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# Toward a Square-Grid Polymer: Synthesis and Structure of Pedestal-Mounted Tetragonal Star Connectors, $C_4R_4{-}Co{-}C_5Y_5$

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We report the synthesis of (cyclobutadiene)cyclopentadienylcobalt derivatives, $C_4R_4{-}Co{-}C_5Y_5$, where R is a rigid arm capable of linear coupling through its para position and the tentacle Y carries a functionality with a large affinity for the surface of mercury. The compounds are needed for a proposed synthesis of a square-grid polymer by 2-dimensional cross-linking polymerization, which calls for cross-shaped star connector modules mounted horizontally on a flat pedestal with a large affinity to a liquid interface. The substituents are R = 4-pyridyl, 4-iodophenyl, 4-bromophenyl, 4-(ethoxycarbonyl)phenyl, 4-(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl, 4-carboxyphenyl, 4−[(triethylsilyl)ethynyl]phenyl, Y = H; R = phenyl, Y = (trifluoroacetoxy)mercurio, iodo; R = 4-bromophenyl, Y = (trifluoroacetoxy)-mercurio; R = 4-(ethoxycarbonyl)phenyl, Y = [(2-hydroxyethyl)thio]mercurio. Single-crystal X-ray diffraction structures are reported for R = 4-pyridyl, 4-(1,12-dicarba-*closo*-dodecaboran-1-yl)−phenyl, 4-(ethoxycarbonyl)phenyl with Y = H, R = phenyl with Y = (trifluoroacetoxy)-mercurio, and bis[4-(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl]acetylene and phenyl[4−(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl]acetylene.

## Introduction

We are interested in developing and using a molecular-size construction kit analogous to the children's Tinkertoy[1] play set with covalently bound rods and connectors. Our initial efforts concentrated on the synthesis of molecular rods,[2,3] and more recently, we focused on the synthesis of connectors.[4−6] Independently, Stoddart introduced a related concept based on intermolecularly assembled supramolecular components, at first called "molecular Lego"[7] and more recently called "molecular Meccano".[8] Synthesis of rigid-rod molecules of well-defined length has also been examined in many other laboratories.[9] Currently, there is a fair amount of interest in the general subject of modular chemistry, and instead of providing a survey here, we refer to numerous references that will be available in a book that is about to appear.[4b]

Our specific goal[4] is the construction of thin (<1 nm) firmly connected regular ("crystalline") 2-dimensional grid-shaped polymers with a trigonal, square, or hexagonal lattice defining large openings of a controlled size. In a subsequent stage, we hope to bind additional regular grid layers firmly on top of the first. They are to be added one at a time in order to allow each one to be different, ultimately permitting the construction of scaffolding-like thin layers of artificial covalent materials whose structure is periodic in two large dimensions and controlled in an aperiodic fashion in the third thin dimension. Suitable active groups are to be attached to the building elements in order to provide desired optical, electrical, mechanical, or other functions.

The conceptual synthetic approach to this goal has been described elsewhere.[4−6] Briefly, it calls for 2-dimensional cross-linking polymerization of monomeric modules constrained to motion in the two dimensions defined by an atomically flat liquid surface or interface, for which our initial choice is liquid mercury. The modules are to be composed of a horizontally oriented connector mounted on a pedestal that is provided with tentacles that adsorb very strongly to the interface, yet are detachable later by a chemical reaction or convertible into another layer of the grid. Our first choice of

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(1) Tinkertoy is a trademark of Playskool, Inc., Pawtucket, RI 02862, and designates a children's toy construction set consisting of straight wooden sticks and other simple elements insertable into spool-like connectors.

(2) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988,** *110,* 5225. Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H.-C.; Robinson, R. E.; McMurdie, N. D.; Kim, T. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A. Blechert, S., Eds.; NATO ASI Series, Vol. 273; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 463.

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(8) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992,** *114,* 193. Amabilino, D. B.; Ashton, P. R.; Brown, C. L.; Córdova, E.; Godínez, L. A.; Goodnow, T. T.; Kaifer, A. E.; Newton, S. P.; Pietraszkiewicz, M.; Philp, D.; Raymo, F. M.; Reder, A. S.; Rutland, M. T.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1995,** *117,* 1271.

(9) See, among others: Zimmerman, H. E.; King, R. K.; Meinhardt, M. B. *J. Org. Chem.* **1992,** *57,* 5484. Eaton, P. E.; Tsanaktsidis, J. *J. Am. Chem. Soc.* **1990,** *112,* 876. Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992,** *114,* 9719. Bunz, U.; Polborn, K.; Wagner, H.-U.; Szeimies, G. *Chem. Ber.* **1988,** *121,* 1785.

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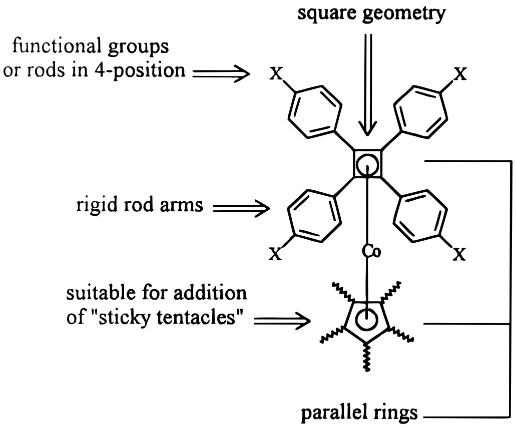


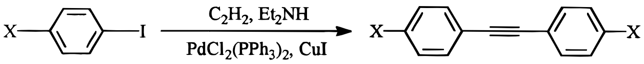
**Figure 1.** Schematic representation of a monomeric module for a square grid.

monomeric modules are metal sandwich complexes, whose bottom deck carries the tentacles and represents a pedestal while the top deck serves as a connector. We started with connectors of the "star" type,[4] and have reported synthetic work toward modules based on the complexes of benzene[5] and porphyrin derivatives.[6] The former carry radially three and the latter four rigid arms capable of linear coupling through their free termini.

The (tetraphenylcyclobutadiene)cyclopentadienylcobalt (**1**) structure (Figure 1) offers yet another promising template for the envisaged monomeric modules. It is thermally stable and chemically resistant to a range of reagents.[10] It possesses the asymmetry needed to differentiate the arms-carrying and the tentacle-carrying decks. The cyclobutadiene and cyclopentadienyl (Cp) rings are parallel, and the cyclobutadiene ring is square.[11−13] If suitable functionalization can be introduced into the para position, the four cross-forming pendant phenyl groups will be well suited as rigid arms capable of linear coupling. The Cp ring is electron rich and promises the reactivity needed for the attachment of a sufficient number of detachable sticky tentacles.

Although some related organometallic complexes suitable for use as star connectors have been synthesized recently,[14] and although a fair number of derivatives of **1** are known, none can serve immediately as the desired module. First, only a few complexes with phenyl rings substituted in the para position are known,[15,16] and they do not have proper functionalities to serve a linear couplers. Second, most of the previously characterized Cp-substituted derivatives carry only one, two, or three substituents on the ring.[14,17,18] These were either attached to the five-membered ring before the formation of the cobalt complex,[14] or were introduced onto the ring by electrophilic aromatic substitution.[17] The only previously reported pentasubstituted derivatives are those containing the pentamethylcyclopentadienyl ligand.[19] None of the known compounds have Cp substituents suitable for use as tentacles.

**Scheme 1**



**2**, X = Br, 61%
**3**, X = I, 42%
**4**, X = COOEt, 70%

We have, therefore, decided to examine synthetic approaches to compounds of type $C_4R_4$−Co−$C_5Y_5$ that would be suitable for our purposes. The standard synthesis of **1** and its derivatives relies on the dimerization of diphenylacetylene or one of its derivatives in the presence of an organometallic cobalt compound.[14,17,20] Three commonly used compounds are tris(triphenylphosphine)cobalt(I) chloride,[14] 1,5-cyclooctadienecyclopentadienylcobalt,[19] and cyclopentadienylcobalt dicarbonyl [CpCo(CO)$_2$].[17] We have chosen to use CpCo(CO)$_2$ because of its ease of synthesis and the usually high yields it offers.[17]

The attachment of five suitable tentacles to the cyclopentadienyl ring potentially represents a challenging synthetic problem. Fortunately, we found that electrophilic aromatic mercuration of the Cp ring permits the preparation of Cp-pentasubstituted cobalt complexes in good yield.

## Results and Discussion

**Precursor Synthesis. 4,4′-Disubstituted Diphenylacetylene Derivatives**. 4,4′-Dipyridylacetylene was prepared by a literature procedure.[21] The known 4,4′-dibromodiphenylacetylene (**2**), 4,4′-diiododiphenylacetylene (**3**), and 4,4′-bis(ethoxycarbonyl)diphenylacetylene (**4**) were prepared in good yields by reaction[22,23] of the appropriate 4-iodophenyl derivative with acetylene gas in the presence of a copper/palladium catalyst in diethylamine (Scheme 1). Bis[4-(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl]acetylene (**5**) was prepared in 25% yield by the palladium-catalyzed cross-coupling of **3** with the copper(I) salt of 1,12-dicarba-*closo*-dodecaborane, using a modification of known procedures (Scheme 2).[5,24] Phenyl[4-(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl]acetylene (**6**) was isolated by column chromatography in 6% yield as a byproduct, presumably formed by the reduction of one of the carbon−iodine bonds. Such reduction has been observed in related reactions.[5]

