7090 *J. Org. Chem.* **2001,** *66,* 7090−7101

Synthesis and Redox Behavior of Azulene-Substituted Benzene Derivatives and (η^5-Cyclopentadienyl)[tetra- and di(6-azulenyl)cyclobutadiene]cobalt Complexes

Shunji Ito,*[†] Haruki Inabe,[†] Tetsuo Okujima,[†] Noboru Morita,[†] Masataka Watanabe,[‡]
Nobuyuki Harada,[‡] and Kimiaki Imafuku[§]

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan,
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
Sendai 980-8577, Japan, and Department of Chemistry, Faculty of Science, Kumamoto University,
Kumamoto 860-8555, Japan

ito@funorg.chem.tohoku.ac.jp

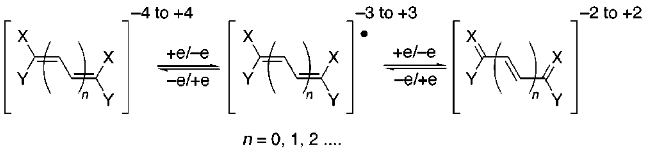
Received May 29, 2001

1,2-Di(6-azulenyl)tetraphenylbenzenes and (6-azulenyl)pentaphenylbenzenes were synthesized by Diels−Alder reactions of di(6-azulenyl)acetylenes and 6-(phenylethynyl)azulenes with tetraphenylcyclopentadienone. Cobalt-mediated cyclooligomerization of mono- and di(6-azulenyl)acetylenes afforded 1,3,5- and 1,2,4-tri(6-azulenyl)benzene derivatives together with (η^5-cyclopentadienyl)-[tetra- and di(6-azulenyl)cyclobutadiene]cobalt complexes. The redox behavior of these novel (6-azulenyl)benzene derivatives and [tetra- and di(6-azulenyl)cyclobutadiene]cobalt complexes was examined by cyclic voltammetry (CV). Mono(6-azulenyl)benzenes exhibited a reduction wave upon CV. In contrast, 1,2-di(6-azulenyl)benzenes showed a two-step reduction wave at the similar potential region upon CV, which revealed the formation of a dianion stabilized by 6-azulenyl substituents under electrochemical reduction conditions. Three 6-azulenyl substituents on benzene in a 1,2,4 relationship also increased electron-accepting properties because of the formation of a closed-shell dianionic structure, whereas 1,3,5-tri(6-azulenyl)benzenes were reduced stepwise.

Introduction

Azulene ($C_{10}H_8$) is a theoretically interesting compound with many unusual properties.[1] The azulene system, especially, has a tendency to stabilize cations, as well as anions, owing to its remarkable polarized properties, which could be utilized to construct advanced materials for electronic and photonic applications.[2] However, to date, molecules with potentially useful electronic properties constructed by using azulene derivatives are fairly scarce. Recently, Hünig et al. proposed a concept of the violene−cyanine hybrid as stabilized organic electrochromics.[3] The hybrid contains the moieties X═C−Y, which represent the "cyanine"-type structure in a fully reduced or oxidized form, as end groups of a violene. The system provides a highly colored closed-shell form as a cyanine dye by an overall two-electron transfer, as illustrated in Scheme 1.

Scheme 1



Hexa(6-azulenyl)benzene (**1**) would be a candidate for a such system. The redox system of **1** could be assumed as one of a violene−cyanine hybrid in which the two cyanine-type structures are connected in two positions, as illustrated in Scheme 2. The compound **1** will provide a delocalized closed-shell dianion $\mathbf{1}_{\mathrm{RED}}{}^{-2}$ by an overall two-electron transfer and could be expected to show significant changes in the absorption spectra in the different oxidation states. We have recently developed a simple route to unknown 1,3,5-tri(1-azulenyl)benzenes by the tetrachlorosilane-mediated cyclotrimerization of 1-acethylazulenes.[4] Hafner et al. reported the ethynylation of azulenes in a five-membered ring, utilizing Pd-catalyzed cross-coupling reactions of bromo- and iodoazulenes with trimethylsiliylacetylene,[5] and the cyclooligomerization of the 1-azulenylacetylenes, catalyzed by $CpCo(CO)_2$, to afford 1-azulenylbenzene derivatives and (cyclobutadiene)cobalt complexes.[6]

Herein, we report two complementary methods to prepare novel 6-azulenylbenzene derivatives toward the synthesis of **1**.[7] One is the Diels−Alder reaction of di(6-azulenyl)acetylenes and 6-(phenylethynyl)azulenes with tetraphenylcyclopentadienone to afford 1,2-di- and mono-

---

* To whom correspondence should be addressed. E-mail: ito@funorg.chem.tohoku.ac.jp. Tel: +81-(0)22-217-7714. Fax: +81-(0)22-217-7714.

[†] Department of Chemistry, Tohoku University.

[‡] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University.

[§] Department of Chemistry, Kumamoto University.

(1) Zeller, K.-P. Azulene. In *Houben-Weyl*; *Methoden der Organischen Chemie,* 4th ed.; Georg Thieme: Stuttgart, 1985; Vol. V, Part 2C, p 127.

(2) See, e.g.: (a) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747. (b) Martin, R. E.; Diederich, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 1350.

(3) (a) Hünig, S.; Kemmer, M.; Wenner, H.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Gescheid, G. *Chem.−Eur. J.* **1999**, *5*, 1969. (b) Hünig, S.; Kemmer, M.; Wenner, H.; Barbosa, F.; Gescheidt, G.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Peters, K. *Chem.−Eur. J.* **2000**, *6*, 2618. (c) Hünig, S.; Perepichka, I. F.; Kemmer, M.; Wenner, H.; Bäuerle, P.; Emge, A. *Tetrahedron* **2000**, *56*, 4203.

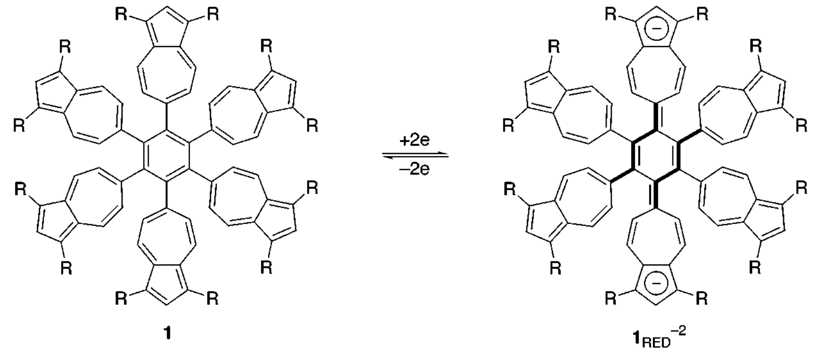
(4) Sato, K.; Yamashiro, S.; Imafuku, K.; Ito, S.; Morita, N.; Fujimori, K. *J. Chem. Res., Synop.* **2000**, 334.

(5) Fabian, K. H. H.; Elwahy, A. H. M.; Hafner, K. *Tetrahedron Lett.* **2000**, *41*, 2855.

(6) Elwahy, A. H. M.; Hafner, K. *Tetrahedron Lett.* **2000**, *41*, 2859.

