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1,3-Steric Induction in Intermolecular Radical Reactions Mediated by a $Co_2(CO)_6$−Metal Core

Gagik G. Melikyan,* Ryan Spencer, and Aaron Rowe

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

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Diastereoselectivity of propargyl coupling reactions can be controlled by using the bulkiness of a γ-substituent as a stereochemical tool. This 1,3-steric induction was observed with γ-t-Bu and γ-Me_3Si groups, both favoring a *d,l*-configuration of the head-to-head coupling products, 3,4-disubstituted 1,5-alkadiynes (*d,l*- 95−100%). X-ray crystallography analysis suggests that the most favorable orientation of converging propargyl radicals is the one in which the bulky γ-substituents are positioned *anti* to each other. Overall, the synthetic strategy of employing a Me_3Si auxiliary group involves five steps and affords, with 28−33% overall yields, pure *d,l*-3,4-diaryl-1,5-hexadiynes, otherwise hardly accessible.

Introduction

Propargyl radical coupling represents a potentially viable approach to generation of acyclic and cyclic alkadiynes with a 1,5-disposition of the triple bonds. The latter can readily be converted, via conventional methods, to a variety of classes of organic compounds (1,5-alkadienes, 1,4-/1,6-diketones, cyclopentenes, cyclopentenones, cycloalkane-1,2-diols, enediynes, fused carbocycles),[1] further highlighting its value and significance to synthetic organic chemistry. In a purely "organic" setting, propargyl−propargyl coupling exhibits a poor regioselectivity due to acetylene−allene rearrangement, forming nearly inseparable mixtures of functional group isomers.[2a] Another drawback is that organic molecules do not provide the anchoring points in proximity to the stereogenic centers so that the stereochemistry of the head-to-head coupling products—1,5-alkadiynes—could be controlled by auxiliary functional groups, either sterically or electronically. Substantial quantities of isomeric allenes (45−50%) are formed in intermolecular coupling of propargyl alcohols with $Ti(OiPr)_2Cl_2$/Mg, along with poor diastereo- and regioselectivities and low conversions (∼70%).[2b] Despite the step economy, metal-catalyzed processes (Ru, Pd) are limited in scope,[2c,d] with their yields and diastereoselectivities declining in the presence of electron-donating and electron-withdrawing substituents (Me; OMe and CF_3, respectively).[2c] In addition, metal-promoted dimerizations exhibit a low regioselectivity because of the formation of isomeric allene-ynes.[2d] Coordination of triple bonds with transition metals has proven to be an effective strategy in stabilizing propargyl cations, such as **1** (Figure 1).[3] Most importantly, the formation of a π-bond between the triple bond and transition metal precludes an unwanted acetylene−allene rearrangement[2] and directs incoming electrophiles, or radicals, exclusively toward the α-carbon atom. The bent geometry of the acetylenic moiety ($\theta_{R\text{-}C\equiv C\text{-}R}$ 140−145°),[3] in tandem with the bulkiness of a $Co_2(CO)_6$ core, provides a unique opportunity for influencing the configurations of the stereocenters generated alpha to the metal cluster. The chemistry of radical counterparts, such as **2**, has been a focus of systematic studies in our laboratory,[4] allowing for discovery of the spontaneous[4b] and THF-mediated[4c] conversion of propargyl cations to the

*To whom correspondence should be addressed. E-mail: gagik.melikyan@csun.edu.

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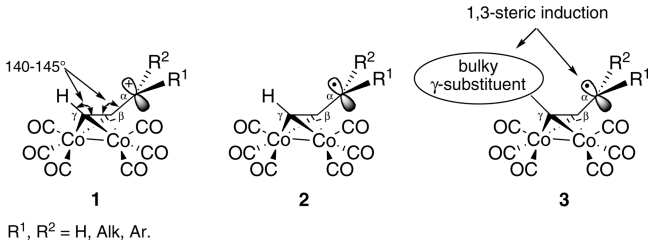

Figure 1

respective radicals, stereoselective synthesis of *d,l*-hexestrol,[4a] formation of topologically diverse *d,l*-1,5-alkadiynes,[4a−c,f,g] efficient assembling of highly sought after 1,5-cyclodecadiynes,[4e] generation of propargyl cations under neutral conditions,[4g] expansion of the temperature range for the spontaneous propargyl cation-to-radical conversion (up to 147 °C),[4f] and reversal of stereoselectivity in intramolecular reactions yielding otherwise inaccessible *meso*-1,5-cyclodecadiynes (up to 97%).[4h]

The bent geometry[3] of cobalt-complexed propargyl radicals **2** provides yet another avenue for controlling the stereochemistry of radical C−C bond formation, *a 1,3-steric induction over the metal-complexed triple bond.* In particular, the presence of a bulky substituent at the γ-carbon atom in propargyl radical **3** could play a dual role. First, due to the 1,3-repulsion, the rotational freedom around a $C_\alpha-C_\beta$ propargyl bond can be constrained. Second, unlike radicals **2** with terminal triple bonds, radicals **3**, while converging, have to place bulky γ-substituents and cobalt−alkyne units further apart from each other. Such a spatial rearrangement could alter the stereochemical outcome of the radical coupling reactions.

The concept of *"remote stereocontrol"* has long been used in organic chemistry to impact the stereoselectivity in ionic and radical reactions.[5] In the cobalt−alkyne series, the 1,4-asymmetric induction was successfully employed in condensation of γ-alkoxy propargyl aldehydes with methyl anions and reduction of γ-alkoxy ketones.[6] The diastereoselectivity of nucleophilic addition reactions was found to reverse, ranging from *anti*:*syn* 96:4 to 6:94.[6] In this account, we report on the *first 1,3-steric induction in radical reactions of the cobalt−alkyne complexes*. The current study was undertaken to determine if the presence of a bulky γ-substituent could favorably affect the stereochemistry of intermolecular propargyl−propargyl coupling reactions. Another objective was to test the efficacy of stereodirecting auxiliary groups that could be subsequently removed, providing an access to 1,5-alkadiynes, which are otherwise inaccessible as individual diastereomers.

