

Convergent Synthesis of Isomeric Pairs of Metallocene-Containing Polyether Macrocycles

Gina A. Virtue, Ninani E. Coyne, and Darren G. Hamilton*

Department of Chemistry, Mount Holyoke College, South Hadley, Massachusetts 01075

hamilton@mtholyoke.edu

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Abstract: A general method for rapid construction of metallocene-based hosts is described. Treatment of polyether bridged bis(diphenylacetylenes) with a source of cyclopentadienyl cobalt at high temperature leads, via macrocyclization and capture of the intermediate cyclobutadiene, to macrocyclic systems tethered to an integral metallocene platform. Equal yields of the two possible structural isomers, the products of parallel or antiparallel cycloaddition of the precursor, are obtained. A combination of X-ray crystallography and NMR is employed to assign structures to the individual isomers and to assess the strength of lithium ion binding by the individual macrocycles.

Numerous metallocene-receptor conjugates, systems designed to provide an electrochemical response to the presence of a guest, have been reported over the past 20 years.¹ The structures of these systems were largely dictated by the employment of the metallocene as an external scaffold on which to hang separate, discrete macrocycles. We sought to circumvent the limitation imposed by the use of distinct, preformed, binding and metallocene units, and against this background we have developed a short (three-step) sequence to metallocene-based macrocyclic receptors that represents a derivation of the elegant work of Brisbois² and Gleiter.³ The approach is illustrated with the preparation of some simple members of a potentially large class of macrocycles based on this general approach.

A simple sketch of a polyether bridged cyclobutadiene, captured by a suitable organometallic fragment (ML: e.g., -CoCp, $-Fe(CO)_3$), is shown in Figure 1. Starting from a sketch of a 1,3-substituted target, retrosynthetic breaking of the cyclobutadiene-metal bond and discon-



FIGURE 1. Reaction considerations: schematic retrosynthetic disconnection of a polyether bridged cyclobutadienemetal complex and possible fates upon cyclization of this precursor.

nection across the four-membered ring yields an *acyclic* bis-acetylene. Forward reaction, i.e. cycloaddition (with attendant macrocyclization) and capture by ML, can lead to products with two substitution patterns. Antiparallel cycloaddition and complexation of the resulting cyclo-butadiene will yield 1,3-substituted systems; the corresponding parallel cycloaddition pathway leads to 1,2-substituted systems.

We selected diphenylacetylene as the alkyne source for these reactions since this material is known to undergo efficient cyclodimerization and capture by a source of cyclopentadienyl cobalt and provides sites on which to locate additional binding functionality in later generation systems.⁴ Alkylation of poly(ethylene glycol) ditosylates 1 or 2 with 2-bromophenol gave the general bridged polyether derivatives 3 and 4 in reasonable yield without recourse to chromatography (Scheme 1). Palladiumcatalyzed coupling of these dibromides with phenyl acetylene gave bridged bis(diphenylacetylene) derivatives 5 and 6, the immediate precursors to the target organometallic systems. Macrocyclization of 5 or 6, via acetylene dimerization, was conducted in refluxing *p*-xylene in the presence of 5.0 equiv of CpCoCl₂.⁵ Both reactions afforded two principal cobalt-containing materials, identified as the structural isomers 7 and 8, or 9 and 10, in essentially identical yields of around 20% of each isomer (Scheme $2).^{6}$

^{*} To whom correspondence should be addressed. Visiting Scholar, Massachusetts Institute of Technology (2002).

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⁽²⁾ Issues of isomer formation and regiocontrol in reactions of this type have been discussed and illustrated: Brisbois, R. G.; Fogel, L. E.; Nicaise, O. J.-C.; DeWeerd, P. J. *J. Org. Chem.* **1997**, *62*, 6708.

⁽³⁾ A family of metallocenophanes has been prepared that contain cyclopentadienyl cobalt capped cyclobutadiene or cyclopentadieneone rings. These systems are derived from *preformed*, acetylene-containing, carbocyclic rings: (a) Haberhauer, G.; Gleiter, R. *Tetrahedron Lett.* **1998**, *39*, 6695. (b) Roers, R.; Rominger, F.; Gleiter, R. *Tetrahedron Lett.* **1999**, *40*, 3141. (c) Roers, R.; Rominger, F.; Nuber, B.; Gleiter, R. *Organometallics* **2000**, *19*, 1578. Conceptually related work has employed similar chemistry in syntheses of endohedral metallocenophanes: Scholz, G.; Gleiter, R.; Rominger, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 2477.