10.1021/jo010540u CCC: $20.00

Scheme 2

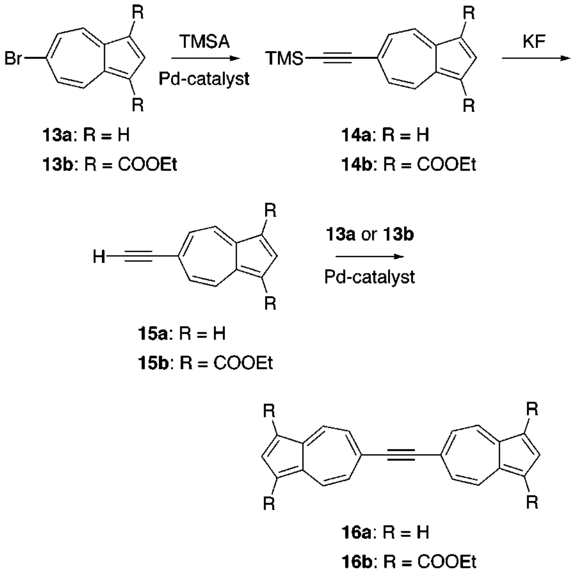


(6-azulenyl)benzene derivatives **2a**, **2b** and **3a**, **3b**, and the other is the cobalt-mediated cyclooligomerization of mono- and di(6-azulenyl)acetylenes to give 1,3,5- and 1,2,4-tri(6-azulenyl)benzene derivatives **4a**, **4b** and **5a**, **5b** together with [(6-azulenyl)cyclobutadiene]cobalt complexes **6**−**12**. 1,2-Di(1-azulenyl)benzene **2a**, **2b** would be a model compound for the formation of a closed-shell dianionic species by electrochemical reduction. 1,2,4-Tri-(6-azulenyl)benzene **5a**, **5b** would be a violene−cyanine hybrid and would exhibit a two-electron transfer to form a colored closed-shell dianionic species by electrochemical reduction. Herein, we also report the redox behavior of these novel 6-azulenylbenzene derivatives **2**−**5** together with those of 6-azulenylacetylenes, diacetylenes, and cobalt complexes **6**−**12** examined by cyclic voltammetry (CV).

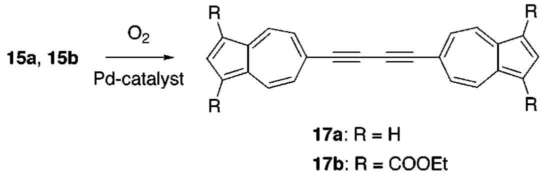
Results and Discussion

Synthesis of 6-Azulenylacetylenes. We found an efficient method of functionalization of azulene in a seven-membered ring utilizing 6-bromoazulenes **13a** and **13b**[8] to produce 6-azulenylacetylenes under Sonogashira−Hagihara conditions.[9] The Pd-catalyzed cross-coupling reactions of **13a** and **13b** with trimethylsilylacetylene (TMSA) at room temperature afforded the 6-(trimethylsilylethynyl)azulenes **14a** and **14b** in 86 and 84% yields, respectively. It is noteworthy that the ethynylation of azulenes in a seven-membered ring proceeded readily by using bromides at room temperature. Treatment of **14a** and **14b** with potassium fluoride in DMF or DMF/tetrahydrofuran furnished 6-ethynylazulenes **15a** and **15b**[10] in 79 and 92% yields, respectively. The cross-coupling reaction of **15a** with **13a** using $PdCl_2(PPh_3)_2$ as a catalyst afforded an inseparable mixture (1:2.2) of di-(6-azulenyl)acetylene (**16a**) and di(6-azulenyl)diacetylene (**17a**). However, we found that the reaction of **15a** with **13a** utilizing $Pd(PPh_3)_4$ as a catalyst exclusively gave the desired **16a** in 98% yield. Similarly, **16b** was obtained by the reaction of **15b** with **13b** in 96% yield (Scheme 3). The diacetylenes **17a** and **17b** were selectively obtained by the Pd-catalyzed oxidative coupling of **15a** and **15b** in 86 and 58% yields, respectively (Scheme 4).[11]

Scheme 3



Scheme 4



Diels−Alder Approach. The Diels−Alder reaction of **16a** and **16b** with a large excess of tetraphenylcyclopentadienone (**18**) in diphenyl ether at 160 °C under an Ar atmosphere for 1−2 d and subsequent chromatographic purification of the reaction mixture on silica gel afforded **2a** and **2b** in 13 and 90% yields, respectively (Scheme 5).[12]

The synthesis of **3a** and **3b** as outlined in Scheme 6 also commenced with **13a** and **13b**, respectively. 6-(Phenylethynyl)azulenes **19a** and **19b** were prepared by the Sonogashira reaction of **13a** and **13b** with phenylacetylene in 90 and 86% yields, respectively. The Diels−Alder

---

(7) A part of this work has been published in a preliminary form: (a) Ito, S.; Inabe, H.; Okujima, T.; Morita, N.; Watanabe, M.; Imafuku, K. *Tetrahedron Lett.* **2000**, *41*, 8343. (b) Ito, S.; Inabe, H.; Okujima, T.; Morita, N.; Watanabe, M.; Nobuyuki, H.; Imafuku, K. *Tetrahedron Lett.* **2001**, *42*, 1085.

(8) McDonald, R. N.; Richmond, J. M.; Curtis, J. R.; Petty, H. E.; Hoskins, T. L. *J. Org. Chem.* **1976**, *41*, 1811.

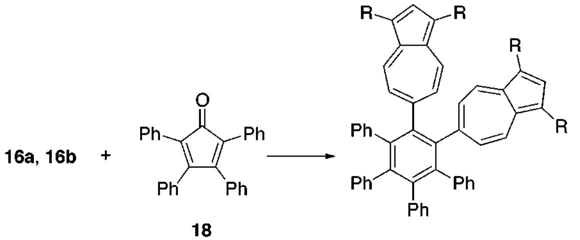
(9) (a) Sonogashira, K. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, Chapter 2.4, p 521. (b) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627. (c) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

(10) (a) Morita, T.; Fujita, T.; Takase, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1647. (b) Fujita, T.; Morita, T.; Takase, K. *Tetrahedron Lett.* **1974**, *30*, 2585.

(11) (a) Rossi, R.; Carpita, A.; Bigelli, C. *Tetrahedron Lett.* **1985**, *26*, 523. (b) Takahashi, A.; Endo, T.; Nozoe, S. *Chem. Pharm. Bull.* **1992**, *40*, 3181.

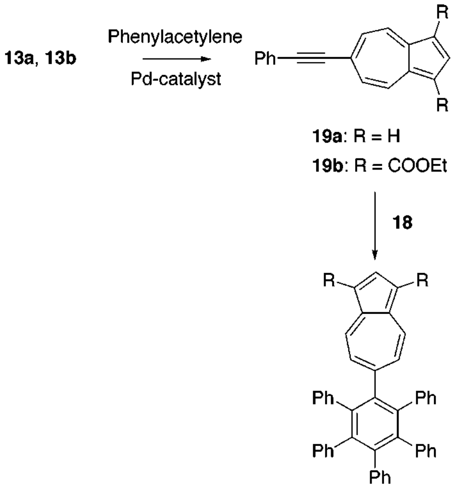
(12) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261.

Scheme 5



2a: R = H
2b: R = COOEt

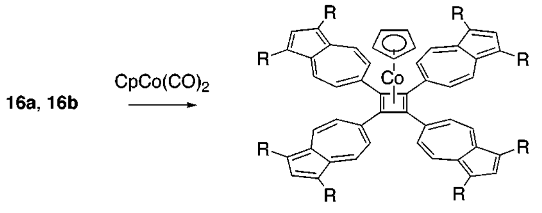
Scheme 6



19a: R = H
19b: R = COOEt

3a: R = H
3b: R = COOEt

Scheme 7



6a: R = H
6b: R = COOEt

reaction of **19a** and **19b** with a large excess of **18** in diphenyl ether for 5 d afforded **3a** and **3b** in 32 and 93% yields, respectively. The spectral features of these azulene-substituted benzenes **2a**, **2b**, **3a**, and **3b** are in agreement with the structures of these products. These compounds are remarkably stable, showing no decomposition even after several weeks at room temperature.