Results and Discussion

Cobalt-complexed propargyl alcohol **4** was involved in dimerization reactions in different settings,[4b−d,f,7] yielding 1,5-hexadiyne **5** as diastereomeric mixtures (Scheme 1). The typical sequence included the conversion to the $Co_2(CO)_6$-complexed propargyl cation **6**, followed by its reduction to radical **7** and the ensuing intermolecular coupling reaction. The level of diastereocontrol was found to be dependent upon the nature of a reducing agent (Zn[4d,7] vs Cp_2Co[4d]), the reaction temperature (0−147 °C),[4d,f] and the type of radical transformation involved (spontaneous,[4b] THF-mediated,[4c] self-coupling,[7] cross-couping[4d]). The lowest stereoselectivities were observed in Zn-[7] and Cp_2Co[4d]-induced reductions (*d,l*-**5**:*meso*-**5**, 75:25 and 76:24, respectively), while THF-mediated self-coupling reactions, albeit with a lower mass efficacy, exhibited a higher level of *d,l*-diastereocontrol (*d,l*-**5**:*meso*-**5**, 92:8).[4d] In order to study the impact of the γ-substituent on the diastereoselectivity of propargyl coupling reactions, the reductions were carried out under standardized conditions (50-fold excess of Zn, −50 °C, 5 min, then 20 °C, 1 h). The formation of dimer **5** occurred with a higher stereoselectivity (*d,l*-**5**:*meso*-**5**, 89:11 vs 75:25[7] or 83:17[4d]) and a good overall yield (67.6%). Incorporation of methoxy groups on the periphery of the aromatic nuclei, in a 3,4,5-pattern, did not affect the stereoselectivity of the dimerization reaction. Thus, the conversion of 3,4,5-$(OMe)_3$ alcohol **8** to radical dimer **9**, via propargyl cation **10** and propargyl radical **11**, afforded a diastereomeric mixture in the ratio of *d,l*-**9**:*meso*-**9**, 87:13 (Scheme 1). The chromatographic mobilities of *d,l*- and *meso*-diastereomers are quite similar, making the isolation of *d,l*-**9** a costly and tedious task (56.6%).

The impact of a γ-substituent upon diastereoselectivity of coupling reactions was first tested by replacing an acetylenic hydrogen with a much bulkier, *tert*-butyl group (ΔV 96 Å^3, PCModel). Propargyl alcohol **12** (R = H) was synthesized by the condensation of lithiated *tert*-butylacetylene and benzaldehyde,[4g,8a] followed by the complexation with dicobaltoctacarbonyl[3,8b] (Scheme 2). Its treatment with HBF_4[3,4] yielded the cation **13**, which was reduced, at −50 °C, with a 50-fold excess of Zn, affording, via requisite radicals **14**, dimeric product **15**. The diastereoselectivity was enhanced by the *tert*-butyl group, forming *d,l*- and *meso*-stereoisomers in the ratio of 95:5. In the case of 3,4,5-$(OMe)_3$ alcohol **16**, the same synthetic protocol formed the expected dimeric product via intermediate propargyl cation **17** and its radical counterpart **18**. Only a single, *d,l*-diastereomer **19** could be isolated and structurally characterized. *These data represent a positive proof of concept that by replacing an acetylenic hydrogen with a bulky, tert-butyl group, the d,l-diastereoselectivity can be significantly enhanced, yielding d,l-diastereomers **15** and **19** with an excellent stereoselectivity* (*95:5 and 100:0, respectively*).

d,l-Diastereomer **19** features an unusual NMR spectrum in which 3-OMe and 5-OMe groups are "collapsed" instead of being represented by sharp singlets.[4e,f] Molecular modeling confirmed that the *d,l*-configuration is extremely crowded, with its conformational freedoms being severely restrained. A high degree of steric hindrance might be the reason for its limited stability, even at ambient temperature. To unambiguously establish the relative configuration of *d,l*-**19**, its structure was resolved by means of X-ray crystallography (Figure 2).[9] As an ORTEP diagram suggests, the bulky *tert*-butyl groups are

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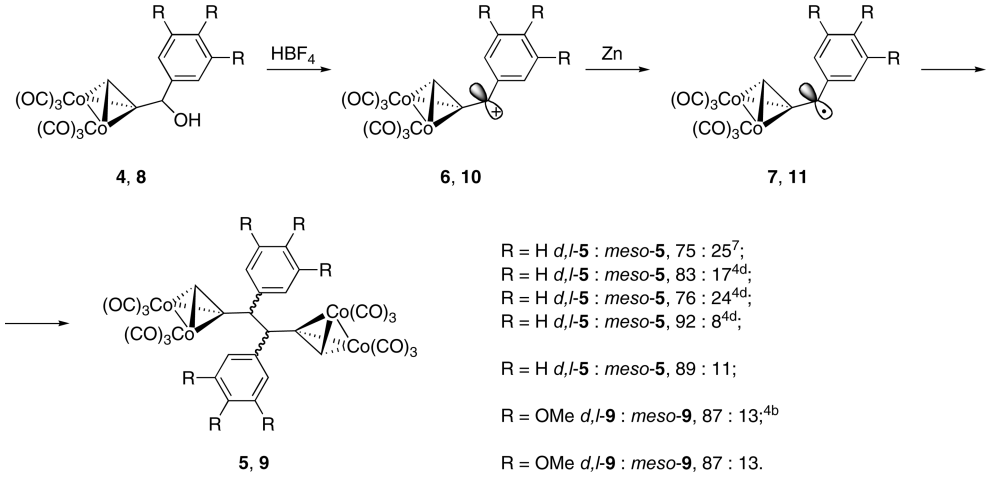
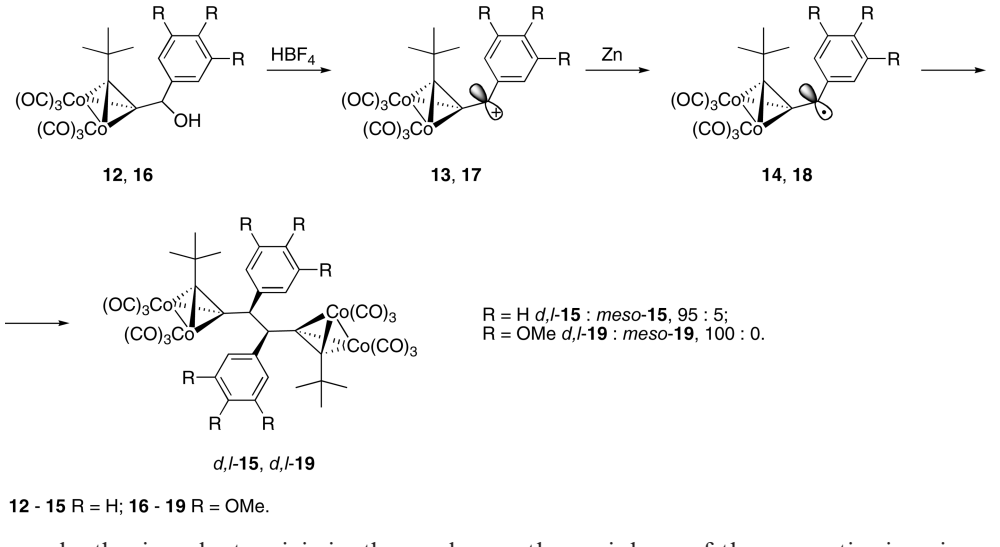
Scheme 1. Propargyl Alcohols with Terminal Triple Bonds: Dimerization with a Low to Moderate Stereoselectivity