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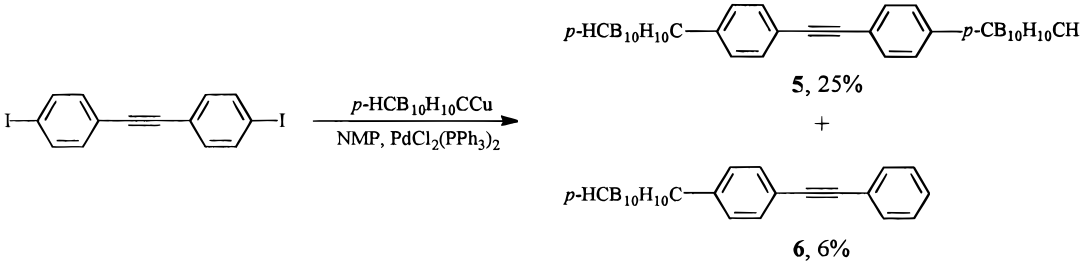
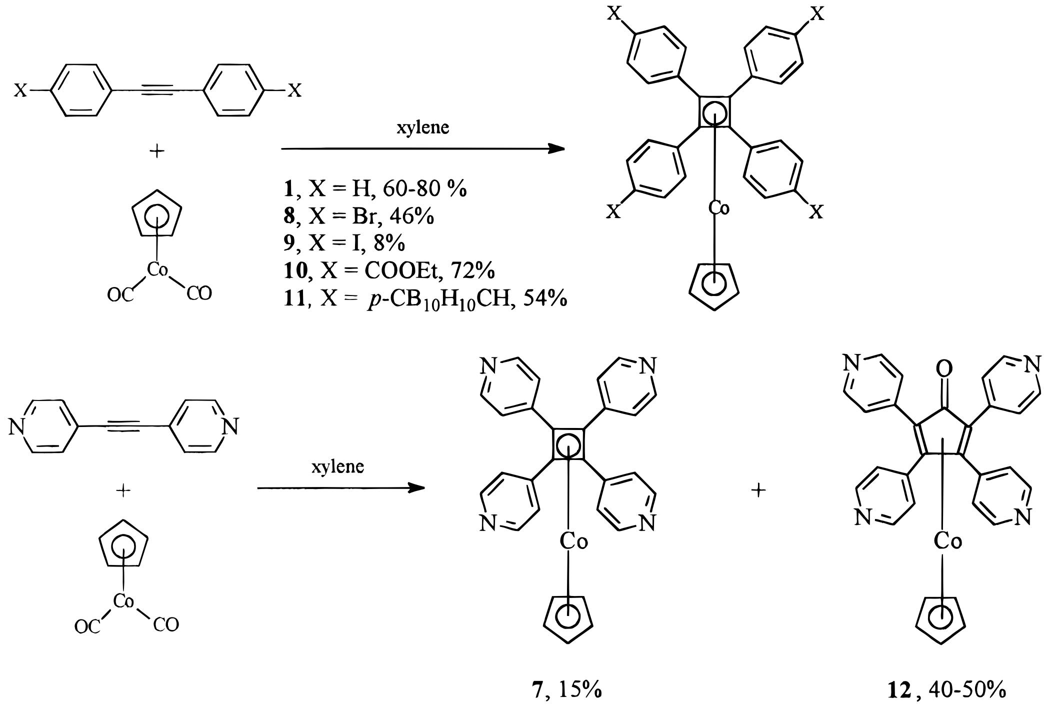
**Scheme 2**



**Scheme 3**



**Tetra-*para*-substituted (Tetraphenylcyclobutadiene)cyclopentadienylcobalt Complexes.** (Tetraphenylcyclobutadiene)cyclopentadienylcobalt (**1**) was needed for initial investigations of electrophilic substitution on the Cp ring. It was prepared in improved yields of 60–80% from diphenylacetylene and CpCo(CO)$_2$, using the method of Rausch[17] (Scheme 3). [Tetrakis(4-pyridyl)cyclobutadiene]cyclopentadienylcobalt (**7**, 15%), [tetrakis(4-bromophenyl)cyclobutadiene]cyclopentadienylcobalt (**8**, 46%), [tetrakis(4-iodophenyl)cyclobutadiene]cyclopentadienylcobalt (**9**, 8%), [tetrakis(4-(ethoxycarbonyl)phenyl)cyclobutadiene]cyclopentadienylcobalt (**10,** 72%), and [tetrakis(4-(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl)cyclobutadiene]cyclopentadienylcobalt (**11**, 54%) were all prepared by the reaction of the appropriate diphenylacetylene derivative and CpCo(CO)$_2$ in xylene (Scheme 3). The quality of the CpCo(CO)$_2$ used in the synthesis strongly influences the yields, and we recommend that it be distilled before use.

Unlike the synthetic procedures for **1**, **8**, **10**, and **11**, which are satisfactory, the synthesis of **7** yields primarily [tetrakis(4-pyridyl)cyclopentadienone]cyclopentadienylcobalt **12** (40–50%), and the synthesis of **9** yielded complicated mixtures. An attempt to avoid the formation of a cyclopentadienone derivative by the use of (Ph$_3$P)$_3$CoCl instead of CpCo(CO)$_2$ in the synthesis of **7** failed. Also, after extensive purification by column chromatography, the best yield of **9** was only 8% and several other derivatives of **1** were isolated in crude form from the reaction mixture. These byproducts were tentatively identified by their $^1$H NMR spectra to be analogues of **9** in which one or more of the carbon–iodine bonds had been reduced, presumably by action of cobalt(I) complexes in the reaction solution. It would thus appear that the Rausch procedure is not suitable for iodoaryl derivatives. Due to the small supply of the potentially useful complex **9**, it has not been examined further.

Initial attempts to synthesize the tetracarborane **11** employed stoichiometric amounts of **5** and CpCo(CO)$_2$ and gave poor yields (~7%). Most of the starting material **5** was recovered from the reaction mixture, suggesting that it is significantly less reactive than the other diphenylacetylenes used. A good yield of **11** was obtained by use of a large excess of CpCo(CO)$_2$ and a reaction time of several days.

(Tetrakis(4-carboxyphenyl)cyclobutadiene)cyclopentadienylcobalt (**13**) was easily obtained by basic hydrolysis of **10** (Scheme 4).

The tetrakis(*para*-bromophenyl) derivative **8** should provide access to many others through the use of transition-metal-catalyzed cross-coupling reactions.[25] To verify this, we have prepared [tetrakis(4-((triethylsilyl)-

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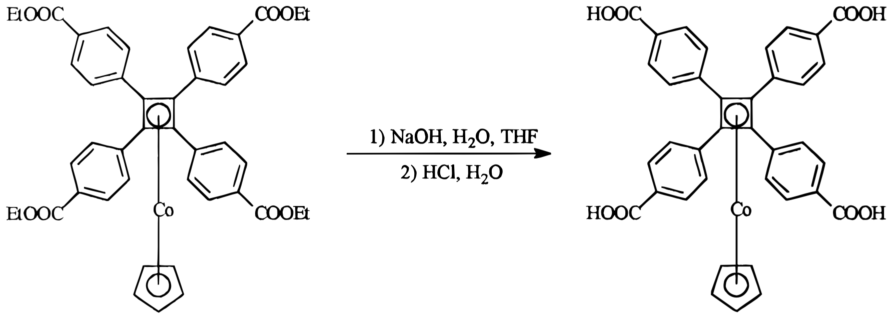
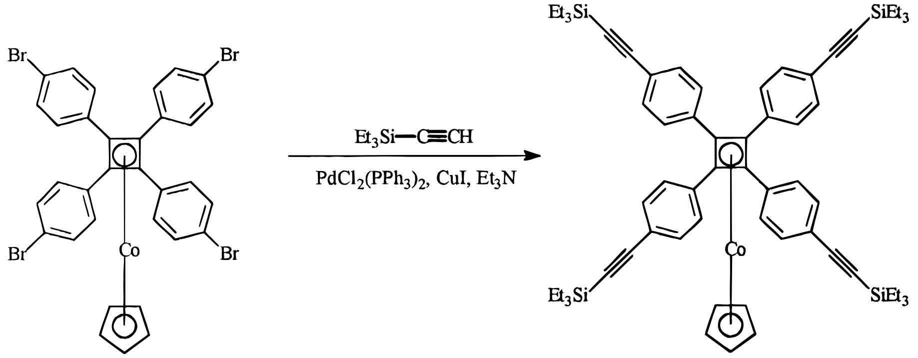
(25) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669.

**Scheme 4**



**13**, 71%

**Scheme 5**



**14**, 58%

ethynyl)phenyl)cyclobutadiene]cyclopentadienylcobalt (**14**) by the palladium-catalyzed cross-coupling[26] of **8** and triethylsilylacetylene (Scheme 5). Long reaction times and high catalyst levels were required to obtain a high yield. The complex **9** would be preferable as a substrate, as aryl iodides are known to react several hundred times faster than the analogous aryl bromides under similar reaction conditions.[25] However, the unfortunate difficulty in preparing large quantities of **9** justifies the preparation of **14** from **8**.

**Penta-Cp-substituted Derivatives**. Initial experiments with electrophilic substitution were performed with the readily available **1** as the substrate. Rausch reported that its Cp ring undergoes facile mercuration with mercury(II) acetate.[17] Mono- and bis(chloromercurio) derivatives of **1** were prepared *via* the respective mercury(II) acetates, which were not isolated. Polymercuration was also observed, but the higher substituted materials were not isolated. Recently, Winter[27] reported that both Cp rings of ruthenocene could be pentamercurated with mercury(II) acetate. Similarly, ferrocene is known to be decamercurated with mercury(II) trifluoroacetate under fairly mild conditions.[28] Prompted by these reports, we set about the pentamercuration of **1** using a similar reaction.

Reaction of 5 equiv of mercury(II) acetate with **1** under a variety of conditions consistently gave a mixture of complexes with one to five mercury substituents on the Cp ring, and conditions could not be found to convert **1** fully into the pentamercurated product. We were unable to separate the resulting mixture effectively by chromatography or crystallization. However, the reaction of **1** with the more electrophilic mercury(II) trifluoroacetate gave a fair yield (60%) of (tetraphenylcyclobutadiene)[pentakis((trifluoroacetoxy)mercurio)cyclopentadienyl]cobalt (**15**) (Scheme 6), soluble in THF and DMSO. Under similar conditions, with **8** as starting material, we obtained [tetrakis(4-bromophenyl)cyclobutadiene][pentakis((trifluoroacetoxy)mercurio)cyclopentadienyl]cobalt **(16)**. Compound **15** was converted into (tetraphenylcyclobutadiene)(pentaiodocyclopentadienyl)cobalt (**17**) by reaction[26] with potassium triiodide (Scheme 6).

Encouraged by the recent results by Bunz,[29] who described the functionalization of metal-complexed periodinated ligands using palladium-catalyzed cross-coupling with acetylene derivatives, we attempted similar chemistry on **17** (Scheme 6). Despite using a variety of acetylene derivatives ($Me_3SiCCH$, $Me_3SiCCSnMe_3$, $ClCH_2CH_2CH_2CCH$), palladium catalysts ($PdCl_2(CH_3CN)_2$, $PdCl_2(dba)$, $PdCl_2(PPh_3)_2$), and solvents (DMF, $Et_3N$), we were unable to find suitable conditions for cross-coupling. In some runs ($Me_3SiCCH$, $PdCl_2(dba)$, $Et_3N$, several days reflux), we observed some mono- and disubstitution of the Cp ring, but in all cases, over 90% of unreacted **17** was recovered from the reaction mixture. This failure does not mean that the reaction cannot be accomplished, since only a small fraction of the known reaction conditions[30] have been examined, and it may be desirable to return to the issue

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(26) Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, Chapter 2.4, p 521 and references therein.