Metal-Mediated Cyclooligomerization. Attempts made toward the cyclooligomerization of **16a** and **16b** in the presence of $CpCo(CO)_2$ in refluxing 1,4-dioxane did not yield hexa(6-azulenyl)benzene (**1**) but exclusively gave (η^5-cyclopentadienyl)[tetra(6-azulenyl)cyclobutadiene]cobalt complexes **6a** and **6b** in 43 and 81% yields, respectively (Scheme 7).[13] The spectral features of **6a** and **6b** are in agreement with the structures of these products. Attempts made toward the cyclooligomerization of **16a** and **16b** in the presence of cobalt carbonyl[14] and dichlorobis(benzonitrile)palladium[15] following literature procedures did not afford satisfactory results. The formation of the cobalt complexes **6a** and **6b** by the reactions of **16a** and **16b** in the presence of $CpCo(CO)_2$ is similar to the results obtained by Hafner et al. with the use of di(1-azulenyl)acetylenes.[6]

Similarly, the reaction of **14b** with $CpCo(CO)_2$ afforded a mixture (1:4.1) of the *cis*- and *trans*-(η^5-cyclopentadienyl)[bis(1,3-diethoxycarbonyl-6-azulenyl)bis(trimethylsilyl)cyclobutadiene]cobalt complexes (**7** and **8**) in 82% yields, which were separable by gel permeation chromatography (GPC) with chloroform (Scheme 8). The regiochemistry of **7** and **8** could not be determined by NMR spectroscopy. Suitable crystals of the major isomer **8** for X-ray structure determination were obtained by slow evaporation of the solution in dichloromethane/hexane, and the molecular structure was determined by X-ray crystallography. Thus, the relative stereochemistry of the major isomer **8** was established as a trans-cobalt complex. The ORTEP plot of **8** has been reported elsewhere.[7b] A synopsis of some key structural features of **8** is provided in Figure 1. Recently, Sekiguchi et al. reported the X-ray structure of *cis*-diphenyl-substituted (cyclobutadiene)-cobalt complex **20**, which exhibited an almost square structure as confirmed by the internal bond angles (89.5, 90.2, 90.3, and 90.4°) (Chart 1.).[16] However, the four-membered ring in **8** is almost planar and forms a rhombus structure.

The reaction of **19b** with $CpCo(CO)_2$ also afforded a mixture (1:1.1) of the *cis*- and *trans*-(η^5-cyclopentadienyl)-[bis(1,3-diethoxycarbonyl-6-azulenyl)di(phenyl)cyclobutadiene]cobalt complexes (**9** and **10**) in 94% yields (Scheme 8). These regioisomers were separable by GPC with chloroform. The regiochemistries of **9** and **10** were tentatively assigned by the comparison of the chemical shifts of their azulene and benzene ring protons in ^1H NMR spectra. The aromaticity of azulene is considerably smaller than that of benzene. Thus, the anisotropy effect of the azulene ring is less than that of the benzene ring.[17] Therefore, the protons on the azulene ring in the trans-configuration **10** ($H_{4',8'} = 9.36$ and $H_{5',7'} = 7.76$ ppm) must be much more shielded than those of the cis-configuration **9** ($H_{4',8'} = 9.47$ and $H_{5',7'} = 7.94$ ppm) because the azulene rings in the trans-configuration are interposed by two phenyl groups. The comparison of the chemical shift of the phenyl groups led to the same conclusion (**9**, 7.45, 7.29, and 7.35; **10**, 7.65, 7.41, and 7.45 ppm). In these three reactions, azulene-substituted benzene derivatives could not be obtained even in trace amounts. The exclusive formation of the (cyclobutadiene)cobalt complexes **6**−**10** would be attributable to the steric effect among the aromatic rings and/or the trimethylsilyl groups.

In contrast to the exclusive formation of the (cyclobutadiene)cobalt complexes **6**−**10**, the cyclooligomerization of **15a** using $CpCo(CO)_2$ afforded 1,3,5- and 1,2,4-tri(6-azulenyl)benzenes **4a** and **5a** in 0.5 and 0.3% yields, respectively, along with (η^5-cyclopentadienyl)[1,2-bis(6-

---

[13] For $CpCo(CO)_2$-mediated cyclooligomerization of alkynes, see, e.g.: (a) Vollhart, K. P. C. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539. (b) Vollhart, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

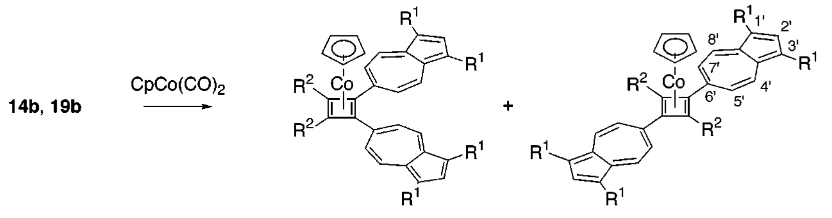
[14] Herwig, P.; Kayser, C. W.; Müllen, K.; Spiess, H. W. *Adv. Mater. (Weinheim, Ger.)* **1996**, *8*, 510.

[15] Keegstra, A.; Feyter, S. D.; Schryver, F. C.; Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 774.

[16] Matsuo, T.; Mizue, T.; Sekiguchi, A. *Chem. Lett.* **2000**, 896.

[17] Esquivel, D. M. S.; De Giambiagi, M. S.; Giambiagi, M.; Makler, S. *Chem. Phys. Lett.* **1979**, *64*, 131.

Scheme 8



7: R^1 = COOEt, R^2 = TMS
9: R^1 = COOEt, R^2 = Ph
8: R^1 = COOEt, R^2 = TMS
10: R^1 = COOEt, R^2 = Ph

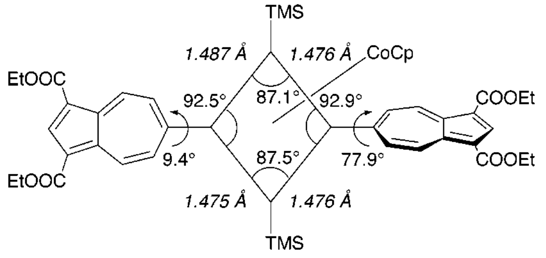
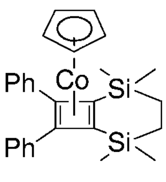


Figure 1. Some key structural features in the cyclobutadiene ring of **8**.

Chart 1



20

azulenyl)cyclobutadiene]cobalt (**11a**) (19%). The cyclooligomerization of **15b** using $CpCo(CO)_2$ afforded similar results to give a mixture (2.5:1) of 1,3,5- and 1,2,4-tri(6-azulenyl)benzenes **4b** and **5b** in 21% yields together with (η^5-cyclopentadienyl)[1,2-bis(1,3-diethoxycarbonyl-6-azulenyl)cyclobutadiene]cobalt (**11b**) (47%). The products **4b** and **5b** were separable by repeated silica gel preparative TLC with ethyl acetate/hexane (Scheme 9). The benzene derivatives **4a**, **4b** and **5a**, **5b** were stable and fully characterized by spectroscopic data as described in the Experimental Section.

The cis-configuration of the cobalt complexes **11a** and **11b** was confirmed by the measurement of the ^{13}C satellite signals of cyclobutadiene protons in the ^1H NMR spectrum. The signals provide very useful information for the analysis of stereochemistry in highly symmetrical compounds such as **11a** and **11b**.[18] The signals of **11b** observed in the cyclobutadiene proton region in $CDCl_3$ are shown in Figure 2b. In the case of **11b**, one of the signals is in the lower slope of the cyclopentadienyl proton signal. For the definite assignment of the signals, we utilized a 2D heteronuclear multiple-quantum coherence (HMQC) spectrum measured under nondecoupling conditions. The 2D spectrum in the region is shown in Figure 3. A slice of the 2D spectrum in the region unequivocally exhibited the signals (**11a**, $^1J_{CH} = 188$ Hz; **11b**, $^1J_{CH} = 189$ Hz) with a negligibly small coupling constant (<1 Hz) between the cyclobutadiene protons (part a of Figure 2). These results clearly show the presence of the 1,2-disubstitution pattern in the cyclobutadiene ring in **11a** and **11b**.[19]

The cis-configuration of **11a** and **11b** was also confirmed by the preparation and observation of the ^{13}C satellite signals of the trans-isomer **12**. The deprotection of the trimethylsilyl groups of **8** was furnished by treatment with tetrabutylammonium fluoride in tetrahydrofuran in 53% yield (Scheme 10). In contrast to **11a** and **11b**, the ^{13}C satellite signals of **12** ($^1J_{CH} = 189$ Hz) in the ^1H NMR spectrum exhibited a large coupling constant between the cyclobutadiene protons (8.1 Hz), which consists of the 1,3-disubstitution of the cyclobutadiene ring.[19] The signals were also identified definitely by a 2D HMQC spectrum measured under nondecoupling conditions. The coupling constants could be determined by both normal ^1H NMR spectrum and the 2D HMQC spectrum. The use of a 2D HMQC spectrum under nondecoupling conditions for the definite observation of ^{13}C satellite signals could be a powerful method for the analysis of the stereochemistry of highly symmetrical compounds. The details of this method will be reported elsewhere.[20]

The formation of both the benzene derivatives **4a**, **4b** and **5a**, **5b** could not be explained by the single intermediate **21** in this reaction, because the intermediate **21** could not afford **4a** and **4b** by further reaction with **15a** and **15b**. The formation of **4a**, **4b** and **5a**, **5b** is assumed by the existence of **22** as an intermediate in this reaction.[21] The exclusive formation of the cis-cobalt complexes **11a** and **11b** in this reaction exhibits the existence of **21** as an intermediate and the relatively high reactivity of the intermediate **22** toward **15a** and **15b**, when compared with reductive elimination to give trans-cobalt complexes (Chart 2).

