis of complex molecular assemblies and as a novel carbon framework in drug development can be envisioned.

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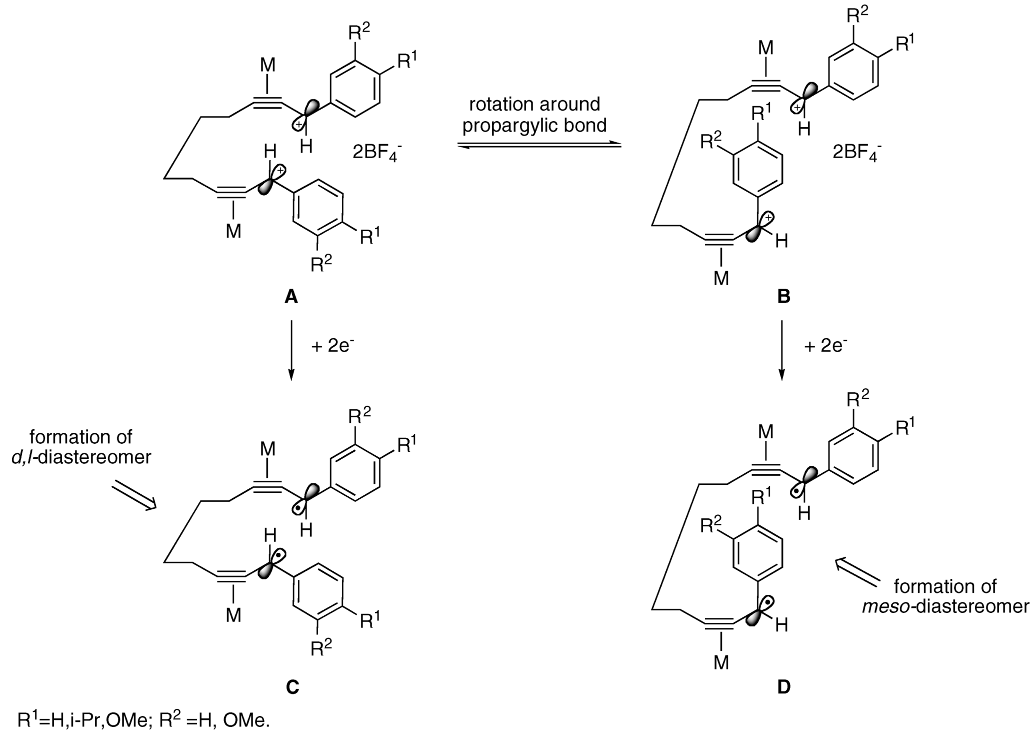
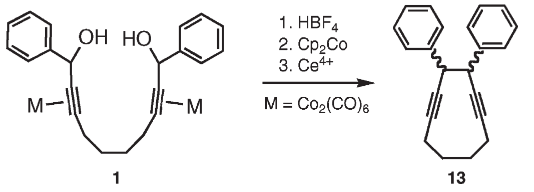


FIGURE 3. Conformational equilibrium of the cobalt-complexed bis-cations (**A**, **B**) and bis-radicals (**C**, **D**).

TABLE 2. Diastereoselectivity as a Function of Temperature



		diastereoselectivity		
entry	temp, °C	bis-cluster **10** *meso*:*d,l*	**13** *meso*:*d,l*	yield, % (over 2 steps)
1	−78	95:5	95:5	36.3
2	−40	87:13	89:11	39.7
3	0	58:42	60:40	45.0
4	+40	42:58	41:59	44.0