Scheme 2. Propargyl Alcohols with γ-*tert*-Butyl Substituents: Highly Stereoselective Dimerization



pushed away from each other in order to minimize the repulsion ($\theta_{C9-C8-C7-C6}$ 135.3°). Such an arrangement stands in sharp contrast with that of 1,5-alkadiynes, having terminal triple bonds:[4a,7] cobalt−alkyne units are located *gauche* to each other, along with an *anti* disposition of hydrogen atoms. The aromatic rings are partially stacked on top of each other with a dihedral angle $\theta_{C24-C8-C7-C15}$ being equal to only 34.1°. Internal H atoms are arranged nearly orthogonally ($\theta_{H7-C7-C8-H8}$ = 93°), which represents a significant deviation from an ideal *gauche* or *anti* disposition. A steric hindrance also manifests itself in distorted dihedral angles around the metal-complexed triple bonds ($\theta_{C2-C1-C6-C7}$ = 11.6°; $\theta_{C8-C9-C10-C11}$ = 13.5°). The latter is reflective of the departure from the normally linear geometry found in cobalt−alkyne complexes.[3]

The observed 1,3-steric induction of a γ-*tert*-butyl group upon the relative configuration of radical coupling products can be exploited in a synthetically meaningful manner if the stereodirecting moiety can act in an auxiliary capacity and be removed after the radical carbon−carbon bond formation. Stereoselective synthesis becomes of utmost importance in those cases when the diastereomeric mixtures cannot be easily resolved. In particular, introducing methoxy substituents on the periphery of the aromatic rings impacts the relative chromatographic mobility of *d,l*- and *meso*-diastereomers, with 3,4-$(OMe)_2$[4g] and 3,4,5-$(OMe)_3$[4b,g] derivatives being the most difficult to separate. For this reason, a γ-*tert*-butyl group was replaced with a γ-trimethylsilyl moiety, which could be easily removed under basic conditions, even at ambient temperature.[10] Silicon is a larger atom than carbon (VdW radii: C 1.70 Å; Si 2.10 Å),[11] and consequently, the volume of a Me_3Si group is greater, by ~17 Å^3, than that of its all-carbon counterpart, a t-Bu group.[12] Given the enhanced bulkiness of an auxiliary group, one could anticipate an even higher *d,l*-diastereoselectivity in radical coupling reactions due to the more efficient 1,3-steric induction.

γ-Trimethylsilyl propargyl alcohol **20** was synthesized in two steps (45.3%) from commercial products, by utilizing

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(12) PCModel, version 9.1: Me_4C V = 138.14 Å^3, Me_4Si V = 156.74 Å^3, ΔV = 18.60 Å^3; Me_3CH V = 117.46 Å^3, Me_3SiH V = 133.60 Å^3, ΔV = 16.14 Å^3.

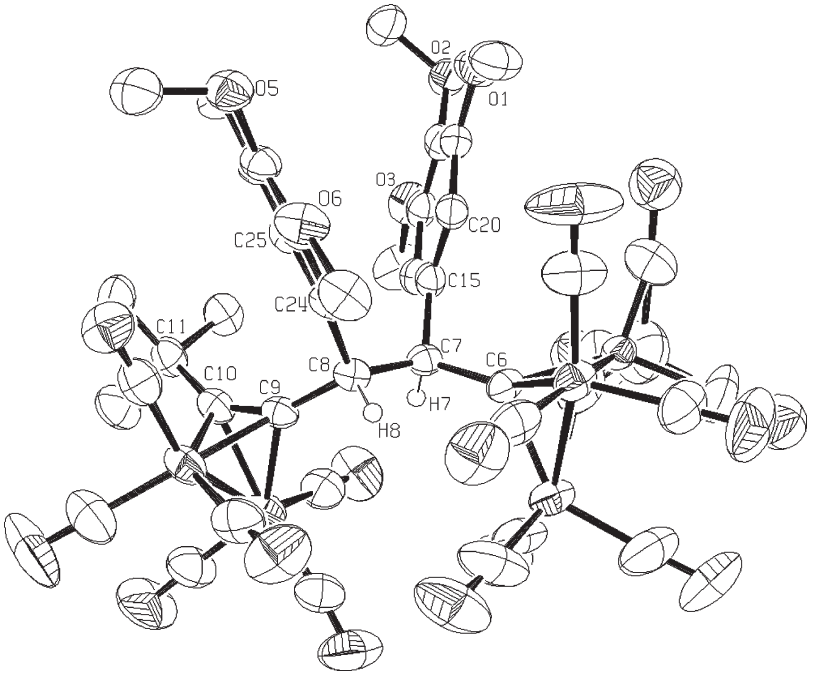
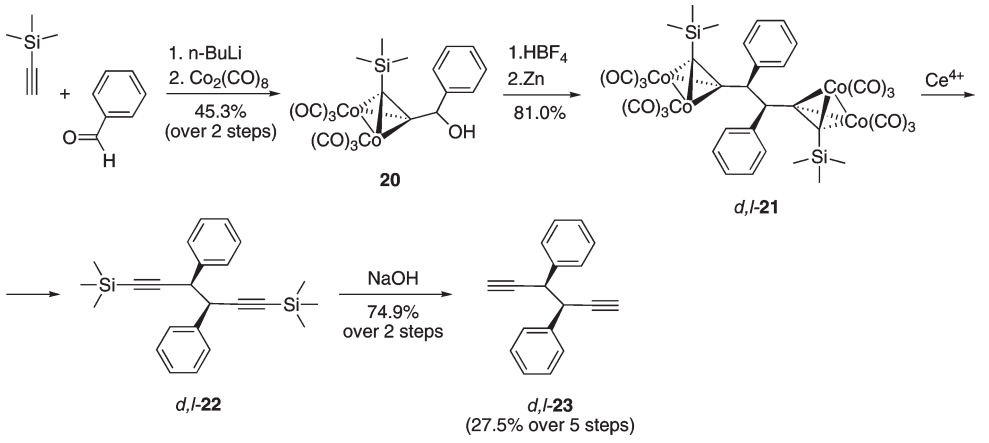