Redox Behaviors of Azulene-Substituted Benzene Derivatives. The redox potentials (V vs Ag/Ag^+) of the azulene-substituted benzenes and the (cyclobutadiene)cobalt complexes measured by CV are summarized in Table 1. Mono(6-azulenyl)benzenes **3a** and **3b** showed a reversible one-electron transfer at −2.06 and −1.63 V upon CV, respectively. The less negative reduction potentials of **3b** compared with those of **3a** are attributable to the stabilization of anions by the ethoxycarbonyl groups substituted in the five-membered ring. In contrast

---

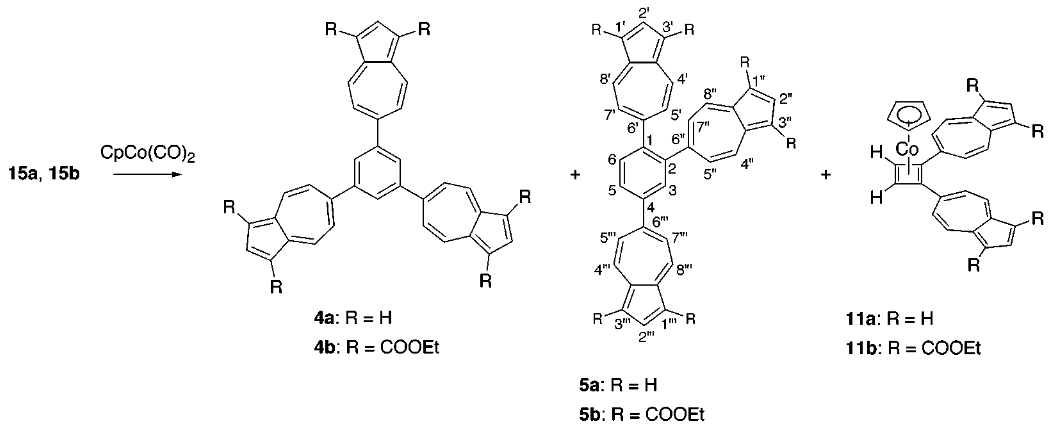
[18] Harada, N.; Li, H.-Y.; Koumura, N.; Abe, T.; Watanabe, M.; Hagiwara, M. *Enantiomer* **1997**, *2*, 349.

[19] (a) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 1545. (b) Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590. (c) Brune, H. A.; Wolff, H. P.; Hüther, H. *Z. Naturforsch., B: Chem. Sci.***1968**, *23B*, 1184.

[20] To be published.

[21] 3,4-Di(6-azulenyl) metallacycle could also be expected as an intermediate in this reaction. However, 3,4-disubstitution is in a poor position to minimize sterics: Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907.

Scheme 9



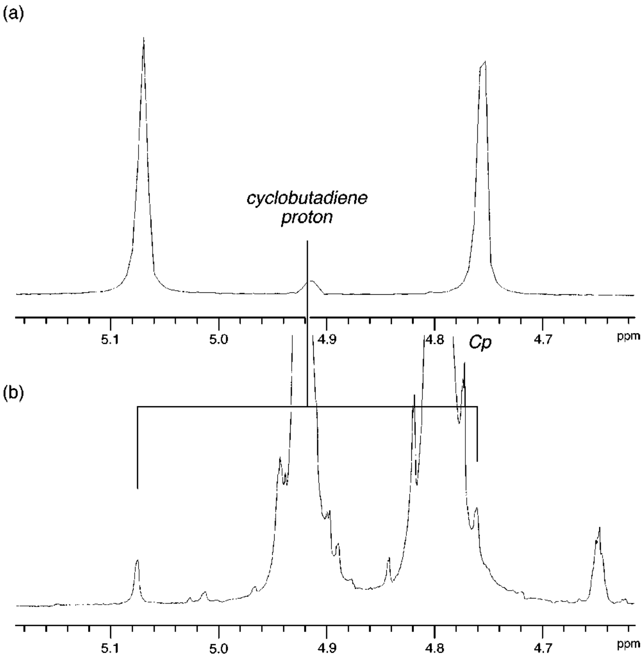


Figure 2. (a) Slice of 2D HMQC spectrum in the cyclobutadiene proton region and (b) ^{13}C satellite signals of the protons measured by ^{1}H NMR spectrum of **11b**.

to the redox behavior of **3a** and **3b**, the benzene derivative **2b** exhibited a barely separated two-step reduction wave at $E_{1/2} = -1.57$ and -1.72 V upon CV.[7a] The compound **2a** also showed a similar two-electron transfer at -2.00 and -2.20 V. The first reduction potentials and even the second ones of **2a** and **2b** are almost comparable with those of **3a** and **3b**, respectively. Therefore, the two 6-azulenyl substituents on a benzene ring in a 1,2 relationship have increased the electron-accepting properties, because of the formation of a closed-shell dianionic structure $\mathbf{2}_{\mathrm{RED}}{}^{-2}$. Thus, the redox system of **2a** and **2b** can be depicted to be a violene **23** as illustrated in Scheme 11.[22] Unfortunately, the reduction waves of **2a** and **2b** showed poor reversibility; they exhibited low stabilities of the expected radical anion and dianion $\mathbf{2}_{\mathrm{RED}}{}^{-2}$ under the electrochemical reduction conditions. Although we tried the electrochemical reduction of **2b** under UV−vis (UV−visible) monitoring, we could not obtain any evidence of the formation of the radical anion and/or dianion $\mathbf{2}_{\mathrm{RED}}{}^{-2}$ due to the instability of these species.

Acetylenes **16a** and **16b** are also examples of such two-electron redox systems stabilized by two 6-azulenyl substituents as illustrated in Scheme 12. In contrast to the poor reversibility of **2a** and **2b**, acetylenes **16a** and **16b** exhibited good reversibility (**16a**, $E_{1/2} = -1.41$ and -1.61 V; **16b**, $E_{1/2} = -0.96$ and -1.15 V, respectively) upon CV.[7a] The potentials are less negative than those of 6-phenylethynylazulenes **19a** (-1.66 V) and **19b** (-1.29 V), respectively. Thus, the two 6-azulenyl substituents on acetylene also increase electron-accepting properties. Diacetylenes **17a** and **17b** also exhibited a reversible two-step reduction wave (**17a**, $E_{1/2} = -1.37$ and -1.50 V; **17b**, $E_{1/2} = -0.98$ and -1.09 V, respectively) upon CV. The potentials are almost comparable with those of **16a** and **16b**, respectively. Thus, the redox system of **17a** and **17b** could also be depicted to be a violene like that of **16a** and **16b**.