(27) Winter, C. H.; Han, Y.; Heeg, M. J. *Organometallics* **1992**, 11, 3169.

(28) Boev, V. I.; Dombrovskii, A. V. *Zh. Obshch. Khim.* **1977**, *47*, 728 (Engl. Transl., 663).

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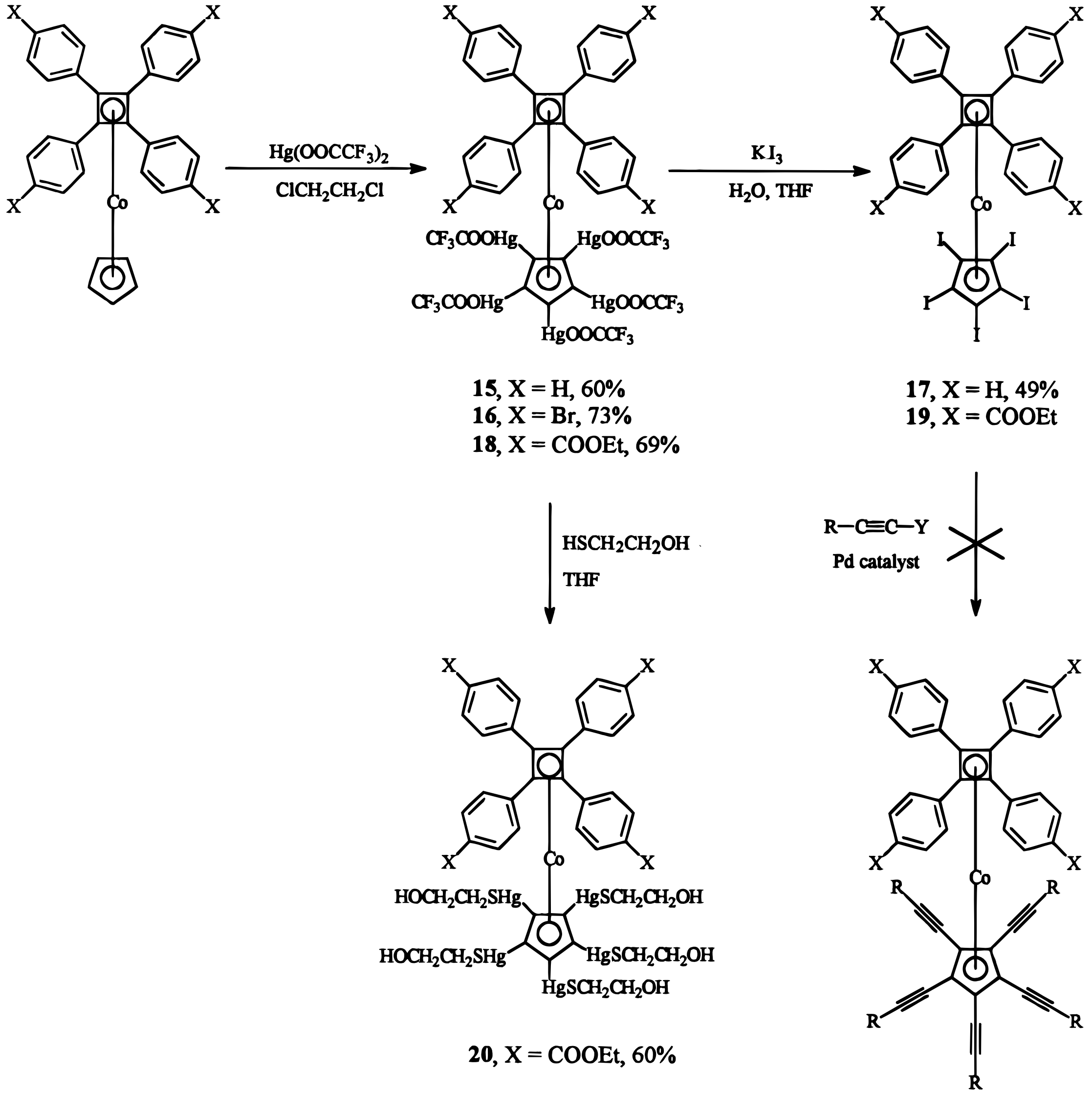
**Scheme 6**



at a later time. However, we note that there is only a limited number of reports on successful coupling of halogenated sandwich complexes with acetylenes and none, that we are aware of, were persubstituted with bulky substituents on one of the rings. It is thus also conceivable that **17** is simply too sterically hindered for the introduction of five ethynyl substituents into the five-membered ring in this fashion.

The tetraester **10** can be similarly pentamercurated to give [tetrakis(4-(ethoxycarbonyl)phenyl)cyclobutadiene]-[pentakis((trifluoroacetoxy)mercurio)cyclopentadienyl]-cobalt **(18)** in 68% yield (Scheme 6). Like the pentamercurio complexes **15** and **16**, **18** is soluble in THF and DMSO. In contrast, the tetrapyridyl derivative **7** cannot be mercurated on the Cp ring in this fashion and the mercuration takes place on the pyridine nitrogen instead.

In a reaction similar to that used to prepare **17**, potassium triiodide smoothly converted **18** to [tetrakis-(4-ethoxycarbonyl)phenyl)cyclobutadiene](pentaiodocyclopentadienyl)cobalt (**19**, Scheme 6) but the product proved difficult to purify. After repeated column chromatography and recrystallization, **19** was only 95% pure. The $^1$H NMR spectrum of the impure sample suggests that the tenacious impurity is the related tetraiodocyclopentadienyl complex. Discouraged by the failure of the cross-coupling reactions of **17** with acetylenes, we have given up plans to complete the synthesis of **19** and have started to look for other ways of attaching suitable tentacles.

One such alternative is to accept the mercury atom as a part of the desired tentacle and to take advantage of the ease of its reductive or oxidative removal at the time when the tentacles are to be cut off after completed polymerization. The reaction of mercuric carboxylates with thiols is facile[31] and, in principle, permits the introduction of a nearly arbitrary chain as long as it can attach through a terminal thiol group. We have chosen to demonstrate the principle with 2-hydroxyethanethiol, and it yielded [tetrakis(4-ethoxycarbonyl)-phenyl)cyclobutadiene][pentakis((2-hydroxyethyl)-thio)mercurio)cyclopentadienyl]cobalt **(20)** without difficulty. Our plans call for the synthesis of a series of

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(31) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, Chapter 17, p 863 and references therein.

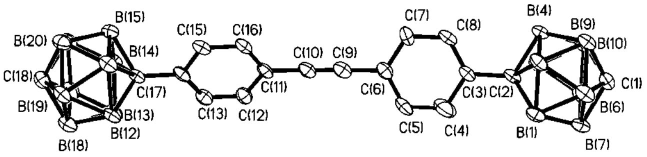

**Figure 2.** Single-crystal X-ray structure of **5**.

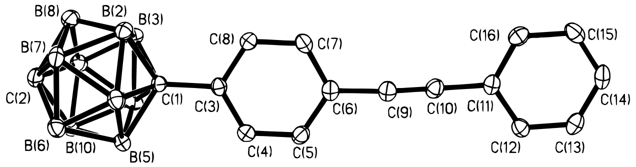

**Figure 3.** Single-crystal X-ray structure of **6**.

**Table 1. Structural Characteristics of Molecular Rods**

| no. | *d* (Å)[a] | α (deg)[b] | *β* (deg)[c] | *γ* (deg)[d] |
|---|---|---|---|---|
| **5**[e] | 18.79 | 42, 21[f] | 4, 5 | 5, 8 |
| | 18.91 | 0 | 5, 5 | 6, 6 |
| **6**[e] | 14.27 | 2 | 5, 6 | 6 |
| | 14.14 | 5 | 9, 6 | 11 |

[a] End-to-end length (C to C). [b] Twist angle between the phenyl rings. [c] Bend angles between the triple bond and the lines from its center to outer carbons on phenyl rings. [d] Bend angles between the triple bond and the lines from its center to terminal carbons of carboranes. [e] Values for two independent molecules in the asymmetric unit. [f] Values for two different conformations in the asymmetric unit.

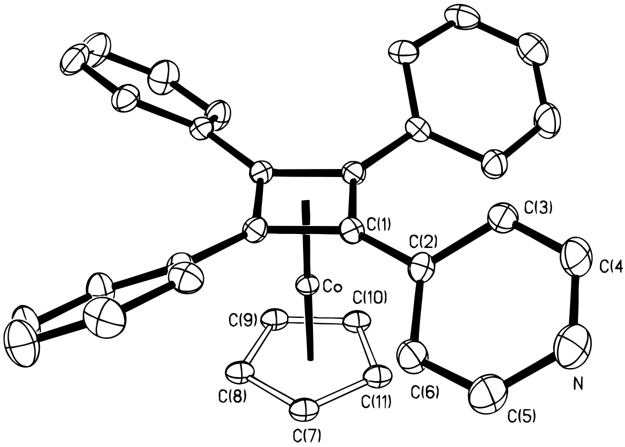

**Figure 4.** Single-crystal X-ray structure of **7**.

such tentacled connectors and investigation of their adhesion to the surface of mercury.

**Crystal and Molecular Structures of Connectors and Rods**. We have characterized the structures of the rods **5** and **6** (Figures 2 and 3, Table 1) and of the cobalt complexes **7**, **10**, **11**, and **15** (Figures 4 −8, Table 2). The two rods are nearly linear, and the slight deviations from linearity are probably due to crystal packing. The connectors possess the expected distance between the two nearly parallel metallocene decks. The length of the arms is as expected, and the phenyl substituents are twisted a little over a third of the way toward orthogonality. The arms are directed almost exactly in the plane of the cyclobutadiene ring. The one connector that has tentacles attached (**15**) has the carbon−mercury bonds within 5° of the plane of the cyclopentadienyl ring. The adjacent oxygen atoms deviate farther from this plane, by as much as 23°. The carbon−mercury bonds are 2.03−2.06 Å and the mercury−oxygen bonds are 2.07−2.11 Å long. The molecules of **15** pack in pairs in which the tentacled rings face each other, with the tentacles staggered (Figure 8).