Figure 2. ORTEP diagram of *d,l*-μ-η^2-[5,6-di(3′,4′,5′-trimethoxyphenyl)-2,2,9,9-tetramethyl-3,7-decadiyne]bis(dicobalthexacarbonyl) (**19**). Selected bond lengths (Å) and angles (deg): C6−C7 1.52, C7−C8 1.57, C8−C9 1.52, C2−C1−C6−C7 11.6, C8−C9−C10−C11 13.5, C9−C8−C7−C6 135.3, C24−C8−C7-C15 34.1, H7−C7−C8−H8 93.0.

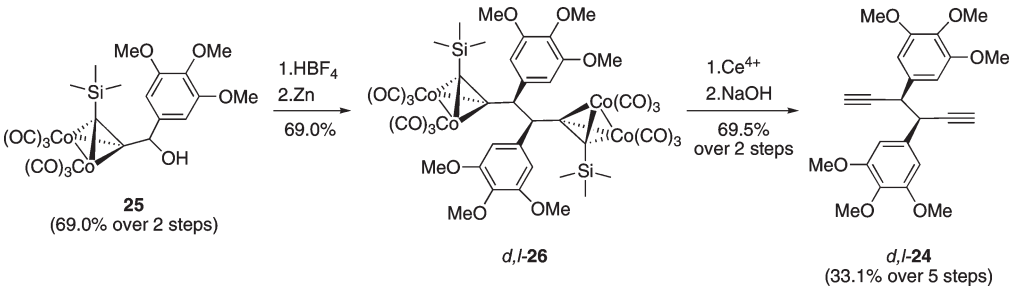
Scheme 3. Propargyl Alcohols with a Removable γ-Me_3Si Substituent: Highly Stereoselectivite Dimerization



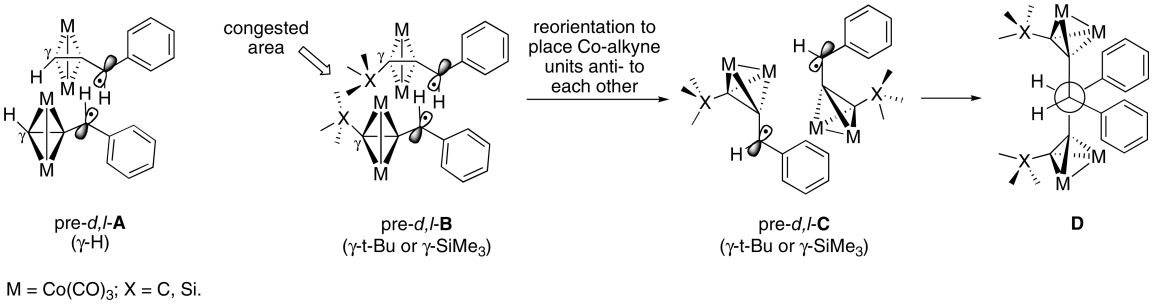
the condensation−complexation sequence[4g,8] (Scheme 3). The treatment with HBF_4 (6 equiv),[3,4] followed by the reduction with a 50-fold excess of Zn, afforded radical dimer **21** in high yield (81.0%) and with an excellent *d,l*-diastereoselectivity (*d,l*:*meso*, 99:1). Decomplexation with ceric ammonium nitrate[3a,g,4] allowed for release of an organic dimer, *d,l*-**22**, which was then treated, without additional purification, with NaOH in order to remove the auxiliary Me_3Si groups.[10] The parent radical dimer, *d,l*-**23**, was isolated as an individual diastereomer in high yield (74.9% over two steps). Thus, a five-step sequence allowed for utilizing the stereodirecting ability of an auxiliary Me_3Si group and assembling *d,l*-diastereomer **23** in an isomerically pure form, in 27.5% overall yield. The same strategy was applied for the stereoselective synthesis of *d,l*-**24** (Scheme 4), for which diastereomers are notoriously difficult to isolate: milligram quantities of individual isomers can be obtained by column chromatography, in 12 h, by using ∼5 gallons of organic solvents! Requisite alcohol **25** was synthesized in two steps (69.0%),[4g,8] then converted to the respective cationic species under acidic conditions[3,4] and reduced with Zn to yield *d,l*-**26** with an excellent *d,l*-diastereoselectivity (*d,l*:*meso*, 98.5:1.5) and in a good yield (69.0%). The decomplexation[3a,g,4]−desilylation[10] sequence released pure *d,l*-**24** in 69.5% yield over two steps. Thus, a five-step sequence again allowed us to exploit a Me_3Si group, as an auxiliary moiety, and synthesize otherwise inaccessible, isomerically pure *d,l*-diastereomer **24** in 33.1% overall yield.