1,3,5-Tri(6-azulenyl)benzene (**4a**) exhibited a quasi-reversible broad reduction wave, centered at around -1.90 V, upon CV. The wave was identified as three waves that were barely separated, at -1.75, -1.87, and -2.00 V, by differential pulse voltammetry (DPV). In contrast to the three-step reduction of **4a**, 1,2,4-tri(6-azulenyl)benzene (**5a**) showed a two-step reduction wave upon CV, i.e., a two-electron reduction wave at -1.74 V and a one-electron transfer at -2.15 V. The waves exhibited good reversibility at the scan rate of 100 mV s^{-1}. 1,3,5- and 1,2,4-tri(6-azulenyl)benzene derivatives **4b** and **5b** also exhibited similar reduction waves upon CV, as shown in Figure 4. Therefore, the three 6-azulenyl substituents on benzene in a 1,2,4 relationship also increased electron-accepting properties because of the formation of a closed-shell dianionic structure $\mathbf{5}_{\mathrm{RED}}{}^{-2}$. Consequently, the redox system of **5a** and **5b** could be illustrated as a violene−cyanine hybrid and could exhibit a significant color change with a different oxidation state (Scheme 13). The three 6-azulenyl substituents on benzene in a 1,3,5 relationship cannot take such a closed-shell dianionic structure. Thus, the three azulene rings of **4a** and **4b** were reduced stepwise. Although good reversibility was observed upon CV, measurement of the UV−vis spectroscopy of **5b** under electrochemical reduction conditions did not afford any evidence of the formation of dianion $\mathbf{5}_{\mathrm{RED}}{}^{2-}$. These results would exhibit the low stability of the dianion species under the conditions of the UV−vis measurement.

---

[22] (a) Deuchert, K.; Hünig, S. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 875. (b) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1959. (c) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1936.

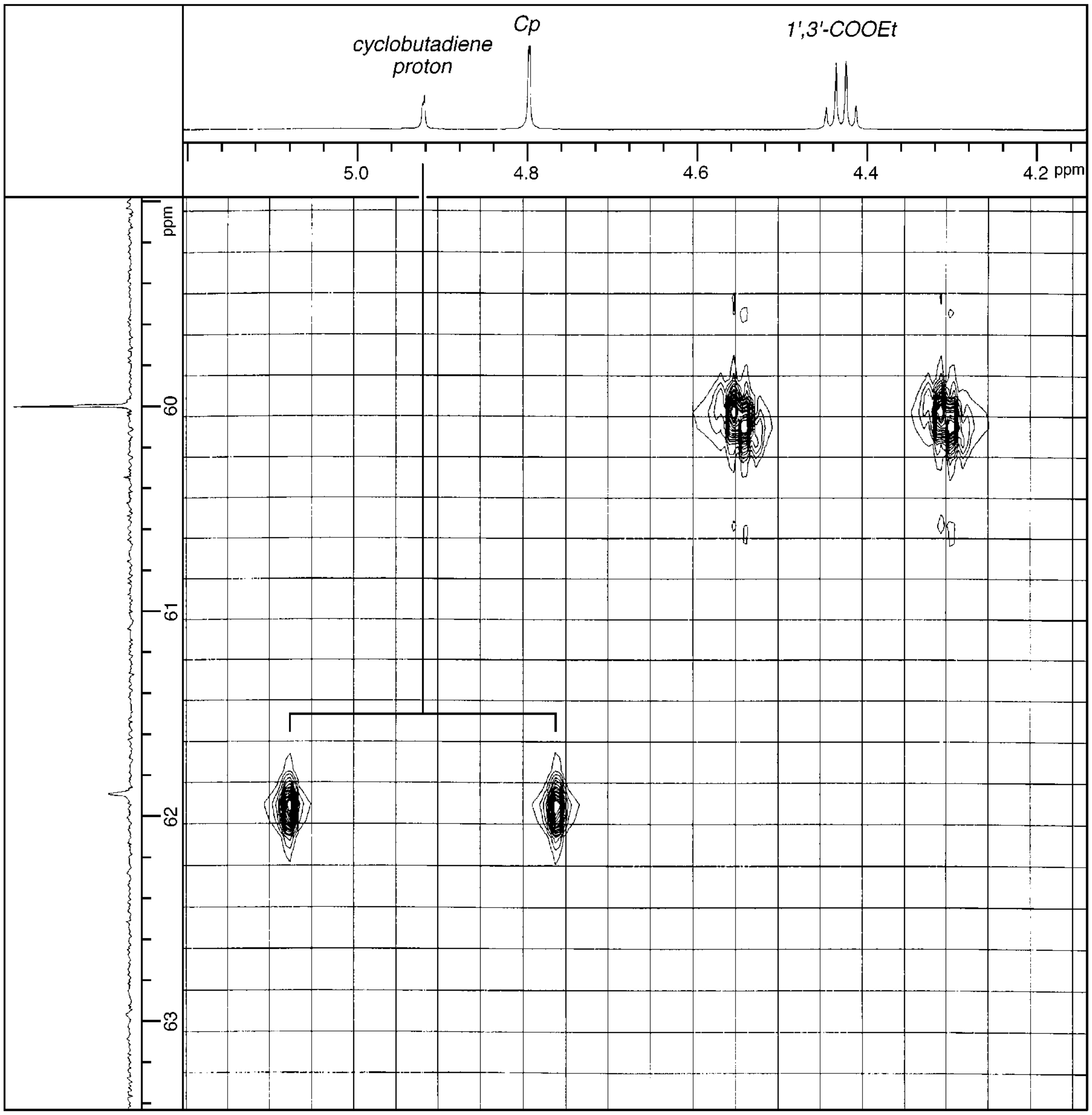
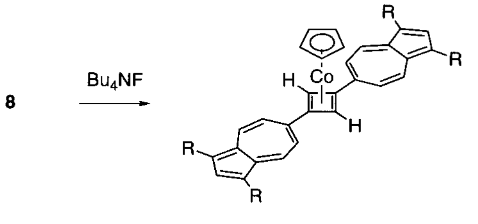


Figure 3. 2D HMQC spectrum of **11b** measured under nondecoupling conditions.

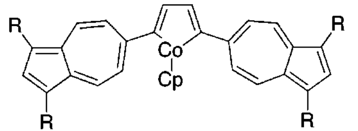
Scheme 10



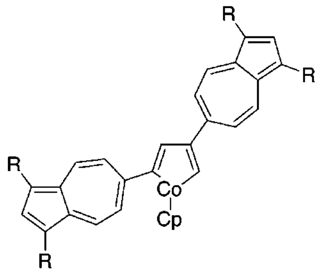
12: R = COOEt

Redox Behavior of Azulene-Substituted Cyclobutadienecobalt Complexes. The voltammogram of **6a** was characterized by two quasi-reversible waves at −1.61 and −1.79 V and the next two irreversible waves at −1.91 and −2.09 V upon CV. The cobalt complex **6b** exhibited a quasi-reversible one-electron transfer at less negative potentials compared with those of **6a**, but the next irreversible two- or three-electron transfer blended into one broad wave centered at −1.42 V. The less negative reduction potentials of **6b** compared with those of **6a** are attributable to the stabilization by the ethoxycarbonyl groups substituted on the five-membered rings. The voltammetric behavior of **6a** and **6b** indicates that the ions of higher charge in the cobalt complexes are considerably less stable under the reduction conditions.

Chart 2



21: R = H or COOEt



22: R = H or COOEt

Table 1. Redox Potentials[a] of the Compounds 2−12

sample	E_1^{ox}	E_2^{ox}	E_1^{red}	E_2^{red}	E_3^{red}
2a[b]	(0.81)		(−2.00)	(−2.20)	
2b[b]			(−1.57)	(−1.72)	
3a[b]	(0.88)		−2.06		
3b[b]			−1.63		
4a[b]	(0.73)	(1.23)	(−1.75)[c]	(−1.87)[c]	(−2.00)[c]
4b[b]			(−1.38)[c]	(−1.46)[c]	(−1.56)[c]
5a[b]	(0.78)	(1.29)	−1.74 (2e)	−2.15	
5b[b]			−1.31 (2e)	−1.63	
6a	(0.71)	(0.91) (1.13)[e]	−1.61	−1.79	(−1.91) (−2.09)[f]
6b	(1.19)	(1.52)	−1.24	(−1.42)[d]	
7	(0.88)	(1.48)	−1.37	−1.53	
8	(0.87)	(1.52)	−1.38	−1.53	
9	(0.84)	(1.43)	−1.33	−1.48	(−2.26)
10	(0.87)	(1.45)	−1.33	−1.49	(−2.26)
11a	(0.58)	(0.83) (1.00)[e]	−1.72	−1.84	(−2.28)
11b	(0.82)	(1.45)	−1.34 (2e)	(−2.23)	
12	(0.80)	(1.33)	−1.33	−1.51	

[a] The redox potentials were measured by CV (0.1 M Et_4NClO_4 in benzonitrile, Pt electrode, scan rate = 100 mV s^{-1}, and Fc/Fc^+ = 0.15 V). In the case of irreversible waves, which are shown in parentheses, E_{ox} and E_{red} were calculated as E_{pa} (anodic peak potential) − 0.03 and E_{pc} (cathodic peak potential) + 0.03 V, respectively. [b] The potentials were measured in 0.1 M Bu_4NBF_4 tetrahydrofuran solution (Fc/Fc^+ = 0.19 V). [c] The values are peak potentials measured by DPV. [d] The value represents two or three electrons in one broad wave. [e] E_3^{ox} value. [f] E_4^{red} value.