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SCHEME 1. Preparation of Polyether Bridged Precursors



SCHEME 2. Macrocyclization and Complex Formation: Isomeric 1,3- and 1,2-Substituted Monomeric Hosts



Simple symmetry arguments predict the same number of resonances for each isomer (at least as drawn in Scheme 2). Assignment of the correct structures to these pairs of isomeric products was thus greatly aided by obtaining X-ray quality crystals of the slower eluting isomer from the macrocyclization reaction involving 5. The structure reveals a 1,3-disposition of the polyether bridge, confirming the identity of this material as 7 (Figure 2). Our bias toward drawing "open" host structures is also laid bare: the system adopts an essentially self-organized structure, the metallocene unit having rotated into the cavity defined by the polyether strap where stabilizing C-H-O contacts are established between cyclopentadienyl protons and oxygen atoms in the polyether chain.⁷ By elimination, the slightly faster eluting fraction from this first reaction had to be the corresponding 1,2-isomer 8 as no other identical molec-



FIGURE 2. X-ray structure of the 1,3-bridged isomer 7 (one conformation only is shown for a small disordered portion of the polyether chain, with hydrogen atoms omitted).

ular weight material was a plausible product of this reaction.

Isomers 7 and 8 both possess symmetry elements that could reduce the number of aromatic carbon environments to 10, as long as rotation of the phenyl substituents is fast with respect to the chemical shift time scale. Ten peaks are indeed observed in the aromatic region of the carbon spectrum of 1,2-isomer 8. However, 1,3-isomer 7 presents 13 peaks, indicating either slow rotation of the phenyl substituents, or an unsymmetrical disposition of the polyether strap with respect to the central plane of the molecule. As there is no obvious reason to expect phenyl group rotation to be retarded in 7 compared to 8, we conclude that the key features of the solid-state conformation of 7 persist in chloroform solution-the noncentral disposition of the polyether strap breaking the predicted symmetry and increasing the number of carbon environments.⁸ High field (600 MHz) ¹H NMR spectra for 7 and 8 support the assertion of the highest possible symmetry for the latter (1,2-isomer), but reduced for the former (1,3-isomer).⁹ The spectra obtained for the products, **9** and **10**, of the reaction of **6** with CpCoCl₂ match the arguments presented for their analogues 7 and 8. No crystals could be obtained for either of these materials, and their structural assignments are therefore made by analogy.¹⁰ These assignments are made with a very high level of confidence as the number of observed aromatic carbon environments is exactly mirrored from 8 to 10 (10), and **7** to **9** (13).¹¹

(11) The parallel extends to coincidence of two resonances (ref 8).

⁽⁵⁾ The concentration of bis(diphenylacetylene) precursors was maintained at around 5-10 mM to attempt to bias monomer formation. During separation small amounts of a number of other cobalt-containing materials were noted, though the amounts were too small for unambiguous characterization. Dimers and perhaps higher order oligomers are likely to be represented among these. The choice of CpCoCl₂ as the cobalt source was motivated by a wish to avoid any products deriving from CO insertion into the cyclobutadiene ring, i.e., cyclopentadienones, in reactions that would necessarily only afford moderate yields of monomeric macrocyclic products.

⁽⁶⁾ Reaction of $CpCo(CO)_2$ with diphenylacetylene yields 50% of the corresponding sandwich complex (Rausch, M. D., Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888); our total yields of **7** and **8**, or **9** and **10**, are comparable.

⁽⁷⁾ Geometry: $O2\cdots H5 = 2.62$ Å, $\angle O2\cdots H5-C5 = 165^{\circ}$; $O4\cdots H6 = 2.43$ Å, $\angle O4\cdots H6-C6 = 172^{\circ}$. These distances and angles place the observed contacts in well-established ranges for interactions of this character: Steiner, T. *Chem. Commun.* **1997**, 727.

⁽⁸⁾ Near coincidence of two resonances reduces the predicted 14 features to the observed 13.