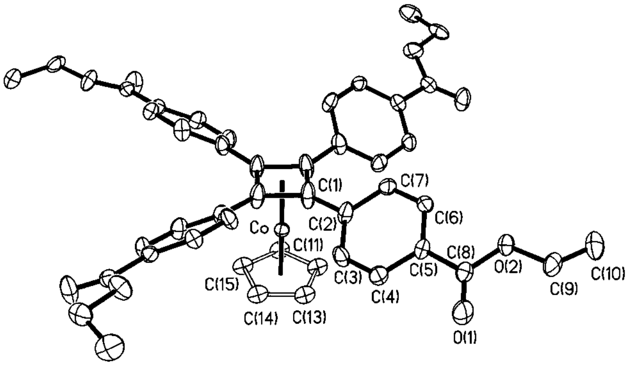

**Figure 5.** Single-crystal X-ray structure of **10**.

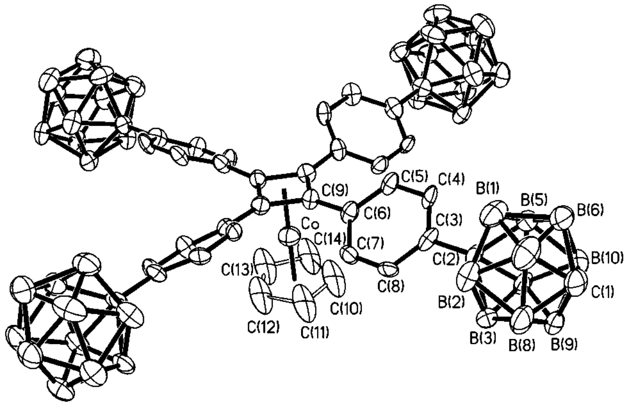

**Figure 6.** Single-crystal X-ray structure of **11**.

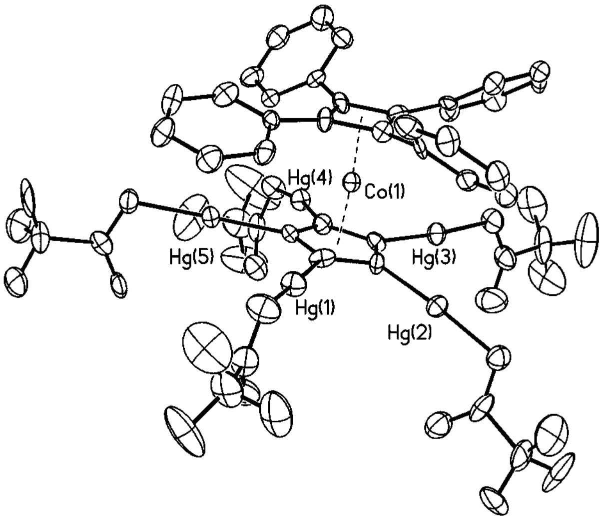

**Figure 7.** Single-crystal X-ray structure of **15**.

## Experimental Section

All reagents were purchased from Aldrich, with the exception of ethyl 4-iodobenzoate (TCI America) and *p*-carborane (Katchem, Prague, Czech Republic), and were used as supplied. All solvents were analytical grade and were freshly distilled before use. (Tetraphenylcyclopentadienyl)(cyclobutadiene)cobalt (**1**) and cyclopentadienylcobalt dicarbonyl, $CpCo(CO)_2$, were prepared by the method of Rausch.[17] Melting points were recorded using a Melt temp II apparatus (Laboratory Devices). $^1H$ and $^{13}C$ NMR spectra were obtained on a Varian VXR-300 S spectrometer at 299.949 and 75.428 MHz, respectively, using $Me_4Si$ as an external reference. IR spectra were obtained on a Nicolet 800 FT-IR spectrometer. Electron impact (EI) and

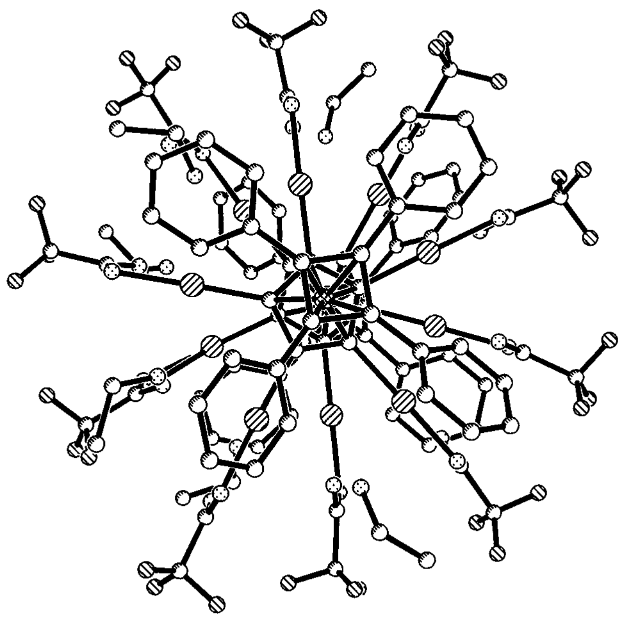

**Figure 8.** Axial view of the asymmetric unit of the single-crystal X-ray structure of **15**.

**Table 2. Structural Characteristics of Square Connectors**

| no. | *d* (Å)[a] | α (deg)[b] | *β* (deg)[c] | *u* (Å)[d] | *γ* (deg)[e] |
|---|---|---|---|---|---|
| **7** | 3.36 | 4 | 35 | 5.33 | 4 |
| **10** | 3.42 | 2 | 33 | 7.40 | 3 |
| **11** | 3.33 | 3 | +31, −31[f] | 9.93 | 2 |
| **15**[g] | 3.39 | 7 | 15, 39, 37, 43 | 5.30 | 0, 5, 7, 4 |
| | 3.40 | 6 | 48, 35, 40, 19 | 5.31 | 5, 6, 3, 3 |

[a] Distance between the two rings. [b] Angle of the two ring planes. [c] Twist angle of the ring - phenyl bond (all four angles are the same in **7**, **10**, and **11**). [d] Arm length from center to the outermost heavy atom (in **10**, to the midpoint of the ester oxygens). [e] Angle between the cyclobutadiene ring plane and the line drawn from ring center to arm end. [f] Two orientations of the phenyl ring are present in the asymmetric unit. [g] Values for two independent molecules in the asymmetric unit.

fast atom bombardment (FAB) mass spectra were obtained on a VG 7070 EQ-HF hybrid tandem Mass spectrometer. UV−vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. Microanalysis were performed by Desert Analytics, Tucson, AZ, and the Microanalytical Laboratory at the University of California, Berkeley, CA.

Crystals for X-ray analysis were selected and mounted onto a glass fiber using Exxon Paratone N oil. Data collections utilized a Siemens SMART CCD diffractometer equipped with a locally modified LT-2A low-temperature apparatus. Unit cell parameters were determined after harvesting reflections from three sets of 20 0.3° $\omega$ scans chosen so that each set was roughly orthogonal to the other two. An arbitrary hemisphere of data was measured for each experiment. Final cell dimensions were calculated using reflections with $I > 10\sigma(I)$ chosen from the entire data set. Data were corrected for Lorentz and polarization effects as well as for absorption.

Structure solution and refinement employed the SHELXTL suite of programs.[32] Scattering factors were from a standard source.[33] Hydrogens were placed at calculated positions with thermal parameters set to 1.2 times the equivalent isotropic thermal parameter of the parent atom. These parameters were then set to ride on the parent values during subsequent refinement. Calculations were performed on a Silicon Graphics Indigo$^2$XL workstation.

Detailed information on single-crystal X-ray analysis of **5**, **6**, **7**, **10**, **11**, and **15** is available in the Supporting Information (for a summary, see Table 3). Some of the results deserve comment: The asymmetric unit of **5** contains 1.5 carborane molecules as well as 1.5 benzene molecules. Inversion completes the fractional molecules. Rotational disorder about the long axis of the molecule was observed in the phenyl ring C(3)−C(8). A second orientation was added to the model; refinement indicates occupancies of 0.46(4) and 0.54(4) for groups {C(4),C(5),C(7),C(8)} and {C(4′),C(5′),C(7′),C(8′)}, respectively. The benzene molecules neatly cap the ends of the carboranes with a contact distance of 2.45 Å from H(1C) to the ring centroid and 2.56 Å from H(18C) by translation.

Two crystallographically independent molecules of **6** comprise the asymmetric unit. Two packing motifs are present. The phenyl groups form parallel planes with an interplanar separation of 2.62 Å. Examples are B(1) to C(16) and B(11) to C(32) which are related by the symmetry operator $(^1/_2 - x, 1 - y, -1^1/_2 + z)$. While the planes of the phenyl rings form close separations, the ring atoms are slipped so that $\pi$-stacking does not appear to be present. The closest contact is H(16A) to H(31A) at 2.56 Å. The second motif observed is reminiscent of the herringbone pattern of benzene. Here, C(5) is 3.03 Å from H(15A) of a neighbor generated by $(^1/_2 - x, -y, ^1/_2 + z)$. Another close approach to C(5) is made by H(23A), 2.85 Å, by $(x, y, -1 + z)$.

Complex **7** crystallizes in noncentrosymmetric space group *I*4. Cobalt lies on a crystallographic 4-fold axis that also passes through the centroids of the cyclobutadiene and cyclobutadienyl ligands. The disorder imposed on the cyclopentadienyl group was modeled as a rigid pentagon with each atom at $^1/_4$ site occupancy. After applying all symmetry operations, this results in 20 positions totaling 5 carbon atoms. No disorder is present in the tetra(4-pyridyl)cyclobutadiene ligand. A small amount of the opposite isomer appears to be present in the crystal. This manifests itself as a persistent peak of residual electron density, approximately 1 $\text{e}^-/\text{Å}^3$, on the 4-fold axis. This peak and the cobalt position are approximately equidistant from the cyclopentadienyl centroid, 1.67 Å for Co and 1.37 Å for the residual peak. The residual peak was modeled as cobalt, and the site occupancies of both cobalt positions were refined to total $^1/_4$, as required by the 4-fold axis. Occupancies refined to 0.24244(3) and 0.0075(3). Attempts to model other atoms at this site were unsatisfactory. Although it would be reasonable to discard such a minor peak, a similar, though larger, residual was also present for compound **10**. Because this minor component is present in such a small quantity, it was not possible to observe any of the lighter atom positions. Columns of molecules form in the direction of the *c* axis. Taking one column as the center, four neighboring columns are slipped $^1/_2$ the magnitude of *c*. This result places the cyclobutadiene and cyclopentadienyl planes of neighboring molecules nearly coplanar and creates a tiling pattern with a cyclopentadiene surrounded by four identical cyclobutadiene groups; the distance from the cyclobutadiene plane to the cyclopentadienyl centroid is 0.08 Å. The linking nitrogens of the pyridyl groups form a 6.61 Å square encompassing the cyclopentadienyl ligand. This void easily accommodates the rotational disorder observed in the cyclopentadienyl ligand.