The electrochemical reduction of the cis-cobalt complex **7** showed a barely separated two-step reduction wave at $E_{1/2} = -1.37$ and −1.53 V, which exhibited good reversibility at the scan rate of 100 mV s^{-1} (Figure 5a). The trans-cobalt complex **8** also showed a similar two-step reduction wave at $E_{1/2} = -1.38$ and −1.53 V, which also exhibited good reversibility under the same conditions (part b of Figure 5). The cobalt complexes **9**−**12** also showed similar reversible two-electron transfers upon CV, as summarized in Table 1. Formally, the reduction of **7**−**12** corresponds to the formation of a rare type of 20-electron cobalt complex.[23]

The electrochemical oxidation of **6b** exhibited two irreversible waves at 1.19 and 1.52 V upon CV. The electrochemical oxidation of **7**−**10**, **11b**, and **12** also exhibited the similar two irreversible waves at 0.80−0.88 and 1.33−1.52 V upon CV. The electrochemical oxidation of **6a** and **11a** showed three irreversible waves at 0.58−1.13 V owing to the lower oxidation potentials of the substituted azulenes. These results are summarized in Table 1. The first irreversible wave of **6b**, **7**−**10**, **11b**, and **12** is probably due to the Co(I) oxidation and the second one is attributable to the redox reaction of 6-azulenyl groups, based on analogy with those of **6a** and **11a** and those of **6b**, **7**−**10**, **11b**, and **12**. The relatively less positive E_2^{ox} value of **12** (1.33 V) could be rationalized by the contribution of the conjugation between two 6-azulenyl groups and the cyclobutadiene ring due to the least steric hindrance among these compounds.

Conclusion. We have demonstrated the Pd-catalyzed ethynylation of azulenes in a seven-membered ring using bromoazulenes. We have demonstrated an efficient preparation of novel 6-azulenylbenzene derivatives by the reaction of 6-azulenylacetylenes with **18**. The cobalt-mediated cyclooligomerization of mono- and di(6-azulenyl)acetylenes also afforded novel 1,3,5- and 1,2,4-tri(6-azulenyl)benzenes together with (η^5-cyclopentadienyl)-[tetra- and di(6-azulenyl)cyclobutadiene]cobalt complexes. We could not detect the radical anion and/or dianion of the azulene-substituted benzene derivatives by UV−vis spectroscopy due to the instability of these species. However, redox behaviors examined by CV of these compounds represented the presumed multielectron redox properties under the electrochemical conditions used.

Experimental Section

6-(Trimethylsilylethynyl)azulene (14a). TMSA (737 mg, 7.50 mmol) was added to a solution of **13a** (1.05 g, 5.07 mmol), PPh_3 (135 mg, 0.515 mmol), CuI (100 mg, 0.525 mmol), and $PdCl_2(PPh_3)_2$ (177 mg, 0.252 mmol) in triethylamine (30 mL) and toluene (60 mL). The resulting mixture was stirred at room temperature for 2.5 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with water and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with hexane to afford **14a** (978 mg, 86%): blue plates; mp 62−63 °C (MeOH/water); MS (70 eV) *m/z* (relative intensity) 224 (M^+, 100); IR (KBr disk) ν_{max} 2153 (C≡C) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.09), 301 (4.88), 305 (4.84), 346 (3.78), 356 (3.96), 363 (3.90), 373 (4.23), 618 (2.56), 671 (2.47), 748 (2.01); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 10.6 Hz, 2H, $H_{4',8'}$), 7.89 (t, *J* = 3.8 Hz, 1H, $H_{2'}$), 7.38 (d, *J* = 3.8 Hz, 2H, $H_{1',3'}$), 7.36 (d, *J* = 10.6 Hz, 2H, $H_{5',7'}$), 0.31 (s, 9H, 1-TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.9 ($C_{3'a,8'a}$), 137.7 ($C_{2'}$), 135.0 ($C_{4',8'}$), 131.2 ($C_{6'}$), 126.2 ($C_{5',7'}$), 119.0 ($C_{1',3'}$), 109.1 (C_2), 96.9 (C_1), −0.1 (1-TMS). Anal. Calcd for $C_{15}H_{16}Si$: C, 80.30; H, 7.19. Found: C, 80.13; H, 7.47.

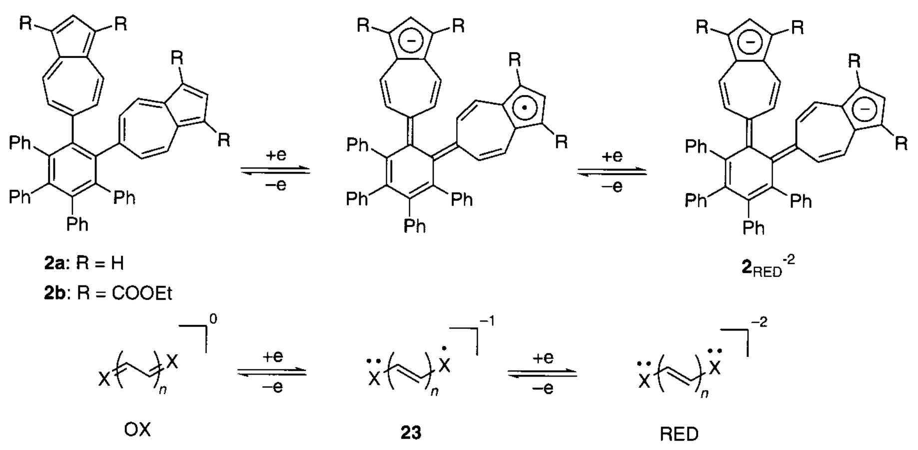
Diethyl 6-(Trimethylsilylethynyl)azulene-1,3-dicarboxylate (14b). The same procedure as was used for the preparation of **14a** was adopted. The reaction of **13b** (1.76 g, 5.01 mmol) with TMSA (760 mg, 7.74 mmol), PPh_3 (132 mg, 0.503 mmol), CuI (103 mg, 0.541 mmol), and $PdCl_2(PPh_3)_2$ (176 mg, 0.251 mmol) in triethylamine (40 mL) and toluene (110 mL) for 1.5 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **14b** (1.55 g, 84%): purple needles; mp 170−174 °C (ethyl acetate); MS (70 eV) *m/z* (relative intensity) 368 (M^+, 100); IR (KBr disk) ν_{max} 2139 (C≡C), 1680 (C═O) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 234 (4.50), 274 (4.18), 329 (4.88), 359 (4.28), 368 (4.32), 540 (2.79); ^1H NMR (400 MHz, $CDCl_3$) δ = 9.63 (d, *J* = 11.1 Hz, 2H, $H_{4',8'}$), 8.77 (s, 1H, $H_{2'}$), 7.84 (d, *J* = 11.1 Hz, 2H, $H_{5',7'}$), 4.43 (q, *J* = 7.1 Hz, 4H, 1′,3′-COOEt), 1.45 (t, *J* = 7.1 Hz, 6H, 1′,3′-COOEt), 0.32 (s, 9H, 1-TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.8 (s, 1′,3′-COOEt), 143.8 ($C_{2'}$), 143.5 ($C_{3'a,8'a}$), 137.5 ($C_{4',8'}$), 135.9 ($C_{6'}$), 133.5 ($C_{5',7'}$), 116.9 ($C_{1',3'}$), 107.4 (C_2), 101.2 (C_1), 60.1 (t, 1′,3′-COOEt), 14.5 (q, 1′,3′-COOEt), −0.3 (1-TMS). Anal. Calcd for $C_{21}H_{24}O_4Si$: C, 68.45; H, 6.56. Found: C, 67.86; H, 6.25.