⁽⁹⁾ Both the aromatic and aliphatic regions of the ¹H NMR spectra are far more complex for 7 than for **8**. Substantial peak overlap (even at 600 MHz) renders the picture less clear than with the corresponding carbon spectra, though it is possible to locate 10 distinct aromatic resonances for 7, the number expected from the persistence in solution of the conformation revealed in the solid-state structure of this material. Similarly, despite a mirror plane bisecting the polyether chain, eight distinct resonances are observed for the methylene groups as these are diastereotopic in the favored conformation.

⁽¹⁰⁾ The only metallocene-macrocycle in this series that we could obtain as a crystalline solid was 7. Crudely, this observation suggests that only 7 has a well-defined structure, while 8-10 possess the conformational flexibility typical of large ring systems.

Addition of a 5-fold excess of LiClO₄ to a solution of **7** (in d_3 -MeCN) did not produce measurable shifts in any of the observed resonances. The corresponding experiment for **8** revealed shifts of several spectroscopically uncluttered resonances and confirmed, as planned, that the cyclopentadienyl singlet, the only noncoupled resonance in the spectrum, offers a useful probe of binding events. Accordingly, NMR titrations were performed to determine binding constants (K)¹² for hosts **8**–**10** with lithium perchlorate.¹³ The choice of lithium was relatively arbitrary and based on the suspicion that the available binding cavities of these first generation hosts would be rather constrained and perhaps best suited to a cation of small diameter.¹⁴

In contrast to 1,3-isomer **7**,¹⁵ 1,2-isomer **8** binds weakly to lithium ion with a binding constant (*K*) of $20 \pm 10 \text{ M}^{-1}$. This weak binding capacity suggests the presence of a rather constrained binding cavity; accordingly, we anticipated stronger interaction with the expanded systems **9** and **10**. Association constants with these hosts were 1 and 2 orders of magnitude greater for 1,2-isomer **10** (*K* = 190 ± 50 M⁻¹) and 1,3-isomer **9** (*K* = 1400 ± 300 M⁻¹), respectively. These values suggest that, at least for ortho strap attachment, the longer chain affords a better lithium ion binding site and that the "bridged" 1,3-isomer represents the better disposition of the polyether strap.¹⁶

Cyclic voltammetric analysis of macrocycles 7-10 reveals the expected one electron oxidation feature at potentials of +620 to +680 mV.¹⁷ The observed peak separations of 70–110 mV are greater than those exhibited by fully reversible systems and were found to vary with sweep rate; the oxidation features of these systems

(14) The hosts presented here were designed as vehicles for establishing a general synthetic method and not as specific ionophores. The NMR binding experiments were conducted in a similar spirit, the aim being to identify general structural characteristics of use in informing the design of second generation systems.

(15) Self-organization, rather than cation interaction, is preferred by 7; no measurable responses to the presence of cations were observed. The NMR analysis supports the retention in solution of the structure revealed in the solid state (Figure 2) and the energetic stabilization provided by the formation of C-H-O contacts must, despite providing only a small energetic benefit, successfully compete with cation coordination. The entropic cost of the establishment of these hydrogen bonding contacts can be expected to be minimal; all that is required is for the cobalt complex to rotate about its 1,3-substitution axis. It seems that by accidental design an ideal length strap was included to prime 7 for efficient self-organization.

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are thus defined as electrochemically quasireversible. The rather weak binding of lithium ion by these macrocycles did not suggest that meaningful data might be obtained from attempting to measure cation-induced shifts of the redox process.¹⁸ However, the identification of an accessible redox process in these systems at least suggests the possibility of electrochemical cation detection in strongly binding systems based on this model.

In conclusion, the employment of poly(ethylene glycol) linkers in macrocycles 7-10 has allowed the establishment of a concise and potentially readily modifiable synthesis of metallocene-containing hosts. Several options for modification of the binding pocket of these prototype systems suggest the possibility of improving binding, and imparting selectivity. Options include alteration of donor atom number and type in the strap, the position of substitution of the phenyl groups bearing the strap, and the inclusion of inward facing coordinating groups on the remaining phenyl rings. It is likely that the position of attachment of the strap plays a significant role in defining the nature of the binding site, and such options may be readily explored by simple changes in the substitution pattern of the starting materials.