Complex **10** crystallizes in noncentrosymmetric space group *I*4. Structural features are similar to those of **7**, including disorder in the cyclopentadienyl group and residual electron density along the 4-fold axis. In this structure, the residual electron density is approximately 6 $\text{e}^-/\text{Å}^3$ and distances from the cyclopentadienyl centroid are 1.63 and 1.40 Å for Co and the residual peak, respectively. Occupancies refined to 0.1982(6) and 0.0517(6). The similarity in packing is striking, given the differences between the two structures. Here, the space occupied by the cyclopentadienyl group is defined by the carbonyl oxygen. Linking these atoms on neighboring molecules forms a 6.15 Å square. The displacement of the

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(32) Sheldrick, G. M. *SHELXTL, A Program for Crystal Structure Determination,* Version 5 beta; Siemens Analytical X-ray Instruments: Madison, WI, 1995.

(33) *International Tables for Crystallography*; Reidel Publishing Co: Boston, MA, 1991; Vols. C, D.

**Table 3. Summary of Crystallographic Parameters**

| compound number | **5** | **6** | **7** | **10** | **11** | **15** |
|---|---|---|---|---|---|---|
| empirical formula | $C_{36}H_{54}B_{30}$ | $C_{32}H_{40}B_{20}$ | $C_{29}H_{21}CoN_4$ | $C_{45}H_{41}CoO_8$ | $C_{10.25}H_{16.25}B_{10}Co_{025}$ | $C_{49}H_{34}CoF_{15}Hg_5O_{13}$ |
| formula mass | 811.09 | 640.84 | 484.43 | 768.71 | 262.32 | 2177.64 |
| cryst syst | triclinic | orthorhombic | tetragonal | tetragonal | tetragonal | triclinic |
| space group | $P\bar{1}$ | $P2_12_12_1$ | $I4$ | $I4$ | $P4/nnc$ | $P\bar{1}$ |
| $a$ = (Å) | 7.3774(5) | 42.1080(6) | 13.2063(2) | 16.233(2) | 21.0073(2) | 15.0547(2) |
| $b$ = (Å) | 15.6765(10) | 7.36570(10) | 13.2063(2) | 16.233(2) | 21.0073(2) | 15.4743(2) |
| $c$ = (Å) | 22.645(2) | 11.64150(10) | 6.8998(2) | 7.0765(8) | 13.9245(2) | 25.3384(2) |
| α = (deg) | 109.7368(6) | 90 | 90 | 90 | 90 | 91.4980(10) |
| $\beta$ = (deg) | 96.4756(12) | 90 | 90 | 90 | 90 | 100.03 |
| $\gamma$ = (deg) | 95.2715(11) | 90 | 90 | 90 | 90 | 90.3260(10) |
| vol, Å$^3$ | 2425.6(3) | 3610.67(8) | 1203.37(4) | 1864.8(4) | 6144.97(12) | 5810.32(12) |
| Z | 2 | 4 | 2 | 2 | 16 | 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.111 | 1.179 | 1.337 | 1.369 | 1.134 | 2.489 |
| $\mu$, cm$^{-1}$ | 0.053 | 0.058 | 0.737 | 0.516 | 0.312 | 13.548 |
| transmission coeff | 0.998−0.988 | 0.997−0.993 | 0.913−0.762 | 0.984−0.966 | 0.981−0.951 | 0.407−0.205 |
| $T$ (K) | 146(2) | 123(2) | 157(2) | 293(2) | 293(2) | 155(2) |
| $\lambda$, Å | 0.710 73 (Mo Kα) | 0.710 73 (Mo Kα) | 0.710 73 (Mo Kα) | 0.710 73 (Mo Kα) | 0.710 73 (Mo Kα) | 0.710 73 (Mo Kα) |
| no. of reflns collected | 12 975 | 24 278 | 4146 | 5343 | 24 939 | 40 036 |
| no. of unique reflns | 8404 ($R_{int}$ = 0.0770) | 8717 ($R_{int}$ = 0.0546) | 1408 ($R_{int}$ = 0.0199) | 1750 ($R_{int}$ = 0.0970) | 2153 ($R_{int}$ = 0.1839) | 26883 ($R_{int}$ = 0.0423) |
| no. of reflns observed | 5387 | 7248 | 1399 | 1238 | 1515 | 17772 |
| $R$ index[a] $[I > 2\sigma(I)]$ | R1 = 0.0952 | R1 = 0.0610 | R1 = 0.0230 | R1 = 0.0667 | R1 = 0.1034 | R1 = 0.0537 |
| $R$ indices[a,b] (all data) | R1 = 0.1483, wR2 = 0.2784 | R1 = 0.0818, wR2 = 0.1468 | R1 = 0.0232, wR2 = 0.0588 | R1 = 0.1092, wR2 = 0.1238 | R1 = 0.1486, wR2 = 0.2368 | R1 = 0.1039, wR2 = 0.1284 |
| weighting coeffs[c] | $a$ = 0.0936 $b$ = 3.6758 | $a$ = 0.0279 $b$ = 2.9672 | $a$ = 0.0356 $b$ = 0.3481 | $a$ = 0.0288 $b$ = 2.1988 | $a$ = 0.0467 $b$ = 30.3415 | $a$ = 0.0271 $b$ = 28.8322 |
| goodness-of-fit[d] on $F^2$ | 1.085 | 1.134 | 1.094 | 1.074 | 1.136 | 1.156 |

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = \{(\sum[w(F_o^2 - F_c^2)^2])/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$. [d] GooF $= \{(\sum[w(F_o^2 - F_c^2)^2])/(M - N)\}^{1/2}$; $M$ = no. of reflns, and $N$ = no. of params refined.

cyclopentadienyl centroid from the plane formed by neighboring cyclobutadiene is 0.12 Å.

While **11** crystallizes in the centrosymmetric space group *P*4/*nnc*, the asymmetric unit is similar to those for **7** and **10**. Just as for those, rotational disorder is present for the cyclopentadienyl group. In this structure, the space occupied by cyclopentadiene may be described by a 7.29 Å square with carborane hydrogen H(8) at its corners. Additional disorder was observed about the carborane arms of the cyclobutadiene ligand in phenyl ring C(3)−C(8). This may be described as opposite in sense to the propeller formed by the phenyl rings. A second orientation was added to the model; refinement indicates occupancies of 0.513(4) and 0.487(4) for groups {C(4),C(5),C(7),C(8)} and {C(4′),C(5′),C(7′),C(8′)}, respectively.

Complex **15** crystallizes in the triclinic space group with two independent molecules in the asymmetric unit. In addition, there are six molecules of ethanol occupying spaces between arms of the ligands. The two cobalt complex molecules are oriented with the cyclopentadiene groups facing each other. These ligands are nearly parallel, 12.1°. Each is rotated with respect to the other so that the arms nest nicely together. The distance between the cyclopentadienyl centroids is 3.84 Å, while some of the pendant atoms are within an angstrom of the best-fit plane. No notable extended structure is present. Several trifluoroacetate groups exhibit rotational disorder, and all display large thermal motion.

**4,4′-Dibromodiphenylacetylene (2).**[34] 1-Bromo-4-iodobenzene (12.5 g, 44 mmol), CuI (57 mg, 0.22 mmol), $PdCl_2(PPh_3)_2$ (210 mg, 0.30 mmol), and diethylamine (200 mL) were charged to a 500 mL three-necked flask fitted with a nitrogen inlet, a gas inlet directly into the reaction mixture, and a gas outlet. The reaction vessel was purged with nitrogen, then a steady stream of acetylene was bubbled through the solution for 7 h, and then the mixture was stirred overnight. The solvent was removed under reduced pressure to give a brown powder. This was dissolved in a mixture of dichloromethane (300 mL) and dilute hydrochloric acid (2 M, 200 mL) and transfered to a separatory funnel. After extraction, the organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic fractions were washed with water (2 × 100 mL) and dried over sodium sulfate, and the solvent was removed to give a brown powder. The crude product was chromatographed (silica gel, dichloromethane/hexane, 30:70) then recrystallized from chloroform to give **2** as white crystals (4.54 g, 61%). Mp: 181−182 °C (lit.[32] 182−184 °C). $^1$H NMR ($CDCl_3$): $\delta$ 7.10 (d, $J = 8$ Hz, 2 H, Ph), 7.54 (d, $J = 8$ Hz, 2 H, Ph). MS (EI$^+$): *m*/*z* 336 (M, correct bromine isotope pattern).

**4,4′-Diiododiphenylacetylene (3).**[22] 1,4-Diiodobenzene (15.0 g, 45 mmol), CuI (100 mg, 0.30 mmol), $PdCl_2(PPh_3)_2$ (210 mg, 0.30 mmol), and diethylamine (100 mL) were charged to a 250 mL three-necked flask. A glass tube was inserted into the flask through a rubber septum and reached well below the surface of the solvent. A balloon filled with acetylene gas was attached to the end of the glass tube. A small purge valve was fitted to the second neck of the flask, and the third neck was stoppered. A slow stream of acetylene from the balloon was passed through the stirred reaction mixture over approximately 5 h, resulting in the formation of a yellow precipitate. Typically, around 2 L of acetylene was used. The solvent was removed, and the crude product was recrystallized twice from toluene to give pure **3**. On a typical run, the yield of **3** was 4.08 g (42%). Yields were as high as 50%, but it was found that insoluble polymeric materials were usually formed when excess acetylene was used in an attempt to increase the yield. Mp: 238−239 °C (lit.[22] 237−238 °C). $^1$H NMR ($CDCl_3$): $\delta$ 7.24 (d, $J = 9$ Hz, 2 H, Ph), 7.69 (d, $J = 9$ Hz, 2 H, Ph). MS (EI$^+$): *m*/*z* 430 (M).