The X-ray structure of *d,l*-**24** represents an extended conformation with aryl groups positioned *anti* to each other ($\theta_{C20-C26-C18-C9}$ 166.0°) (Figure 3). The dihedral angle between two triple bonds is ideally *gauche* ($\theta_{C25-C26-C18-C23}$ 60.2°), while the hydrogen atoms exhibit only a slight deviation from an expected value ($\theta_{H26-C26-C18-H18}$ 68.4°). Conformationally, the X-ray structure of *d,l*-**24** represents a striking departure from its metal-clustered counterpart *d,l*-**19**. The latter was forced to place its bulky, γ-substituted cobalt−alkyne moieties *anti* to each

Scheme 4. 1,3-Steric Induction in the Stereoselective Synthesis of *d,l*-1,5-Hexadiyne 24



Scheme 5. Alternative Pre-d,*l*-dispositions of Converging Propargyl Radicals



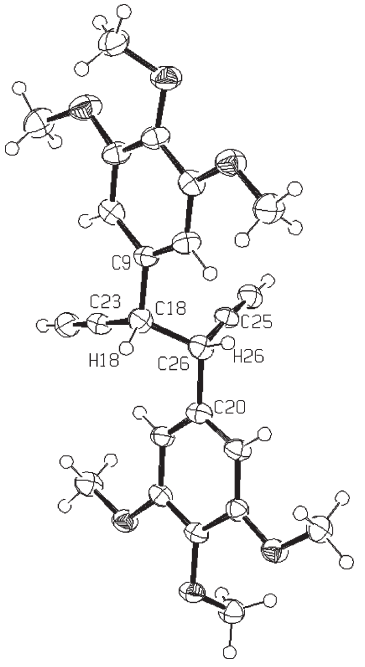


Figure 3. ORTEP diagram of *d,l*-3,4-di(3′,4′,5′-trimethoxyphenyl)-1,5-hexadiyne (**24**). Selected bond lengths (Å) and angles (deg): C9−C18 1.53, C18−23 1.46, C18−C26 1.56, C26−C20 1.52, C26−C25 1.46; C9−C18−C26 112.7, C9−C18−C23 111.9, C18−C26−C20 114.2, C20−C26−C25 110.9; C20−C26−C18−C9 166.0, C25−C26−C18−C23 60.2, H26−C26−C18−H18 68.4.

other, while holding aromatic rings in a partially eclipsed manner. The steric relief attendant with the removal of γ-substituents and metal cores allowed for aromatic rings to spring out (*d,l*-**19** $\theta_{C24-C8-C7-C15}$ 34.1° vs *d,l*-**24** $\theta_{C20-C26-C18-C9}$ 166.0°), while placing the triple bonds *gauche* to each other (*d,l*-**19** $\theta_{C9-C8-C7-C6}$ 135.3° vs *d,l*-**24** $\theta_{C25-C26-C18-C23}$ 60.2°).

The observed 1,3-steric induction can best be accounted for in terms of the repulsion between γ-located, bulky t-Bu or Me_3Si groups (Scheme 5). In the case of terminal propargyl radicals (γ-H), hydrogen atoms, given their size, can be pointed at each other in the pre-*d,l*-arrangement **A**. After the formation of the $C_\alpha-C_\alpha$ bond, according to X-ray crystal structures,[4a,7] cobalt−alkyne units are arranged *gauche* to each other, with acetylenic hydrogens being positioned in close proximity to each other. When bulky t-Bu or Me_3Si groups are introduced, respective pre-*d,l*-arrangement **B** becomes destabilized due to the repulsion between γ-substituents. To facilitate the convergence, propargyl radicals can undergo a spatial rearrangement, placing the bulky cobalt−alkyne units *anti* to each other (pre-*d,l*-arrangement **C**). Dimerization would then form *d,l*-diastereomer **D**, in which hydrogen atoms are positioned *gauche* to each other, while bulky cobalt−alkyne units maintain an *anti* disposition. Conformation **D** is consistent with the X-ray structure of *d,l*-**19** (Figure 2), featuring *gauche*-oriented aromatic rings and methine hydrogens along with the bulky substituents—(t-BuC≡C)$Co_2(CO)_6$—pointed away from each other. Analogous crystal structures were reported by us for topologically related radical dimers—γ-Et,[4j] γ-C_6H_4OMe[4d]—further highlighting the generality of how propargyl radicals respond conformationally to an increased bulkiness at the remote γ-position.

Conclusion

Due to 1,3-steric induction, the diastereoselectivity of intermolecular coupling reactions of $Co_2(CO)_6$-complexed propargyl radicals can be controlled by relatively large γ-substituents. Steric repulsion forces radical species to converge in a manner that places conflicting bulky substituents *anti* to each other. Both permanent t-Bu and auxiliary Me_3Si groups can substantially improve the diastereoselectivity of these reactions, affording *d,l*-1,5-alkadiynes with excellent stereoselectivity (γ-t-Bu 95−100%; γ-Me_3Si 98.5−99%). Overall, the synthetic strategy employing a Me_3Si auxiliary group involves five steps and yields, with 28−33% overall yields, pure *d,l*-diastereomers, which are otherwise hardly accessible.

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 $Ce(NH_4)_2(NO_3)_6$ were purchased from Strem. NMR solvents were supplied by Cambridge Isotope Laboratories. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 (^1H, 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. Melting temperatures (uncorrected) were measured on a Mel-Temp II (Laboratory Devices) apparatus and an 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 are ether (E) and petroleum ether (PE). Mass spectra were run at the Regional Center on Mass-Spectroscopy, UC Riverside, Riverside, CA (Agilent 6210 LCTOF instrument with a Multimode source). X-ray structures were determined at the crystallographic facility at Emory University, Atlanta, GA.