6-Ethynylazulene (15a). A solution of KF (610 mg, 10.5 mmol) in water (3 mL) was added to a solution of **14a** (1.15 g, 5.13 mmol) in DMF (40 mL). After the mixture was stirred at room temperature for 3 h, the reaction mixture was poured into water and extracted with hexane. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by recrystallization from MeOH/water to afford **15a** (613 mg, 79%): blue plates; mp 82−84 °C; MS (70 eV) *m/z* (relative intensity) 152 (M^+, 100); IR (KBr disk) ν_{max} 3305 (C≡CH), 2103 (C≡C) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 234 (4.05), 293 (4.86), 338 (3.62), 353 (3.76), 368 (3.84), 616 (2.54), 670 (2.46), 745 (2.04); ^1H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 10.5 Hz, 2H, $H_{4',8'}$), 7.89 (t, *J* = 3.8 Hz, 1H, $H_{2'}$), 7.38 (d, *J* = 3.8 Hz, 2H, $H_{1',3'}$), 7.35 (d, *J* = 10.5 Hz, 2H, $H_{5',7'}$), 3.26 (s, 1H, H_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.0 ($C_{3'a,8'a}$), 138.1 ($C_{2'}$), 134.9 ($C_{4',8'}$), 130.7 ($C_{6'}$), 126.2 ($C_{5',7'}$), 119.2 ($C_{1',3'}$), 87.6 (C_1), 78.9 (C_2). Anal. Calcd for $C_{12}H_8$: C, 94.70; H, 5.30. Found: C, 94.54; H, 5.36.

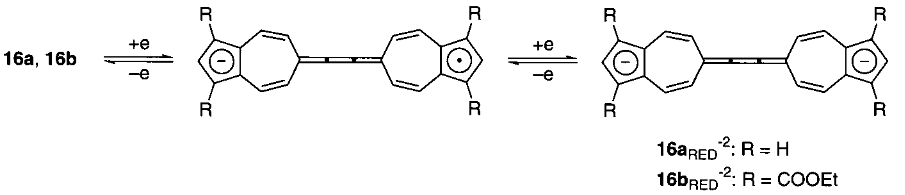
---

(23) Little is known about the reduction potentials of (cyclobutadiene)cobalt complexes: (a) Brotin, T.; Pospísil, L.; Fiedler, J.; King, B. T.; Michl, J. *J. Phys. Chem. B* **1998**, *102*, 10062. (b) Iyoda, M.; Sultana, F.; Sasaki, S.; Butenschön, H. *Tetrahedron Lett.* **1995**, *36*, 579.

Scheme 11



Scheme 12



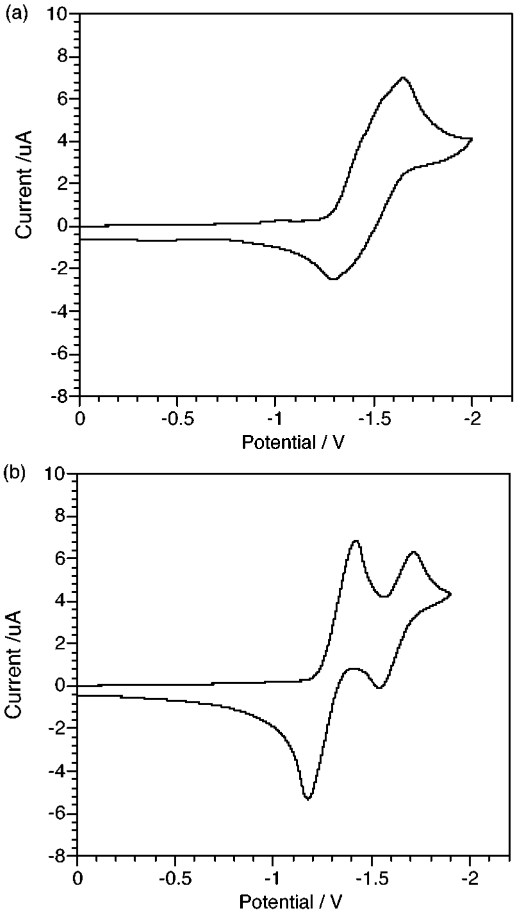
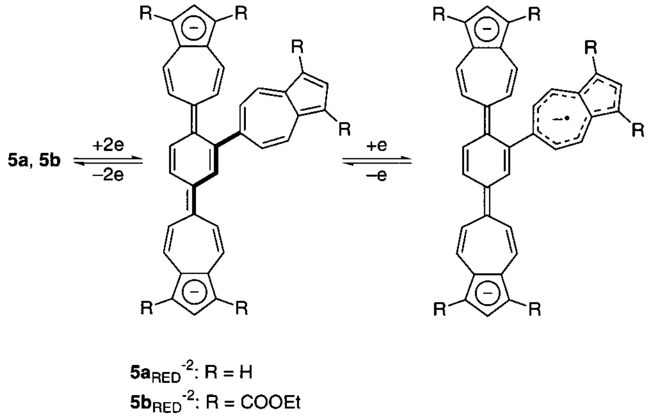


Figure 4. Cyclic voltammograms of (a) **4b** and (b) **5b** in THF containing n-$Bu_4N^+BF_4^-$ (0.1 M) as a supporting electrolyte.

Scheme 13



Diethyl 6-Ethynylazulene-1,3-dicarboxylate (15b). The same procedure as was used for the preparation of **15a** was adopted. The treatment of a solution of **14a** (505 mg, 1.37 mmol) in THF (27 mL) and DMF (15 mL) with a solution of KF (159 mg, 2.72 mmol) in water (0.5 mL) for 50 min followed by column chromatography on silica gel with CH_2Cl_2 afforded **15b** (375 mg, 92%): purple needles; mp 175−176 °C dec (lit.[10] 164−165 °C); MS (70 eV) *m/z* (relative intensity) 296 (M^+, 100); IR (KBr disk) ν_{max} 3235 (C≡CH), 2093 (C≡C), 1688 (C=O) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 233 (4.47), 274 (4.24), 321 (4.88), 346 (4.06), 354 (4.13), 378 (3.75), 541 (2.75); ^1H NMR (400 MHz, $CDCl_3$) δ = 9.64 (d, J = 11.1 Hz, 2H, $H_{4',8'}$), 8.79 (s, 1H, $H_{2'}$), 7.85 (d, J = 11.2 Hz, 2H, $H_{5',7'}$), 4.43 (q, J = 7.1 Hz, 4H, 1′,3′-COOEt), 3.48 (s, 1H, H_2), 1.45 (t, J = 7.1 Hz, 6H, 1′,3′-COOEt); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.7 (s, 1′,3′-COOEt), 144.1 ($C_{2'}$), 143.6 ($C_{3'a,8'a}$), 137.5 ($C_{4',8'}$), 134.7 ($C_{6'}$), 133.5 ($C_{5',7'}$), 117.1 ($C_{1',3'}$), 86.2 (C_1), 82.3 (C_2), 60.2 (t, 1′,3′-COOEt), 14.5 (q, 1′,3′-COOEt). Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.91; H, 5.52.