**4,4′-Bis(ethoxycarbonyl)diphenylacetylene (4).** The procedure is similar to that reported for related structures.[21] Ethyl 4-iodobenzoate (11.1 g, 40 mmol), $PdCl_2(PPh_3)_2$ (315 mg, 0.45 mmol), copper(I) iodide (171 mg, 0.9 mmol), and diethylamine (400 mL) were charged to a 500 mL three-necked flask fitted with a introgen inlet, a gas inlet directly into the reaction mixture, and a gas outlet. The reaction vessel was purged with nitrogen, then a steady stream of acetylene was bubbled through the solution for 7 h, and then the mixture was stirred overnight. The solvent was removed, the residual powder was dissolved in a mixture of dichloromethane (300 mL) and dilute hydrochloric acid (2 M, 200 mL) and transfered to a separatory funnel. After extraction, the organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic fractions were washed with water (2 × 100 mL) and dried over sodium sulfate, the solvent was removed, and the crude product was chromatographed (silica gel, dichloromethane/hexane, 1:1) and then recrystallized from dichloromethane/hexane to give **4** as white crystals (4.57 g, 70%). Mp: 147−148 °C. $^1$H NMR ($CDCl_3$): $\delta$ 1.40 (t, $J = 7$ Hz, 3 H, $CH_3$), 4.39 (q, $J = 7$ Hz, 2 H, $CH_2$), 7.60 (d, $J = 8$ Hz, 2 H, Ph), 8.04 (d, $J = 8$ Hz, 2 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 14.22 ($CH_3$), 61.13 ($CH_2$), 91.30 (ethynyl), 127.22, 129.52, 130.26, 131.57 (Ph), 165.95 (C=O). MS (EI$^+$): *m*/*z* (relative intensity) 322 (M, 100), 277 (M − $C_2H_5O$, 89), 249 (M − $C_4H_{10}O$, 28), 176 (M − $C_6H_{10}O_4$, 32). IR (KBr, cm$^{-1}$): 3076 (w, C−H aromatic), 2906 (w, C−H aliphatic), 1710 (s, C=O), 1274 (s, C−O). Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.82; H, 5.58.

**Bis[4-(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl]acetylene (5) and Phenyl[4-(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl]acetylene (6).** Related literature procedures[5] were followed closely. 1,12-Dicarba-*closo*-dodecaborane (837 mg, 5.8 mmol) was dissolved in THF (50 mL) in a 100 mL two-necked flask, and the solution was cooled to −30 °C. *n*-Butyllithium (1.6 M in hexane, 3.6 mL) was added to the solution *via* syringe over 5 min. The mixture was allowed to rise to room temperature over 1 h and was stirred for a further 4 h. The solution was again cooled to −30 °C, and CuI (580 mg, 5.8 mmol) was added to the solution. After slowly warming to room temperature, the mixture was heated to 50 °C for 14 h to give a dark brown solution. On cooling, the solvent was removed under reduced pressure. *N*-Methyl-2-pyrolidinone (30 mL), $Pd_2Cl_2(PPh_3)_2$ (75 mg, 0.11 mmol), and **3** (1.0 g, 2.3 mmol) were added to the reaction vessel, and the solution was heated to 100 °C for 18 h. On cooling, the mixture was transfered to a separatory funnel and hexane (150 mL) and dilute HCl (150 mL) were added to the mixture. After extraction, the organic layer was collected, and the aqueous layer was again extracted with hexane (100 mL). The combined organic fractions were extracted with dilute HCl (3 × 75 mL) and dried over sodium sulfate. After removal of the solvent, the residue was chromatographed (silica gel, hexane). 1,12-Dicarba-*closo*-dodecaborane (118 mg) was isolated as the first fraction from the column. Pure **5** (260 mg, 25%) was next to elute from the column, followed by pure **6** (44 mg, 6%). Both were recrystallized from EtOH. Analysis for **5**: mp 231−232 °C. $^1$H NMR ($CDCl_3$): $\delta$ 1.30−3.42 (br, 11 H, $H_{carborane}$), 7.16 (d, $J = 8$ Hz, 2 H, Ph), 7.28 (d, $J = 8$ Hz, 2 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 59.98 ($C_{carborane}$−H), 85.75 ($C_{carborane}$−C), 89.60 (ethynyl), 123.20, 127.08, 131.21, 136.84 (Ph). $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta$ −13.39 (s, 10 B), −15.92 (s, 10 B). MS (EI$^+$): *m*/*z* 463 (M, boron cluster center, isotope pattern fits the calculated cluster for the ion $[C_{18}H_{30}B_{20}]^+$). IR (KBr, cm$^{-1}$): 3070 (w, C−H aromatic), 2612 (s, B−H), 1631 (m, Ph), 1519 (m, Ph), 1088 (m, Ph). UV−vis ($CH_2Cl_2$): $\lambda$ ($\epsilon$) 316 (43 500), 256 (48 000) nm (L mol$^{-1}$ cm$^{-1}$). Anal. Calcd for $C_{18}H_{30}B_{20}$: C, 46.73; H, 6.54. Found: C, 46.68; H, 6.59. Analysis for **6**: mp 132−133 °C. $^1$H NMR ($CDCl_3$): $\delta$ 1.24−3.44 (br, 11 H, $H_{carborane}$), 7.19 (d, $J = 8$ Hz, 2 H, Ph), 7.31−7.36 (m, 5 H, Ph), 7.47−7.54 (m, 2 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 59.94 ($C_{carborane}$−H), 85.83 ($C_{carborane}$−C), 88.34, 90.68 (ethynyl), 122.93, 123.54, 127.05, 128.24, 128.45, 131.17, 131.63, 136.60 (Ph). $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta$ −13.39 (s, 5 B), −15.92 (s, 5 B). IR

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(34) Barber, H. J.; Slack, R. *J. Chem. Soc.* **1944**, 612.

($CCl_4$, cm$^{-1}$): 3066 (w, C−H aromatic), 2614 (s, B−H), 1551 (w, Ph), 1513 (w, Ph), 1088 (m, Ph). MS (EI$^+$) *m/z* 321 (M, boron cluster center, isotope pattern fits the calculated cluster for the ion $[C_{16}H_{20}B_{10}]^+$). HRMS Calcd for $C_{16}H_{20}11B_{10}$: 322.2496. Found: 322.2520.

**(Tetraphenylcyclobutadiene)cyclopentadienylcobalt (1).**[17] Diphenylacetylene (2.94 g, 16.5 mmol), freshly distilled $CpCo(CO_2)$ (1.49 g, 8.3 mmol), and xylene (80 mL) were charged to a 250 mL round-bottom flask and heated under reflux for 22 h under an argon atmosphere in the dark. After the reaction mixture was cooled, the solution was poured directly onto a dry silica column and the orange band at the solvent front was eluted with benzene. The solvent was evaporated, and the solid residue was washed with pentane (100 mL) and then rechromatographed on silica gel with benzene to give yellow crystals of **1** (3 g, 75%). The product was then recrystallized from benzene and heptane. Mp: 262 °C (lit.[17] 262−264 °C). $^1H$ NMR ($C_6D_6$): $\delta$ 4.47 (s, 5 H, Cp), 7.04 (m, 12 H, Ph), 7.59 (m, 8 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 75.0 (Cb), 83.2 (Cp), 126.2 (Ph), 127.9 (Ph), 128.9 (Ph), 136.5 (Ph). IR (KBr, cm$^{-1}$): 3050 (w, C−H aromatic), 1596 (s, C=C aromatic), 1498 (s, Ph). MS (EI$^+$) *m/z* (relative intensity) 480 (100), 302 (50), 105 (39), 71 (54), 57 (85).

**[Tetrakis(4-pyridyl)cyclobutadiene]cyclopentadienylcobalt (7).** 4,4′-Dipyridylacetylene (4.86 g, 27 mmol), $CpCo(CO)_2$ (2.44 g, 13.6 mmol), and xylene (240 mL) were charged to a 500 mL round bottom flask and heated under reflux for 24 h under an argon atmosphere in the dark. After the reaction mixture was cooled, the solvent was evaporated and the solid residue was washed with a few milliliters of a mixture of acetone and pentane (1:1). The solid was chromatographed on silica gel (eluent, $CHCl_3/EtOH$, 4:1). Crude **7** was eluted first, followed by **12**. The former was then rechromatographed on silica gel ($CHCl_3/EtOH$, 85:15) to give pure **7** (0.95 g, 15%). The product was recrystallized from chloroform and pentane. X-ray quality crystals were obtained from chloroform and acetonitrile. Mp: 330 °C (dec). $^1H$ NMR ($CDCl_3$): $\delta$ 4.71 (s, 5 H, Cp), 7.25 (d, 8 H, $J$ = 6 Hz, Pyr), 8.51 (d, 8 H, $J$ = 6 Hz, Pyr). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 73.1 (Cb), 84.0 (Cp), 122.8, 143.7, 149.9. MS (EI$^+$) m/z (relative intensity) 484 (M, 100), 304 (40), 180 (7), 124 (62), 91 (64). IR (KBr, cm$^{-1}$): 3072−3019 (w, C−H aromatic), 1607−1590 (s, C=C aromatic). UV−vis ($CH_2Cl_2$): $\lambda$ ($\epsilon$) 400 sh (3 000), 298 (34 500) nm (L mol$^{-1}$ cm$^{-1}$). HRMS Calcd for $C_{29}H_{21}N_4Co$: 484.1098. Found: 484.1076. Anal. Calcd for $C_{29}H_{21}N_4Co$: C, 71.90; H, 4.37; N, 11.57. Found: C, 71.65; H, 4.31; N, 11.54.

**[Tetrakis(4-pyridyl)cyclopentadienone]cyclopentadienylcobalt (12).** After chromatography on silica gel, the solvent was evaporated and the solid residue was washed with a few milliliters of acetone and recrystallized from chloroform and pentane to give dark red crystals of **12** (3.47 g, 50%). Mp: 270−280 °C (dec). $^1H$ NMR ($CDCl_3$): $\delta$ 5.01 (5, 5 H, Cp), 7.03 (d, 4 H, $J$ = 5.4 Hz, Pyr), 7.46 (d, 4 H, $J$ = 5.4 Hz, Pyr), 8.52 (m, 8 H, Pyr). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 74.2, 85.9, 91.5, 124.5, 126.4, 139.9, 141.2, 149.4, 157.2. MS(EI$^+$) m/z (relative intensity) 512 (M), 120 (13), 83 (100). IR (KBr, cm$^{-1}$): 3095−3023 (w, C−H aromatic), 1613 (s, C=C aromatic), 1593 (s, C=O). Anal. Calcd for $C_{30}H_{21}N_4OCo\cdot{}^1/_2CHCl_3$: C, 64.03; H, 3.79; N, 9.79. Found: C, 64.28; H, 3.73; N, 9.75.