Zinc-Induced Dimerization of $Co_2(CO)_6$-Complexed Propargyl Cations (Protocol A): *d,l- and meso*-μ-η^2-(3,4-Diphenyl-1,5-hexadiyne)bis(dicobalthexacarbonyl) (5). Under an atmosphere of nitrogen, $HBF_4 \cdot Me_2O$ (161 mg, 1.20 mmol) was added dropwise (1 min) to a solution of **4** (83.6 mg, 0.2 mmol) in dry ether (20 mL) at −20 °C and stirred for 45 min. The ethereal layer was removed, and the cation was washed with dry ether (2 × 15 mL) at −30 °C. The residual amount of ether was removed under reduced pressure at −30 °C, and the cation was suspended in dry CH_2Cl_2 (20 mL), cooled to −50 °C, and stirred for 15 min. Zinc (650 mg, 10 mmol) was added to the reaction mixture at −50 °C and stirred for 5 min and then for an additional hour at 20 °C (TLC control). The crude mixture was filtered though a short bed of Florisil (1 cm), concentrated under reduced pressure (NMR: *d,l*-**5**: *meso*-**5**, 89:11), and fractionated on preparatory TLC (PE, 2 runs) to give *d,l*-**5** (49.3 mg, 61.4%) and *meso*-**5** (5.0 mg, 6.2%). Spectral data were identical to those previously published by us.[4c]

***d,l- and meso*-μ-η^2-[3,4-Di(3′,4′,5′-trimethoxyphenyl)-1,5-hexadiyne]bis(dicobalthexacarbonyl) (9).** According to protocol A, alcohol **8** (101.6 mg, 0.2 mmol) was converted to the mixture of *d,l*-**9** and *meso*-**9** in the ratio of 87:13 (NMR). Fractionation on a silica gel column (50 g, degassed, PE:E, 1:2) afforded *d,l*-**9** (55.6 mg, 56.6%) as dark red-brown crystals and *meso*-**9** (5 mg, 5.1%; contains minute quantities of inseparable impurities) as brown crystals. Spectral data were identical to those previously published by us.[4b]

Condensation of Lithium Acetylides with Aromatic Aldehydes (Protocol B): μ-η^2-(4,4-Dimethyl-1-phenylpent-2-yn-1-ol)dicobalt Hexacarbonyl (12). Under an atmosphere of nitrogen, 3,3-dimethyl-1-butyne (246 mg, 3 mmol) in THF (10 mL) was added dropwise (10 min) to a solution of n-BuLi (2.8 mL, 1.6 M) in THF (30 mL) at −10 °C. The reaction mixture was stirred for 5 h at −10 °C; then a solution of PhCHO (318 mg, 3 mmol) in THF (10 mL) was added dropwise (10 min) at −10 °C. After stirring for 20 h at 20 °C, the reaction mixture was cooled to 0 °C and quenched with saturated NH_4Cl_{aq} (20 mL). An aqueous layer was extracted with ether (3 × 50 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 (564 mg, 3 mmol; assuming 100% yield) was added to a solution of dicobaltoctacarbonyl (1.13 g, 3.3 mmol) in dry ether (20 mL) at 0 °C. The mixture was stirred for 3 h at 0 °C, concentrated, and fractionated on silica gel (100 g, PE:E, 10:1). The compound was reisolated on silica gel (18 g, PE:E, 10:1) to yield **12** (300 mg, 21.1%) as a dark red oil. TLC (PE:E, 3:1): R_f 0.56. ^1H NMR (400 MHz, $CDCl_3$): δ 1.27 (9H, s, $3CH_3$), 2.30 (1H, d, OH, J = 3.2), 5.91 (1H, d, CH), 7.28−7.50 (5H, m, aromatic H). MS TOF: m/z calcd for $C_{19}H_{15}O_6Co_2$ $[M - OH]^+$ 456.9527, found 456.9535.

***d,l*-μ-η^2-(2,2,9,9-Tetramethyl-5,6-diphenyl-3,7-decadiyne)bis(dicobalthexacarbonyl) (15).** According to protocol A, alcohol **12** (94.8 mg, 0.2 mmol) was converted to the mixture of *d,l*-**15** and *meso*-**15** in the ratio of 95:5 (NMR). Fractionation on preparatory TLC (PE) afforded *d,l*-**15** (56.9 mg, 62.2%) as dark brown crystals and (t-BuC≡CCH_2Ph)$Co_2(CO)_6$ (5 mg, 5.5%) as a red oil. Isolation of *meso*-**15** was not carried out due to its instability. *d,l*-**15** TLC (PE:E, 10:1): R_f 0.65. T_{dec}: 110−135 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (18H, s, $6CH_3$), 4.89 (2H, s, 2CH), 7.14−7.33 (10H, m, aromatic H). ^{13}C NMR (100 MHz, C_6D_6): δ 32.4 (2($\underline{C}H_3)_3C$), 36.6 (C2, C9), 57.0 (C5, C6), 103.5, 114.2 (C3, C4, C7, C8), 127.2, 127.9, 132.8, 139.8 (aromatic C), 200.3 (C═O). MS TOF: m/z calcd for $C_{36}H_{30}O_{10}Co_4$ $[M - 2CO]^-$ 857.9172, found 857.9150. (t-BuC≡CCH_2Ph)$Co_2(CO)_6$ TLC (PE): R_f 0.43. ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (9H, s, $3CH_3$), 4.06 (2H, s, CH_2), 7.24−7.41 (5H, m, aromatic H).