Experimental Section

General. All starting materials were obtained from commercial sources with the exception of hexa(ethylene glycol) ditosylate, which was prepared according to a literature procedure.¹⁹ NMR spectra (300 or 600 MHz) were recorded in CDCl₃ or CD₂Cl₂ and referenced to residual solvent. Electrochemical measurements, at 1 mM concentrations of macrocycle, were made in acetonitrile solution containing 0.1 M "Bu₄PF₆ as the supporting electrolyte with Pt auxiliary and working electrodes and an Ag/AgCl reference electrode. Twenty cycles of 0 to +1.0 V at a sweep rate of 200 mV s⁻¹ were made and runs 5–15 averaged to afford the quoted potentials.

1,13-Di(2-bromophenyl)-1,4,7,10,13-pentaoxapentadecane (3). A mixture of 2-bromophenol (4.35 g, 25 mmol), tetra-(ethylene glycol) ditosylate 1 (5.00 g, 10 mmol), anhydrous K_2CO_3 (6.90 g, 50 mmol), and anhydrous MeCN (80 mL) was heated at reflux in an argon atmosphere for 16 h. After cooling and filtering the solvent was removed under vacuum. The residue was dissolved in CH₂Cl₂ (100 mL) and extracted with 10% aq. NaOH (3 \times 100 mL) and water (100 mL). The organic phase was separated, dried over anhydrous MgSO₄, and evaporated to yield an amber oil that was further dried under high vacuum to afford 3 as an oil (1.70 g, 34%): C₂₀H₂₄O₅Br₂ requires C 47.64, H 4.80, found C 47.80, H 4.76; HR ESI-MS (positive ion) $\begin{array}{l} C_{20}H_{24}O_5Br_2Na~([M+Na]^+)~requires~524.9888,~found~524.9880;\\ {}^{13}C~NMR~(CDCl_3,~67~MHz)~\delta~155.38,~133.48,~128.55,~122.20, \end{array}$ 113.74, 112.48, 71.33, 70.91, 69.69, 69.20 ppm; ¹H NMR (CDCl₃, 250 MHz) δ 7.52 (d, J = 8 Hz, 2H), 7.23 (m, 2H), 6.90 (d, J = 8Hz, 2H), 6.82 (m, 2H), 4.17 (t, J = 5 Hz, 4H), 3.91 (t, J = 5 Hz, 4H), 3.79 (m, 4H), 3.70 (m, 4H) ppm.

1,19-Di(2-bromophenyl)-1,4,7,10,13,16,19-heptaoxaheptadecane (4). This material was prepared in a manner analogous to that described for **3** from 2-bromophenol (3.70 g, 21 mmol), hexa(ethylene glycol) ditosylate **2** (5.00 g, 8 mmol), and

⁽¹²⁾ *K* represents the 1:1 binding constant between lithium cation and the respective macrocycle and is quoted to two significant figures to take account of errors involved in the determination.

⁽¹³⁾ All titrations were performed in d_2 -MeCN at 298 K. Hosts were purified by preparative TLC and rigorously dried under high vacuum prior to use; lithium perchlorate was recrystallized from ethanol and dried at 160 °C for 48 h. Deuterated acetonitrile was taken from fresh ampules, and every reasonable precaution made to minimize exposure to the atmosphere during solution preparation and aliquot addition. In a typical titration 0.5 mL of a 5 mM solution of host was titrated with up to 0.7 mL of a 100–500 mM solution of alkali metal perchlorate, the concentration of guest solution being matched to an estimate of the binding constant obtained from a rough first titration to ensure good coverage of the 1:1 binding isotherm. Data were analyzed using Macintosh routines custom written within the research group of Professor Christopher A. Hunter (available at http://www-.shef.ac.uk/uni/projects/smc/software.html). See: Bisson, A. P.; Hunter, C. A.; Morales, J. C.; Young, K. *Chem. Eur. J.* **1998**, *4*, 845. (14) The hosts presented here were designed as vehicles for establishing a general synthetic method and not as specific ionophores. The

⁽¹⁶⁾ Some experiments with potassium perchlorate were also performed, but the data obtained from these NMR titrations could only be fitted to a 2:1 host:guest binding model. Potassium ion's propensity to form "sandwich"-type complexes with crowns is well-known, and it is likely that the binding processes were accurately modeled by a 2:1 curve fitting analysis (e.g., yielding $K \approx 2100 \text{ M}^{-1}$ for the dimeric (**10**)₂· K⁺ complex).