**[Tetrakis(4-bromophenyl)cyclobutadiene]cyclopentadienylcobalt (8).** The procedure described for **1** was followed, using $CpCo(CO)_2$ (1.0 g, 5.5 mmol), **2** (2.73 g, 8.125 mmol), and xylene (80 mL) in a 200 mL flask and refluxing for 24 h. In the chromatographic separation, the orange band at the solvent front was eluted with hexane and the product rechromatographed on silica gel. Unreacted **2** (380 mg) was first to be eluted with hexane, and **8** was eluted with hexane/dichloromethane (3:1). Recrystallization of the crude product from benzene/hexane gave pure **8** as brown crystals (1.08 g, 46% based on **2** consumed). Mp: 307−308 °C. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 4.62 (s, 5 H, Cp), 7.26 (d, $J$ = 9 Hz, 8 H, Ph), 7.30 (d, $J$ = 9 Hz, 8 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 73.64 (Cb), 83.38 (Cp), 120.31, 130.11, 131.43, 134.73 (Ph). IR (KBr, cm$^{-1}$): 3044 (w, C−H aromatic), 1632 (m, Ph), 1493 (s, Ph), 1069 (m, Ph). MS (EI$^+$) *m/z* 796 (M). Anal. Calcd for $C_{33}H_{21}Br_4Co$: C, 49.79; H, 2.66. Found: C, 50.09; H, 2.49.

**[Tetrakis(4-iodophenyl)cyclobutadiene]cyclopentadienylcobalt (9)**. The procedure described for **1** was followed, using $CpCo(CO)_2$ (223 mg, 1.24 mmol), **3** (1.07 g, 2.48 mmol), and xylene (50 mL) in a 100 mL flask and refluxing for 24 h. In the chromatographic separation, the product was eluted with chloroform and rechromatographed on silica gel with hexane. Unreacted **3** was eluted first. The second band contained **9** mixed with **3** and was rechromatographed (silica gel, hexane) to give pure **9** (102 mg, 8%). Recrystallization from benzene/hexane gave orange-brown crystals. Mp: 300−301 °C (dec with evolution of iodine); single crystals were obtained from a mixture of chloroform and acetonitrile. $^1H$ NMR ($CDCl_3$): $\delta$ 4.58 (s, 5 H, Cp), 7.12 (d, $J$ = 9 Hz, 8 H, Ph), 7.54 (d, $J$ = 5 Hz, 8 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 73.71 (Cb), 83.40 (Cp), 91.68, 130.30, 135.34, 137.30 (Ph). IR (KBr, cm$^{-1}$): 3055 (w, C−H aromatic), 1633 (m, Ph), 1489 (s, Ph), 1057 (m, Ph), 1004 (s, C−I). MS (FAB$^+$, 3-NOBA): *m/z* 984 (M). Anal. Calcd for $C_{33}H_{21}CoI_4$: C, 40.28; H, 2.15. Found: C, 40.02; H, 2.00.

**[Tetrakis(4-(ethoxycarbonyl)phenyl)cyclobutadiene]-cyclopentadienylcobalt (10)**. The procedure described for **1** was followed, using **4** (0.42 g, 1.3 mmol), $CpCo(CO)_2$ (117 mg, 0.65 mmol), and xylene (50 mL) in a 100 mL flask and refluxing for 20 h. A precipitate formed on cooling to 0 °C was collected on a frit and washed with hexane. The solid residue was chromatographed (silica gel $CHCl_3$) to give pure **10** (0.36 g, 72%). Crystallization from toluene gave **10** as a orange-red crystals. Mp: 282−284 °C; single crystals were obtained from a mixture of chloroform and acetonitrile. $^1H$ NMR ($CDCl_3$): $\delta$ 1.40 (t, $J$ = 8 Hz, 12 H, $CH_3$), 4.39 (q, $J$ = 8 Hz, 8 H, $CH_2$), 4.64 (s, 5 H, Cp), 7.46 (d, $J$ = 8 Hz, 8 H, Ph), 7.91 (d, $J$ = 8 Hz, 8 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 14.35 ($CH_3$), 61.00 ($CH_2$), 74.76 (Cb), 83.68 (Cp), 128.49, 128.62, 129.42, 140.94 (Ph), 166.36 (C=O). MS (FAB$^+$, 3-NOBA): *m/z* 768 (M), 769 (M + H). IR (KBr, cm$^{-1}$): 3057 (w, C−H aromatic), 2911 (w, C−H aliphatic), 1713 (s, C=O), 1269 (s, C−O). UV−vis ($CH_2Cl_2$): $\lambda$ ($\epsilon$) 418 sh (5000), 318 (46 000), 276 (40 000) nm (L mol$^{-1}$ cm$^{-1}$). Anal. Calcd for $C_{45}H_{41}CoO_8$: C, 70.31; H, 5.38. Found: C, 70.34 ; H, 5.48.

**[Tetrakis(4-(1,12-dicarba-*closo*-dodecaboran-1-yl)phenyl)cyclobutadiene]cyclopentadienylcobalt (11).** The procedure described for **1** was followed, using **5** (250 mg, 0.54 mmol), $CpCo(CO)_2$ (100 mg, 0.55 mmol), and xylene (50 mL) in a 100 mL round bottom flask and refluxing for 24 h. After the reaction mixture was cooled, $CpCo(CO)_2$ (100 mg, 0.55 mmol) was added and the mixture was again heated under reflux for 24 h. More $CpCo(CO)_2$ (100 mg, 0.55 mmol) was added to the cooled solution, and the reaction was heated under reflux for 72 h. In the chromatographic separation, the orange-brown band at the solvent front was eluted with hexane and rechromatoraphed (silica gel, hexane). A trace of unreacted **5** was first to elute from the column, followed by an unidentified blue band. **11** was eluted as a yellow band, which on removal of the solvent gave pure **11** (152 mg, 54%) as a yellow powder. Dark red crystals were obtained by slow evaporation from a mixture of dichloromethane and ethanol. Mp: >300 °C. $^1H$ NMR ($CDCl_3$): 1.30−3.42 (br, 44 H, $H_{carborane}$), 4.85 (s, 5 H, Cp), 6.98 (d, $J$ = 7 Hz, 8 H, Ph), 7.07 (d, $J$ = 7 Hz, 8 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 59.73 ($C_{carborane}$−H), 73.76 (Cb), 83.20 (Cp), 86.50 ($C_{carborane}$−C), 126.65, 128.06, 134.67, 136.28 (Ph). $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta$ −13.32 (s, 20 B), −15.98 (s, 20 B). IR (KBr, cm$^{-1}$): 3060 (w, C−H aromatic), 2610 (s, B−H), 1631 (m, Ph), 1517 (m, Ph), 1084 (m, Ph). MS (FAB$^+$, NOBA): *m/z* 1049 (M). Anal. Calcd for $C_{41}H_{65}B_{40}Co$: C, 46.93; H, 6.24. Found: C, 46.45; H, 6.51.

**[Tetrakis(4-carboxyphenyl)cyclobutadiene]cyclopentadienylcobalt (13).** **10** (200 mg, 0.26 mmol), sodium hydroxide (1.0 g, 25 mmol), THF (20 mL), and water (30 mL) were charged to a 100 mL round bottom flask and heated under reflux for 20 h. After the reaction mixture was cooled, concentrated HCl was added to the strirred mixture until the solution became acidic. Water (50 mL) was added to the solution, and the THF was removed by evaporation to give an orange precipitate, which was collected on a frit. The crude material was recrystallized from EtOH at −70 °C to give **13** (120 mg, 71%) as an orange powder. An analytical sample was prepared by recrystallization from EtOH/$H_2O$. Mp: >300 °C. $^1$H NMR (DMSO-$d_6$): $\delta$ 4.75 (s, 5 H, Cp), 7.45 (d, $J$ = 8 Hz, 2 H, Ph), 7.83 (d, $J$ = 8 Hz, 2 H, Ph). $^{13}$C{$^1$H} NMR (DMSO-$d_6$): $\delta$ 74.38 (Cb), 83.74 (Cp), 128.55, 128.87, 129.43, 140.43 (Ph), 167.22 (COOH). MS (FAB$^+$, glycerol and DMSO): $m/z$ 657 (M + H). MS (FAB$^-$, glycerol and DMSO): $m/z$ 655 (M − H). IR (KBr, cm$^{-1}$): 3231 (m br, OH), 1705 (s, C═O), 1274 (m, C−O). Anal. Calcd for $C_{37}H_{25}O_8Co\cdot{}^1/_2H_2O$: C, 66.77; H, 3.94. Found: C, 66.62; H 4.14.

**[Tetrakis(4-((triethylsilyl)ethynyl)phenyl)cyclobutadiene]cyclopentadienylcobalt (14).** **8** (200 mg, 0.25 mmol), (triethylsilyl)acetylene (700 mg, 5.0 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), CuI (25 mg, 0.13 mmol), and triethylamine (50 mL) were charged to a round bottom flask, cooled to −50 °C, and degassed under high vacuum for 1 h. The reaction mixture was heated to a gentle reflux for 48 h under argon, and then cooled to room temperature. (Triethylsilyl)acetylene (400 mg, 2.8 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (25 mg, 0.13 mmol) were added, and the mixture was refluxed for 48 h. After the reaction mixture was cooled to room temperature, (triethylsilyl)acetylene (400 mg, 2.8 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (25 mg, 0.13 mmol) were added and the reflux was continued for a further 96 h. On cooling, hexane (30 mL) was added to the solution and the mixture was filtered into a separatory funnel. The solid black residue was washed with hexane (70 mL), and the yellow washings were added to the separatory funnel. The mixture was extracted with dilute HCl (2 × 100 mL) and water (100 mL) and dried over sodium sulfate, and the solvent was removed to give a dark orange-brown oil. This oil was chromatographed (alumina, hexane, then hexane/dichloromethane, 9:1). Elution of the orange band gave pure **14** (149 mg, 58%) as an orange powder, which was recrystallized from ethanol to give long orange needles. Mp: 210−212 °C (dec). $^1$H NMR ($CDCl_3$): $\delta$ 0.69 (q, $J$ = 8 Hz, 8 H, $SiCH_2$), 1.07 (t, $J$ = 8 Hz, 12 H, $CH_3$), 4.55 (s, 5 H, Cp), 7.32 (s,16 H, Ph). $^{13}$C-{$^1$H} NMR ($CDCl_3$): $\delta$ 4.35 ($SiCH_2$), 7.47 ($CH_3$), 74.47 (Cb), 83.38 (Cp), 92.35, 106.50 (ethynyl), 121.09, 128.44, 131.81, 136.52 (Ph). IR (KBr, cm$^{-1}$): 3035 (vw, C−H aromatic), 2954 (s, C−H aliphatic), 2153 (ethynyl), 1631 (Ph), 1509 (Ph). MS (FAB$^+$, 3-NOBA): $m/z$ 1033 (M). UV−vis ($CH_2Cl_2$): $\lambda$ ($\epsilon$) 412 sh (5000), 300 (83 000) nm (L mol$^{-1}$ cm$^{-1}$). Anal. Calcd for $C_{65}H_{81}CoSi_4$: C, 75.53; H, 7.90. Found: C, 75.37; H, 8.12.