Experimental Section

***meso*-3,4-Diphenyl-1,5-cyclodecadiyne (13).** Under an atmosphere of nitrogen, a solution of the bis-alcohol **1** (89.0 mg, 0.1 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 −20 °C. The reaction mixture was stirred at −20 °C for 15 min, the ethereal layer was removed, and the bis-cation **4** was washed with dry ether (2 × 15 mL) at −30 °C. The residual amount of ether was removed under reduced pressure, and the cation was dissolved in dry CH_2Cl_2 (15 mL) at −78 °C. A solution of Cp_2Co (75.6 mg, 0.4 mmol) in CH_2Cl_2 (5 mL) was added dropwise (2 min) to the reaction flask at −78 °C and the mixture was stirred for 15 min (TLC control). The crude mixture was filtered through a short bed of Florisil (1 cm), and organic solvents were stripped away under reduced pressure (NMR: *meso*-**10**:*d,l*-**10** 95:5). The residue was dissolved in acetone (10 mL, degassed) and treated with a solution of $Ce(NH_4)_2(NO_3)_6$ (219 mg, 0.4 mmol; molar ratio 1:4 assuming 100% yield of **10**) in acetone (4 mL, degassed; N_2, −78 °C). Upon addition (4 min), the reaction mixture was stirred at −78 °C for 15 min, and then at −50 °C for 30 min. An additional portion of $Ce(NH_4)_2(NO_3)_6$ (109.6 mg, 0.2 mmol) was added (degassed acetone, 2 mL) dropwise at −78 °C (2 min), and the reaction mixture was stirred for 15 min, then at −50 °C for 30 min (TLC control). A degassed saturated solution of $NaCl_{aq}$ (20 mL) was added at −78 °C, and the mixture was transferred to a separatory funnel and extracted with ether (2 × 15 mL). The combined organic layers were dried (molecular sieves 4 Å), organic solvents were removed under reduced pressure, and the crude mixture was fractionated by preparative TLC (10:1, PE:E) to afford a mixture of *meso*-**13** and *dl*-**13** (NMR: *meso*-**13**: *dl*-**13**, 95:5) as a light yellow solid (10.3 mg, 36.3%). Mp 93−94 °C (sealed capillary; dried at 58 deg/1 mm/5 h). TLC (5:1 PE:E) R_f 0.53. Spectral characteristics are identical with those reported earlier.[7]

Under analogous conditions, at −40, 0 and +40 °C the ratios and yields of *meso*-**13** and *dl*-**13** were equal to 89:11 (39.7%), 60:40 (45.0%), and 41:59 (44.0%), respectively.

***meso*-3,4-Bis(4′-isopropylphenyl)-1,5-cyclodecadiyne (14).** Under an atmosphere of nitrogen, a solution of the bis-alcohol **2** (97.4 mg, 0.1 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 −20 °C. The reaction mixture was stirred at −20 °C for 15 min, the ethereal layer was removed, and the bis-cation **5** was washed with dry ether (3 × 15 mL) at −10 °C. The residual amount of ether was removed under reduced pressure, and the cation was dissolved in dry CH_2Cl_2 (15 mL) at −78 °C. A solution of Cp_2Co (75.6 mg, 0.4 mmol) in CH_2Cl_2 (5 mL) was added dropwise (2 min) to the reaction flask at −78 °C and the mixture was stirred for 15 min (TLC control). The crude mixture was filtered through a short bed of Florisil (1 cm), and organic solvents were stripped away under reduced pressure (NMR: *meso*-**11**:*d,l*-**11** 90:10). The residue was dissolved in acetone (10 mL, degassed) and treated with a solution of $Ce(NH_4)_2(NO_3)_6$ (219 mg, 0.4 mmol; molar ratio 1:4 assuming

100% yield of **11**) in acetone (4 mL, degassed). Upon addition (4 min), the reaction mixture was stirred at −78 °C for 15 min, then at −50 °C for 30 min. An additional portion of $Ce(NH_4)_2(NO_3)_6$ (219 mg, 0.4 mmol) was dissolved in acetone (4 mL, degassed), added dropwise (4 min) at −78 °C to the reaction mixture, stirred for 15 min, then stirred at −50 °C for 30 min (TLC control). The mixture was treated (−78 °C, N_2) with a degassed saturated solution of $NaCl_{aq}$ (20 mL), transferred to a separatory funnel, and extracted with ether (2 × 15 mL). The combined organic layers were dried (molecular sieves 4 Å), organic solvents were removed under reduced pressure, and the crude mixture was fractionated by preparative TLC (20:1 PE:E) to afford a mixture of *meso*-**14** and *dl*-**14** (NMR: *meso*-**14**:*d,l*-**14**, 95:5) (10.1 mg, 28.0%) as a light yellow oil. TLC (10:1 PE:E) R_f 0.58. Spectral characteristics are identical with those reported earlier.[7] ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 24.1, 24.2, 28.0, 33.8, 45.9, 83.3, 88.7, *meso*- 125.6, *d,l*- 126.5, 127.8, *meso*- 128.6, 135.2, *d,l*- 138.6, *meso*- 147.4.