⁽¹⁷⁾ The specific oxidation potentials for the individual macrocycles are 7, +620 mV; 8, +660 mV; 9, +680 mV; 10, +645 mV.

⁽¹⁸⁾ The huge excesses of lithium ion that would have been required to achieve substantial occupancy of the macrocyclic binding sites of **8** and **10** argued against attempts to measure possible shifts in oxidation potential in the presence of this cation. Such an experiment was attempted for the best binding macrocycle **9**, but no measurable change in the peak oxidation potential was noted and general interpretation of the trace was hampered by the irreversibility of oxidation in this case.

⁽¹⁹⁾ Ouchi, M.; Yoshihisa, I.; Yu, L.; Nagamune, S.; Nakamura, S.; Wada, K.; Tadao, H. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1260.

anhydrous K₂CO₃ (5.85 g, 42 mmol), in anhydrous MeCN (50 mL). We found that more exhaustive base extraction was required to remove excess phenol from this preparation, but relatively pure material could still be obtained without recourse to chromatography. Compound **4** was obtained as an oil (1.85 g, 37%): C₂₄H₃₂O₇Br₂ requires C 46.83, H 5.00, found C 46.53, H 5.07; HR ESI-MS (positive ion) C₂₄H₃₂O₇Br₂Na ([M + Na]⁺) requires 613.0412, found 613.0399; ¹³C NMR (CDCl₃, 67 MHz) δ 155.38, 133.45, 128.52, 122.20, 113.78, 112.48, 71.30, 70.88, 70.77 (two unresolved peaks), 69.69, 69.20 ppm; ¹H NMR (CDCl₃, 250 MHz) δ 7.50 (d, J = 8 Hz, 2H), 7.23 (m, 2H), 6.90 (d, J = 8 Hz, 2H), 6.85 (m, 2H), 4.17 (t, J = 5 Hz, 4H), 3.90 (t, J = 5 Hz, 4H), 3.78 (m, 4H), 3.69–3.65 (m, 12H) ppm.

1,13-Di[2-(ethynylphenyl)phenyl)]-1,4,7,10,13-pentaoxapentadecane (5). A mixture of dibromide 3 (1.00 g, 2 mmol), bis(diphenylphosphino)palladium(II) dichloride (70 mg, 1 mmol), triphenylphosphine (50 mg, 0.2 mmol), copper(I) iodide (20 mg, 0.1 mmol), and anhydrous triethylamine (75 mL) was heated at reflux in an argon atmosphere for 40 h. After cooling the entire reaction mixture was added dropwise to a stirred mixture of 10% aqueous H₂SO₄ (500 mL) and CHCl₃ (200 mL). The organic layer was separated, washed with 10% aqueous H_2SO_4 (2 \times 100 mL) and water (2 \times 100 mL), dried (MgSO₄), and evaporated to afford a dark red oily residue. Chromatography (SiO₂; 1:3, EtOAc/ hexanes) gave the desired bis(diphenylacetylene) **5** ($R_f = 0.22$ under given conditions) as a pale yellow oil (0.62 g, 56%): $C_{36}H_{34}O_5$ requires C 79.10, H 6.27, found C 79.22, H 6.17; HR ESI-MS (positive ion) $C_{36}H_{34}O_5Na$ ([M + Na]⁺) requires 569.2304, found 569.2309; ¹³C NMR (CDCl₃, 67 MHz) δ 159.47, 133.45, 131.63, 129.78, 128.42, 128.17, 123.84, 120.94, 113.22, 112.52, 93.58, 86.11, 71.33, 70.88, 69.79, 68.96 ppm; ¹H NMR (CDCl₃, 250 MHz) δ 7.53–7.49 (m, 4H), 7.32–7.23 (m, 10H), 6.95–6.86 (m, 4H), 4.18 (t, J = 5 Hz, 4H), 3.90 (t, J = 5 Hz, 4H), 3.78 (m, 4H), 3.60 (m, 4H) ppm.