**(Tetraphenylcyclobutadiene)[pentakis((trifluoroacetoxy)mercurio)cyclopentadienyl]cobalt (15).** The cobalt complex **1** (1.95 g, 4.07 mmol) was dissolved in 1,2-dichloroethane (300 mL). Mercury(II) trifluoroacetate (9.02 g, 21.17 mmol) was added in portions over 15 min. The solution turned dark red and was stirred for 18 h at room temperature, after which time, a large amount of orange precipitate had formed. The reaction mixture was transferred to a separatory funnel, and THF (50 mL) was added to give a clear organic fraction on shaking. If the THF is not added, an emulsion forms and extraction becomes difficult. The organic solution was extracted with water (2 × 300 mL), and the solvent was removed to give an orange powder. Recrystallization of the crude product from EtOH/THF gave **15** (4.88 g, 60%) as deep red crystals. An analytically pure material was prepared by a second recrystallization from EtOH/THF. Mp: 226−228 (dec) °C. $^1$H NMR (DMSO-$d_6$): $\delta$ 7.17−7.24 (m, 3 H, Ph), 7.69−7.73 (m, 2 H, Ph). $^{13}$C{$^1$H} NMR (DMSO-$d_6$): $\delta$ 75.24 (Cb), 110.73 (Cp), 118.49 (q, $^1J_{CF}$ = 290 Hz, $CF_3$), 126.65, 128.40, 128.63, 136.09 (Ph), 158.65 (q, $^2J_{CF}$ = 37 Hz, C═O). IR (KBr, cm$^{-1}$): 3058 (w, C−H aromatic), 1680 (s, C═O), 1209 (s, $CF_3$), 1131 (s, $CF_3$). UV−vis (THF): $\lambda$ ($\epsilon$) 440 sh (2000), 346 (17 000), 316 (18 500), 276 sh (33 500), 244 (44 500) nm (L mol$^{-1}$ cm$^{-1}$). Anal. Calcd for $C_{43}H_{20}CoF_{15}Hg_5O_{10}$: C, 25.27; H, 0.97. Found: C, 25.07; H, 0.91.

**[Tetrakis(4-bromophenyl)cyclobutadiene][pentakis((trifluoroacetoxy)mercurio)cyclopentadienyl]cobalt (16).** The cobalt complex **8** (0.15 g, 0.19 mmol) was dissolved in freshly distilled 1,2-dichloroethane (20 mL). Then mercury(II) trifluoroacetate (0.43 g, 10 mmol) was added in portions over 5 min. The solution was stirred and heated at 70 °C under argon for 22 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated. The crude product was dissolved in a minimum of diethyl ether, and pentane was added. Concentration of the solution afforded a yellow-brown precipitate (0.32 g, 73%), which was collected on a frit, washed with pentane, and dried under vaccum. Mp: 195−200 °C (dec, change of color). $^1$H NMR ($CDCl_3$): $\delta$ 7.36 (d, $J$ = 8.7 Hz, 8 H, Ph), 7.59 (d, $J$ = 8.7 Hz, Ph). $^{13}$C {$^1$H} NMR ($CDCl_3$): $\delta$ 73.73 (Cb), 111.20 (Cp), 118.38 (q, $^1J_{CF}$ = 290 Hz, $CF_3$), 119.78, 130.37, 130.40, 131.40, 134.74, 158.67 (q, $^2J_{CF}$ = 38 Hz, C═O). IR (KBr, cm$^{-1}$): 1682 (s, C═O), 1207 (s, $CF_3$), 1132 (s, $CF_3$). MS (FAB$^+$, 3-NOBA): $m/z$ maximum calcd at 2359, found at 2358. Anal. Calcd for $C_{43}H_{16}Br_4CoHg_5F_{15}O_{10}$; C, 21.89; H, 0.68. Found: C, 22.06; H, 0.65.

**(Tetraphenylcyclobutadiene)(pentaiodocyclopentadienyl)cobalt (17).** Potassium iodide (1.18 g, 7.1 mmol) and iodine (1.81g, 7.1 mmol) were stirred in water (100 mL) for 2 h to prepare a solution of $KI_3$. **15** (2.79 g, 1.37 mmol) in THF (65 mL) was added to the solution, and the mixture was stirred for 2 days at room temperature. Most of the THF was removed under vacuum, and the mixture was transfered to a separatory funnel and extracted with toluene (3 × 100 mL). The combined organic fractions were extracted with an aqueous sodium thiosulfate solution (2 × 100 mL) and water (2 × 100 mL) and dried over $Na_2SO_4$, and the solvent was removed to give an orange powder. The crude product was chromatographed (silica gel, dichloromethane/hexane, 30:70) and recrystallized from toluene to give **17** (747 mg, 49%) as orange crystals. Mp: 260−280 (dec) °C. $^1$H NMR ($CDCl_3$): $\delta$ 7.32−7.40 (m, 3 H, Ph), 7.53−7.58 (m, 2 H, Ph). $^{13}$C{$^1$H} NMR (DMSO-$d_6$): $\delta$ 71.43 (Cb), 79.37 (Cp), 127.72, 128.19, 129.09, 131.54 (Ph). MS (EI$^+$) $m/z$ (relative intensity) 1109 (M, 100), 983 (M − I, 20). IR (KBr, cm$^{-1}$): 3056 (w, C−H aromatic), 1607 (s), 1274 (s), 574 (s, C−I), 556 (s, C−I). Anal. Calcd for $C_{33}H_{20}CoI_5$: C, 35.68; H, 1.81. Found: C, 35.60; H, 1.63.

**[Tetrakis(4-(ethoxycarbonyl phenyl)cyclobutadiene]-[pentakis((trifluoroacetoxy)mercurio)cyclopentadienyl]-cobalt (18).** **10** (300 mg, 0.390 mmol), mercury(II) trifluoroacetate (890 mg, 2.09 mmol), and 1,2-dichloroethane (30 mL) were charged to a 250 mL flask and heated at 70 °C for 22 h. After the reaction mixture was cooled, hexanes (200 mL) were added to the stirred solution to precipitate **18**, which was collected on a frit as an yellow-orange solid (630 mg, 69%). This compound is nearly pure, and only very small peaks of impurities remained in the aromatic region of the $^1$H NMR spectrum. An analytical sample was obtained as a few crystals by slow evaporation of the filtrate. Mp: >250 °C. $^1$H NMR (DMSO-$d_6$): $\delta$ 7.82 (s, 4 H, Ph), 4.26 (q, $J$ = 6 Hz, 2 H, $CH_2$), 4.26 (t, $J$ = 6 Hz, 3 H, $CH_3$). $^{13}$C{$^1$H} NMR (DMSO-$d_6$): $\delta$ 13.79 ($CH_3$), 60.32 ($CH_2$), 74.94 (Cb), 111.52 (Cp), 118.18 (q, $^1J_{CF}$ = 290 Hz, $CF_3$), 127.80, 128.58, 129.22, 140.89 (Ph), 158.55 (q, $^2J_{CF}$ = 38 Hz, C═O), 165.29 (C═O). IR (KBr, cm$^{-1}$): 2982 (w, C−H aromatic), 1685 (s, C═O), 1280 (s, COO), 1209 (s, $CF_3$), 1129 ($CF_3$). UV−vis (THF): $\lambda$ ($\epsilon$) 440 sh (4000), 340 (36 000), 288 (43 500), 258 (43 000) nm (L mol$^{-1}$ cm$^{-1}$). Anal. Calcd for $C_{55}H_{36}O_{18}F_{15}Hg_5Co$: C, 28.33; H, 1.56. Found: C, 28.55; H, 1.70.

**[Tetrakis(4-(ethoxycarbonyl)phenyl)cyclobutadiene]-[pentakis(((2-hydroxyethyl)thio)mercurio)cyclopentadienyl]cobalt (20).** The cobalt complex **18** (0.2 g, 0.086 mmol) was dissolved in THF (5 mL). The solution was cooled to 0 °C, and 2-hydroxyethanethiol (0.04 g, 0.52 mmol) in THF

(1 mL) was added in one portion. The dark red solution was allowed to stir for 1 min. Hexanes (50 mL) were added to quench the reaction and to precipitate **20**. The precipitate was collected on a frit and washed with a copious amount of hexanes to give **20** as a yellow-orange solid (0.111 g, 60%), which was then recrystallized from a mixture of THF and ethanol (red crystals). Mp. 175−180 °C (dec, change of color). $^1$H NMR (DMSO-$d_6$): $\delta$ 7.83 (d, $J$ = 8.4 Hz, 8 H, Ph), 7.76 (d, $J$ = 8.4 Hz, 8 H, Ph), 4.98 (t, $J$ = 5.1 Hz, 5 H, OH), 4.30 (q, $J$ = 7.5 Hz, 8 H, $OCH_2$), 3.42 (q, $J$ = 5.4 Hz, 10 H, $CH_2O$), 2.77 (t, $J$ = 6 Hz, 10 H, $SCH_2$), 1.31 (t, $J$ = 7.5 Hz, 12 H, $CH_3$). $^{13}$C{$^1$H} NMR (DMSO-$d_6$): $\delta$ 14.24, 29.68, 60.47, 64.39, 73.17 (Cb), 126.30 (Cp), 127.65 (Ph), 128.34 (Ph), 129.40 (Ph), 142.48 (Ph), 165.43 (COO). IR (KBr, cm$^{-1}$): 3430 (s, OH), 2920 (w, C−H aliphatic), 1713 (s, CO), 1602 (s, C═C), 1384 (s, $CH_3$ deformation), 1274 (s, C−O), 1175 (w), 1115 (m), 1058 (w), 1017 (w), 860 (w), 756−726 (w). MS (FAB$^+$, 3−NOBA) $m/z$ maximum calcd at 2152, found at 2151. UV−vis (THF): $\lambda$ ($\epsilon$) 440 sh (6500), 362 (38 500), 282 sh (39 000), 254 sh (48 500) nm (L mol$^{-1}$ cm$^{-1}$). Anal. Calcd for $C_{55}H_{61}O_{13}S_5Hg_5Co$: C, 30.69; H, 2.86. Found: C, 30.92; H, 2.94.

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**Supporting Information Available:** Tables of crystal data, data collection, structure solution and refinement, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **5**, **6**, **7**, **10**, **11**, and **15** (83 pages). Ordering information is given on any current masthead page.

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