μ-η^2-[1-(3′,4′,5′-Trimethoxyphenyl)-2-pentyne-4,4-dimethyl-1-ol]dicobalt Hexacarbonyl (16). According to protocol B, 3,3-dimethyl-1-butyne (1.80 g, 22 mmol), n-BuLi (15 mL, 1.6 M, 24.0 mmol), 3,4,5-trimethoxybenzaldehyde (5.10 g, 26.0 mmol), and dicobaltoctacarbonyl (8.27 g, 24.0 mmol) were converted, upon washing the crude product with cold petroleum ether (0 °C, 6 × 50 mL), to complex **16** (2.62 g, 21.2%) as dark red crystals. T_{decomp}: 75−110 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (ether): R_f 0.68. ^1H NMR (400 MHz, $CDCl_3$): δ 1.30 (9H, s, t-Bu) 2.40 (1H, d, OH, J = 2.8), 3.80 (3H, s, OMe), 3.88 (6H, s, OMe), 5.85 (1H, d, CH), 6.70 (2H, s, 2′-H, 6′-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.89, 36.81 (C4, C5), 56.39, 61.36, 74.54 (3′/5′-OMe; 4′-OMe; C1), 102.49, 111.86 (C≡C), 103.87, 138.48, 139.94, 153.58 (arom. C), 200.00 (CO). MS FAB$^+$: m/z 565 (M^+ + H), 547 (M^+ − OH), 536 (M^+ −CO), 508 (M^+ −2CO), 480 (M^+ −3CO), 463 (M^+ −3CO −OH), 452 (M^+ − 4CO), 435 (M^+ − 4CO − OH), 424 (M^+ − 5CO), 396 (M^+ − 6CO), 348 (M^+ − 6CO − OMe − OH), 261 (M^+ − 6CO − 2Co − OH). HR-MS/FAB$^+$: calcd for M^+ − CO $C_{21}H_{22}O_9Co_2$ 535.992778, found 535.994600.

***d,l*-μ-η^2-[5,6-Di(3′,4′,5′-trimethoxyphenyl)-2,2,9,9-tetramethyl-3,7-decadiyne]bis(dicobalthexacarbonyl) (19).** According to protocol A, alcohol **16** (423 mg, 0.75 mmol) was converted to *d,l*-**19** (285 mg, 69.5%), a red-brown solid unstable at ambient temperature, which was isolated by using preparatory TLC (4 plates, 20 × 20 cm; PE:E, 2:1). TLC (PE:E, 1:3): R_f 0.59. ^1H NMR (400 MHz, $CDCl_3$): δ 1.44 (18H, s, t-Bu), 3.53 (∼6H, br s, 3′/5′-OMe), 3.71 (∼6H, s, 4′-OMe), 3.83 (∼6H, br s, 3′/5′-OMe), 4.79 (2H, s, 2CH), 6.17 (2H, br s, arom. H), 6.84 (2H, br s, arom. H). MS FAB$^+$: m/z 1010 (M^+ − 3CO), 1009 (M^+ − 3CO − H), 982 (M^+ − 4CO), 926 (M^+ − 6CO), 898 (M^+ − 7CO), 870 (M^+ − 8CO), 871 (M^+ − 8CO − H), 843 (M^+ − 9CO − H), 814 (M^+ − 10CO), 786 (M^+ − 11CO), 758 (M^+ − 12CO), 727 (M^+ − 12CO − OMe), 699 (M^+ − 12CO − Co), 668 (M^+ − 12CO − OMe − Co), 640 (M^+ − 12CO − 2Co). HR-MS/DEI: calcd for $C_{41}H_{42}O_{15}Co_4$ (M^+ − 3CO) 1009.985162, found 1009.990300. Single crystals suitable for X-ray structure analysis (Figure 2) were obtained at ambient temperature by a slow evaporation of dichloromethane solution (NMR tube) under N_2 atmosphere.

X-ray Crystallography of *d,l*-19 and *d,l*-24.[9] Suitable crystals of *d,l*-**19** and *d,l*-**24** 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 SMART APEX CCD sealed-tube diffractometer with graphite-monochromated Mo Kα (0.71073 Å) radiation. Data were measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame

widths. Data collection, indexing, and initial cell refinements were all carried out using SMART[9a] software. Frame integration and final cell refinements were done using SAINT[9b] software. The SADABS[9c] program was used to carry out absorption corrections.

The structures were solved using direct methods and difference Fourier techniques (SHELXTL, V6.12).[9d] 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 nonhydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.[9e] Structure solution, refinement, graphics, and generation of publication materials were performed by using SHELXTL, V6.12 software.

***μ*-η^2-(3-Trimethylsilyl-1-phenylprop-2-yn-1-ol)dicobalt Hexacarbonyl (20).** According to protocol B, trimethylsilyl acetylene (294 mg, 3 mmol), n-BuLi (2.8 mL, 1.6 M), PhCHO (318 mg, 3 mmol), and dicobaltoctacarbonyl (1.13 g, 3.3 mmol) were converted, upon fractionation on a silica gel column (200 g, PE:E, 10:1), to alcohol **20** (666 mg, 45.3%) as a dark red powder. Mp: 51−52 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (PE:E, 3:1): R_f 0.63. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.23 (9H, s, $3CH_3$), 2.34 (1H, d, OH, J = 3.2), 5.92 (1H, d, CH), 7.27−7.48 (5H, m, aromatic H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 0.59 (Me_3Si), 74.82 (C3), 78.22, 116.37 (C1, C2), 125.84, 128.32, 128.53, 143.90 (aromatic C), 199.71 (CO). MS TOF: m/z calcd for $C_{18}H_{15}O_6SiCo_2$ $[M - OH]^+$ 472.9296, found 472.9307. MS TOF FD$^+$: m/z M^+ 490. Anal. Found: C, 43.71; H, 3.31. $C_{18}H_{16}O_7SiCo_2$ requires: C, 44.10; H, 3.29.

***d,l*-*μ*-η^2-[1,6-Di(trimethylsilyl)-3,4-diphenyl-1,5-hexadiyne]bis(dicobalthexacarbonyl) (21).** According to protocol A, alcohol **20** (98.0 mg, 0.2 mmol) was converted to *d,l*-**21** (76.6 mg, 81.0%; *d,l*-**21**:*meso*-**21**, 99:1) as dark brown crystals. TLC (PE:E, 10:1): R_f 0.62. T_{dec}: 87−92 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.16 (18H, s, $6CH_3$), 4.88 (2H, s, 2CH), 6.97 (4H, br d, aromatic H, J = 6.0), 7.17−7.31 (6H, m, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.84 (Me_3Si), 61.41 (C3, C4), 77.73, 114.12 (C1, C2, C5, C6), 127.70, 127.94, 131.46, 140.44 (aromatic C), 199.72, 200.58 (CO). MS TOF: m/z calcd for $C_{34}H_{30}O_{10}Si_2Co_4$ $[M - 2CO]^-$ 889.8711, found 889.8685. MS TOF FD$^+$: m/z M^+ 946. Anal. Found: C, 45.52; H, 3.45. $C_{36}H_{30}O_{12}Si_2Co_4$ requires: C, 45.68; H, 3.19.