1,19-Di[2-(ethynylphenyl)]-1,4,7,10,13,16,19-heptaoxaheptadecane (6). This material was prepared in a manner analogous to that described for 5 from dibromide 4 (1.85 g, 3.1 mmol), bis(diphenylphosphino)palladium(II) dichloride (110 mg, 0.16 mmol), triphenylphosphine (82 mg, 0.31 mmol), and copper(I) iodide (30 mg, 0.16 mmol), in anhydrous triethylamine (75 mL). Workup and isolation as described above (SiO₂; 1:1, EtOAc/hexanes) gave 6 ($R_f \approx 0.4$ under given conditions) as a pale yellow oil (0.83 g, 42%): $C_{40}H_{42}O_7$ requires C 75.69, H 6.67, found C 75.45, H 6.80; HR ESI-MS (positive ion) C₄₀H₄₂O₇-Na ([M + Na]⁺) requires 657.2828, found 657.2840; ¹³C NMR $(CDCl_3, 67 \text{ MHz}) \ \bar{\delta} \ 159.37, \ 133.27, \ 131.45, \ 129.64, \ 128.28,$ 128.03, 123.73, 120.80, 113.08, 112.38, 93.41, 86.00, 71.23, 70.74 (two unresolved peaks), 70.60, 69.69, 68.89 ppm; $^1{\rm H}$ NMR (CDCl_3, 250 MHz) δ 7.51–7.45 (m, 4H), 7.32–7.25 (m, 10H), 6.92-6.87 (m, 4H), 4.20 (t, J = 5 Hz, 4H), 3.91 (t, J = 5 Hz, 4H), 3.80 (m, 4H), 3.62-3.57 (m, 12H) ppm.

Cobalt-Containing Macrocycles from 5. 1,2-Isomer 8 and 1,3-Isomer 7. A solution of bis(diphenylacetylene) 5 (0.29 g, 0.52 mmol) in an hydrous m-xylene (100 mL) was prepared in a flask equipped with a reflux condenser, a Pasteur pipet through which a slow, continuous stream of nitrogen was passed, and a mineral oil bubbler. CpCoCl2 (0.5 mL) was added via syringe to the stirred solution, and the mixture heated to reflux for 40 h. After cooling the solvent was removed to leave a dark residue, which was subjected to an initial purification on a short column (SiO₂; DCM/MeOH, 99.5:0.5), and the orange fractions were collected. These materials were separated by preparative TLC (SiO₂; DCM/MeOH, 99.5:0.5) to yield two orange materials. The faster eluting fraction $(R_f = 0.45)$ was identified as the 1,2isomer 8, a sticky low-melting solid (80 mg, 23%), and the slower $(R_f = 0.40)$ as 1,3-isomer 7, an orange crystalline material (70) mg, 20%). Data for 8: C₄₁H₃₉O₅Co requires C 73.42, H 5.86, found C 73.67, H 5.89; HR ESI-MS (positive ion) C41H39O5CoNa ([M + Na]⁺) requires 693.2022, found 693.2017; ¹³C NMR $(CDCl_3, 75 \text{ MHz}) \delta 156.25, 138.59, 132.19, 128.77, 127.68,$ 127.52, 125.99, 125.67, 119.85, 111.76, 83.52, 74.99 (second cyclobutadienyl resonance obscured by solvent peaks), 71.20, 70.79, 69.27, 67.45 ppm; ¹H NMR (300 MHz, CDCl₃) 5 7.48 (d, J = 8 Hz, 2H), 7.43 (m, 4H), 7.24–7.18 (m, 8H), 6.84 (d, J = 8Hz, 2H), 6.78 (d, J = 8 Hz, 2H), 4.72 (s, 5H), 3.76-3.69 (m, 4H), 3.54-3.43 (m, 8H), 3.21-3.14 (m, 2H), 3.00-2.93 (m, 2H) ppm. Data for 7: mp 217–219 °C; $C_{41}H_{39}O_5$ Co requires C 73.42, H 5.86, found C 73.62, H 5.90; HR ESI-MS (positive ion) $C_{41}H_{39}O_5$ -CoNa ([M + Na]⁺) requires 693.2022, found 693.2024; ¹³C NMR (CDCl₃, 75 MHz) δ 156.07, 140.14, 138.96, 132.77, 129.83, 127.96, 127.69, 126.94, 125.32, 125.00, 124.62, 119.96, 111.32, 83.79, 73.65 (second cyclobutadienyl resonance obscured by solvent peaks), 71.60, 70.99, 69.14, 67.67 ppm; ¹H NMR (300 MHz, CDCl₃) δ 7.63–7.58 (m, 3H), 7.56–7.52 (m, 3H), 7.28–7.22 (m, 2H), 7.16–7.09 (m, 3H), 7.03–7.01 (m, 3H), 6.89 (d, J = 7 Hz, 2H), 6.83 (d, J = 7 Hz, 2H), 4.96 (s, 5H), 4.29–4.23 (m, 2H), 3.92–3.81 (m, 4H), 3.72–3.55 (m, 8H), 3.26–3.21 (m, 2H).