***meso*-[μ-η^2-3,4-Bis(3′,4′-dimethoxyphenyl)-1,5-cyclodecadiyne]-bis(dicobalthexacarbonyl) (12) and *meso*-3,4-Bis(3′,4′-dimethoxyphenyl)-1,5-cyclodecadiyne (15).** Under an atmosphere of nitrogen, a solution of the bis-alcohol **3** (101 mg, 0.1 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 −20 °C. The reaction mixture was stirred at −20 °C for 15 min, the ethereal layer was removed, and the bis-cation **6** was washed with dry ether (2 × 15 mL) at −30 °C. The residual amount of ether was removed under reduced pressure, and the cation was dissolved in dry CH_2Cl_2 (15 mL) at −78 °C. A solution of Cp_2Co (75.6 mg, 0.4 mmol) in CH_2Cl_2 (5 mL) was added dropwise (2 min) to the reaction flask at −78 °C and the mixture was stirred for 15 min (TLC control). The crude mixture was filtered through a short bed of Florisil (1 cm), and organic solvents were stripped away under reduced pressure (NMR *meso*-**12**:*d,l*-**12**:**16**[17] 82:3:15, *meso*-**12**:*d,l*-**12** 97:3). Major diastereomer—*meso*-**12**—can be isolated by preparative TLC (1:2 PE:CH_2Cl_2, 2 runs). Spectral characteristics are identical with those reported earlier.[7] Single crystals suitable for X-ray structure analysis were obtained by methanol vapor diffusion into a solution of *meso*-**12** in CH_2Cl_2 (+5 °C, 1 day). The residue (*meso*-**12** + *d,l*-**12** + **16**) was dissolved in acetone (10 mL, degassed) and treated with a solution of degassed $Ce(NH_4)_2(NO_3)_6$ (438 mg, 0.8 mmol; molar ratio of 1:8 assuming 100% yield of **12**) in acetone (8 mL, degassed; N_2, −78 °C). Upon addition (10 min), the reaction mixture was stirred at −78 °C for 15 min, then at −50 °C for 30 min. An additional portion of $Ce(NH_4)_2(NO_3)_6$ (54.8 mg, 0.1 mmol) dissolved in acetone (1 mL, degassed) was added dropwise (1 min) at −78 °C, and the reaction mixture was stirred for 15 min, then stirred at −50 °C for 30 min (TLC control). The mixture was treated (−78 °C, N_2) with a degassed saturated solution of $NaCl_{aq}$ (20 mL), transferred to a separatory funnel, and extracted with ether (2 × 15 mL). The combined organic layers were dried (molecular sieves 4 Å), organic solvents were removed under reduced pressure, and the crude mixture was fractionated by preparative TLC (PE) to afford *meso*-**15** (11.8 mg, 28.1% over two steps; *meso*-**15**:*d,l*-**15** 97:3) as a yellow amorphous solid. TLC (E) R_f 0.43 (PMA); ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (m, 4H), 2.33 (m, 4H), 3.67 (s, 6H), 3.80 (s, 6H), 4.10 (s, 2H), 6.57 (ABC-spectrum, $J_{H(A)-H(B)}$ = 8.0 Hz, $J_{H(B)-H(C)}$ = 2.0 Hz, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 21.1, 28.0, 46.0, 55.6, 55.8, 83.2, 88.7, 110.4, 112.0, 112.1, 120.8, 130.3, 147.9, 148.1; HRMS (TOF) *m*/*z* calcd for $C_{26}H_{29}O_4$ $[MH]^+$ 405.2060, found 405.2070. Single crystals suitable for X-ray structure analysis were obtained by methanol vapor diffusion into a solution of *meso*-**15** in EA (+5 °C, 3 days).

[μ-η^2-1,10-Bis(3′,4′-dimethoxyphenyl)-2,8-decadiyne]bis(dicobalthexacarbonyl) (16). Under an atmosphere of nitrogen, $HBF_4 \cdot Me_2O$ (32.2 mg, 0.24 mmol) was added dropwise (30 s) to a solution of the bis-alcohol **3** (40.2 mg, 0.04 mmol) in dry ether (10 mL) at 0 °C and the mixture was stirred for 15 min. The ethereal layer was removed, then the bis-cation was washed with dry ether (2 × 15 mL) at −30 °C and suspended in ether (10 mL). Tributyltinhydride (46.6 mg, 0.16 mmol) was added dropwise (30 s) at 0 °C and the mixture was stirred for 30 min (TLC control). The crude mixture was concentrated under reduced pressure and fractionated on preparative TLC (1:1 PE:E) to afford **16** (27.2 mg, 70.1%) as a brown-red oil. TLC (CH_2Cl_2) R_f 0.45; ^1H NMR (400 MHz, $CDCl_3$) δ 1.81 (m, 4H), 2.88 (m, 4H), 3.87 (s, 6H), 3.89 (s, 6H), 4.05 (s, 4H), 6.76−7.88 (m, 6H); HRMS (TOF) *m*/*z* calcd for $C_{38}H_{30}O_{16}ClCo_4$ $[M + Cl]^-$ 1012.8556, found 1012.8548.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for products, tables of crystallographic details, bond distances and angles, atomic coordinates, and equivalent isotropic displacement parameters, as well as torsion angles for *meso*-**12** and *meso*-**15** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.