Decomplexation−Desilylation Sequence (Protocol C): *d,l*-3,4-Diphenyl-1,5-hexadiyne (23). Under an atmosphere of nitrogen, at −78 °C, a solution of degassed $Ce(NH_4)_2(NO_3)_6$ (333 mg, 0.608 mmol) in acetone (8 mL, degassed) was added (10 min) to a solution of *dl*-**21** (71.9 mg, 0.076 mmol) in acetone (10 mL, degassed). The reaction mixture was stirred at −78 °C for 15 min, then at −50 °C for 30 min. An additional amount of $Ce(NH_4)_2(NO_3)_6$ (125 mg, 0.228 mmol; 3 portions) was added to bring the reaction to completion (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), and ether was removed under reduced pressure. At 0 °C, the crude product **22** and $BnMe_3NCl$ (3.5 mg, 0.019 mmol) were combined and dissolved in acetonitrile (3 mL). A solution of NaOH (30.4 mg, 0.76 mmol) in H_2O (2 mL) was added dropwise (2 min), the temperature was raised to 20 °C, and the reaction mixture was stirred for 16 h. The suspension was diluted with ether (3 mL), and the organic layer was washed with saturated $NaCl_{aq}$ (3 × 5 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Fractionation on a preparative TLC plate (1/2; PE, 2 runs) afforded *dl*-**23** (13.1 mg, 74.9% over two steps), which was fully characterized in the previous account.[4g]

***μ*-η^2-[3-Trimethylsilyl-1-(3′,4′,5′-trimethoxyphenyl)prop-2-yn-1-ol]dicobalt Hexacarbonyl (25).** According to protocol B, trimethylsilyl acetylene (588 mg, 6 mmol), n-BuLi (4.5 mL, 1.6 M), 3,4,5-$(MeO)_3C_6H_2CHO$ (1.18 g, 6 mmol), and dicobaltoctacarbonyl (2.26 g, 6.6 mmol) afforded, upon fractionation on a silica gel column (300 g, PE:E, 2:1), alcohol **25** (2.40 g, 69.0%) as a brick red powder. Mp: 98−107 °C (sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). TLC (PE:E, 1:1): R_f 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.25 (9H, s, $3CH_3$), 2.39 (1H, d, OH, J = 2.8), 3.80 (3H, s, OCH_3), 3.88 (6H, s, $2OCH_3$), 5.84 (1H, d, CH), 6.69 (2H, s, aromatic H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 0.66 (Me_3Si), 56.04 (OMe), 60.91 (OMe), 74.75 (C3), 78.13 (C1/C2), 103.02 (aromatic C), 116.20 (C2/C1), 138.17, 139.73, 153.31 (aromatic C), 199.83 (CO). MS TOF: m/z calcd for $C_{21}H_{26}NO_{10}SiCo_2$ $[MNH_4]^+$ 597.9984, found 597.9978. Anal. Found: C, 43.48; H, 3.64. $C_{21}H_{22}O_{10}SiCo_2$ requires: C, 43.46; H, 3.82.

***d,l*-*μ*-η^2-[1,6-Di(trimethylsilyl)-3,4-di(3′,4′,5′-trimethoxyphenyl)-1,5-hexadiyne]bis(dicobalthexacarbonyl) (26).** According to protocol A, alcohol **25** (116 mg, 0.2 mmol) was converted to the mixture of *d,l*-**26** and *meso*-**26** in the ratio of 98.5:1.5 (NMR). Fractionation on a preparatory TLC plate (PE:E, 1:1) afforded *d,l*-**26** (78.0 mg, 69.0%) as dark brown crystals. TLC (PE:E, 1:1): R_f 0.44. Mp: 97−126 °C (w/dec; sealed capillary; dried by coevaporation with benzene, 3 × 1 mL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.14 (18H, s, $6CH_3$), 3.60−3.90 (12H, br s, $4OCH_3$), 3.78 (6H, s, $2OCH_3$), 4.80 (2H, s, 2CH), 6.00−6.90 (4H, br, aromatic H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.82 (Me_3Si), 56.45 (OMe), 60.86 (C3, C4, OMe), 78.35 (C1/C6 or C2/C5), 110.55 (aromatic C), 115.16 (C1/C6 or C2/C5), 136.28, 138.83, 152.45 (aromatic C), 199.79, 200.71 (CO). MS TOF: m/z calcd for $C_{42}H_{46}NO_{18}Si_2Co_4$ $[MNH_4]^+$ 1143.9576, found 1143.9608. Anal. Found: C, 45.35; H, 3.89. $C_{42}H_{42}O_{18}Si_2Co_4$ requires: C, 44.77; H, 3.76.

***d,l*-3,4-Di(3′,4′,5′-trimethoxyphenyl)-1,5-hexadiyne (24).** According to protocol C, *dl*-**26** (22.5 mg, 0.02 mmol) was treated with $Ce(NH_4)_2(NO_3)_6$ (132 mg, 0.24 mmol; 6 portions), $BnMe_3NCl$ (0.9 mg, 0.005 mmol), and NaOH (8.0 mg, 0.2 mmol) to afford, upon fractionation on a preparatory TLC plate (1/4; PE:E, 1:2), *d,l*-**24** (5.7 mg, 69.5% over two steps), which was fully characterized in the previous account.[4g] Single crystals suitable for X-ray structure analysis (Figure 3) were obtained by ethanol vapor diffusion into a solution of *d,l*-**24** in ethyl acetate at ambient temperature (4 days).

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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*-**19** and *d,l*-**24**. This material is available free of charge via the Internet at http://pubs.acs.org.