Cobalt-Containing Macrocycles from 6. 1,2-Isomer 10 and 1,3-Isomer 9. These materials were prepared in a manner analogous to that described for 7 and 8 from bis(diphenylacetylene) 6 (0.31 g, 0.49 mmol), in anhydrous *m*-xylene (100 mL), and CpCoCl₂ (0.5 mL). Initial purification on a short column (SiO₂; DCM/MeOH, 98:2) gave two mixed orange fractions, which were separated by preparative TLC (SiO₂; DCM/MeOH, 98:2) to yield two orange-yellow oils. The faster eluting fraction (R_f = 0.71; CHCl₃/MeOH, 95:5) was the 1,2-isomer 10 (70 mg, 19%), and the slower ($R_f = 0.68$; CHCl₃/MeOH, 95:5) the 1,3-isomer **9** (67 mg, 18%). Data for 10: C₄₅H₄₇O₇Co requires C 74.37, H 6.52, found C 74.30, H 6.52; HR ESI-MS (positive ion) C₄₅H₄₇O₇CoNa ([M + Na]⁺) requires 781.2546, found 781.2546; ¹³C NMR (CDCl₃, 75 MHz) & 156.19, 138.33, 130.90, 128.98, 127.59, 127.45, 126.53, 125.67, 119.84, 111.54, 83.33, 74.81 (second cyclobutadienyl resonance obscured by solvent peaks), 70.94, 70.84 (two coincident peaks), 70.53, 69.19, 67.28 ppm; ¹H NMR (300 MHz, CDCl₃) δ 7.40–7.37 (m, 4H), 7.28–7.16 (m, 10H), 6.83 (d, J = 7 Hz, 2H), 6.74 (t, J = 7 Hz, 2H), 4.78 (s, 5H), 3.84 (br m, 4H), 3.70-3.63 (m, 4H), 3.61-3.53 (m, 8H), 3.46-3.41 (m, 4H), 2.94-2.89 (m, 2H), 2.83 (br m, 2H) ppm. Data for 9: C₄₅H₄₇O₇Co requires C 74.37, H 6.52, found C 74.31, H 6.50; HR ESI-MS (positive ion) $C_{45}H_{47}O_7CoNa$ ([M + Na]⁺) requires 781.2546, found 781.2552; ¹³C NMR (CD₂Cl₂, 75 MHz) δ 157.31, 140.15, 134.75, 132.55, 132.42, 129.13, 128.92, 128.11, 127.14, 125.84, 125.23, 120.94, 113.20, 83.44, 76.69, 74.62, 71.25, 71.03, 70.92, 70.83, 69.26, 68.57 ppm; ¹H NMR (300 MHz, CDCl₃) δ 8.01 (dd, J = 7 Hz, 2 Hz, 2H), 7.72-7.65 (m, 4H), 7.58-7.53 (m, 2H), 7.50-7.47 (m, 2H), 7.36-7.31 (m, 2H), 7.13-7.07 (m, 4H), 6.86 (d, J = 8 Hz, 2H), 4.69 (s, 5H), 3.78 (t, J = 5 Hz, 4H), 3.57-3.52 (m, 8H), 3.45-3.36 (m, 8H), 2.92 (t, J = 5 Hz, 4H) ppm.

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Supporting Information Available: Details of the data collection, structure solution, and refinement of **7**. A crystallographic data file in CIF format is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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