Di(6-azulenyl)acetylene (16a). $Pd(PPh_3)_4$ (298 mg, 0.258 mmol) was added to a degassed solution of **13a** (1.03 g, 4.97 mmol), **15a** (761 mg, 5.00 mmol), PPh_3 (134 mg, 5.11 mmol), and CuI (108 mg, 5.67 mmol) in triethylamine (40 mL) and toluene (200 mL). The resulting mixture was stirred at room temperature for 18 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by recrystallization from CH_2Cl_2/hexane to afford **16a** (1.35 g, 98%): green plates; mp 240−250 °C dec (1,4-dioxane); MS (70 eV) *m/z* (relative intensity) 278 (M^+, 100);

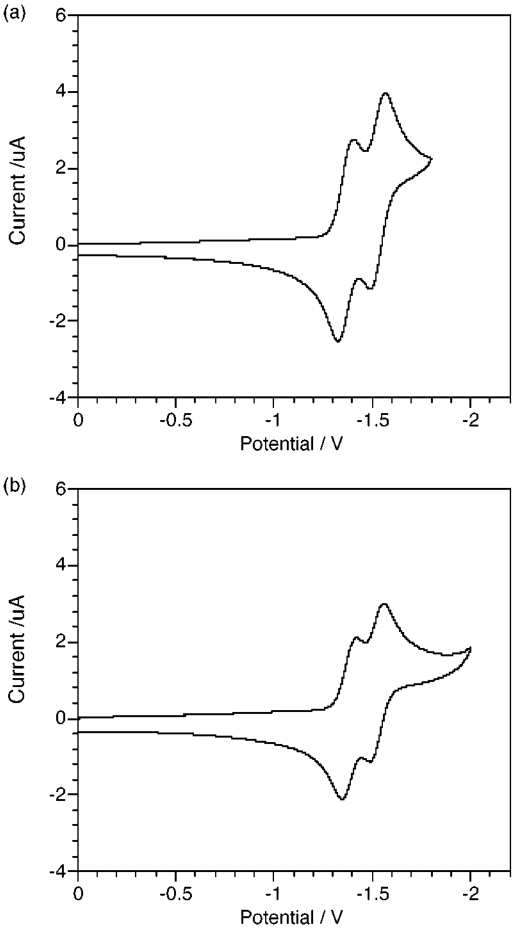


Figure 5. Cyclic voltammograms of (a) cis-cobalt complex **7** and (b) trans-cobalt complex **8** in benzonitrile containing $Et_4N^+ClO_4^-$ (0.1 M) as a supporting electrolyte.

UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 255 (4.33), 288 (4.45), 309 (4.66), 326 (4.86), 421 (4.72), 628 (2.91); ^1H NMR (500 MHz, $CDCl_3$) $\delta = 8.29$ (d, $J = 10.5$ Hz, 4H, $H_{4',8'}$), 7.92 (t, $J = 3.7$ Hz, 2H, $H_{2'}$), 7.47 (d, $J = 10.5$ Hz, 4H, $H_{5',7'}$), 7.42 (d, $J = 3.7$ Hz, 4H, $H_{1',3'}$); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 139.9$ ($C_{3'a,8'a}$), 138.1 ($C_{2'}$), 135.0 ($C_{4',8'}$), 131.6 ($C_{6'}$), 126.1 ($C_{5',7'}$), 119.2 ($C_{1',3'}$), 96.1 ($C_{1,2}$). Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.44; H, 5.01.

Bis(1,3-diethoxycarbonyl-6-azulenyl)acetylene (16b). The same procedure as was used for the preparation of **16a** was adopted. The reaction of **13b** (633 mg, 1.80 mmol) with **15b** (524 mg, 1.77 mmol), $Pd(PPh_3)_4$ (107 mg, 0.093 mmol), PPh_3 (47 mg, 0.16 mmol), and CuI (34 mg, 0.18 mmol) in triethylamine (10 mL) and toluene (80 mL) for 1.5 h followed by column chromatography on silica gel with $CHCl_3$ afforded **16b** (961 mg, 96%): green needles; mp 272−278 °C dec (1,4-dioxane); MS (70 eV) *m/z* (relative intensity) 566 (M^+, 100); IR (KBr disk) ν_{max} 1694 (C═O) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.74), 266 (4.49), 360 (4.82), 378 (4.81), 401 (4.74), 425 (4.85), 551 (3.29); ^1H NMR (400 MHz, $CDCl_3$) $\delta =$ 9.70 (d, $J = 11.1$ Hz, 4H, $H_{4',8'}$), 8.82 (s, 2H, $H_{2'}$), 7.95 (d, $J =$ 11.1 Hz, 4H, $H_{5',7'}$), 4.45 (q, $J = 7.1$ Hz, 8H, 1′,3′-COOEt), 1.47 (t, $J = 7.1$ Hz, 12H, 1′,3′-COOEt); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 164.7$ (s, 1′,3′-COOEt), 144.5 ($C_{2'}$), 143.6 ($C_{3'a,8'a}$), 137.5 ($C_{4',8'}$), 134.6 ($C_{6'}$), 133.3 ($C_{5',7'}$), 117.4 ($C_{1',3'}$), 97.0 ($C_{1,2}$), 60.3 (t, 1′,3′-COOEt), 14.5 (q, 1′,3′-COOEt). Anal. Calcd for $C_{34}H_{30}O_8$: C, 72.07; H, 5.34. Found: C, 71.89; H, 5.58.

Di(6-azulenyl)diacetylene (17a). $PdCl_2(PPh_3)_2$ (18 mg, 0.026 mmol), CuI (5 mg, 0.03 mmol), and triethylamine (0.6 mL) were added to a solution of **15a** (200 mg, 1.31 mmol) in toluene (2.6 mL). The resulting mixture was stirred at room temperature for 1 h under an O_2 atmosphere. The reaction mixture was poured into a 5% NH_4Cl solution, extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by recrystallization from toluene to afford **17a** (171 mg, 86%): green needles; mp 200−210 °C dec (toluene); MS (70 eV) *m/z* (relative intensity) 302 (M^+, 100); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 248 (4.39), 296 (4.76), 316 (4.78), 335 (4.70), 395 (4.65), 425 (4.73), 636 (2.94); ^1H NMR (500 MHz, $CDCl_3$) $\delta = 8.25$ (d, $J = 10.4$ Hz, 4H, $H_{4',8'}$), 7.92 (t, $J = 3.7$ Hz, 2H, $H_{2'}$), 7.42 (d, $J = 3.7$ Hz, 4H, $H_{1',3'}$), 7.40 (d, $J = 10.4$ Hz, 4H, $H_{5',7'}$); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 140.2$ ($C_{3'a,8'a}$), 138.6 ($C_{2'}$), 134.8 ($C_{4',8'}$), 130.2 ($C_{6'}$), 126.3 ($C_{5',7'}$), 119.5 ($C_{1',3'}$), 87.8 ($C_{1,4}$), 76.0 ($C_{2,3}$). Anal. Calcd for $C_{24}H_{14}\cdot{}^1/_2H_2O$: C, 92.58; H, 4.86. Found: C, 92.23; H, 4.70.

Bis(1,3-diethoxycarbonyl-6-azulenyl)diacetylene (17b). The same procedure as was used for the preparation of **17a** was adopted. The reaction of **15b** (100 mg, 0.337 mmol) with $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), CuI (2 mg, 0.01 mmol), and triethylamine (0.15 mL) at 60 °C for 1 h under an O_2 atmosphere afforded **17b** (58 mg, 58%): green needles; mp >300 °C (1,4-dioxane); MS (70 eV) *m/z* (relative intensity) 590 (M^+, 100); IR (KBr disk) ν_{max} 1694 (C═O) cm^{-1}; UV−vis ($(CHCl_2)_2$) λ_{max}, nm (log ϵ) 361 (4.79), 380 (4.80), 402 (4.73), 436 (4.79), 558 (3.26); ^1H NMR (500 MHz, $CDCl_3$) $\delta = 9.70$ (d, $J = 11.1$ Hz, 4H, $H_{4',8'}$), 8.84 (s, 2H, $H_{2'}$), 7.91 (d, $J = 11.1$ Hz, 4H, $H_{5',7'}$), 4.45 (q, $J = 7.1$ Hz, 8H, 1′,3′-COOEt), 1.46 (t, $J =$ 7.1 Hz, 12H, 1′,3′-COOEt); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) $\delta = 164.7$ (s, 1′,3′-COOEt), 144.7 ($C_{2'}$), 143.9 ($C_{3'a,8'a}$), 137.4 ($C_{4',8'}$), 133.8 ($C_{6'}$), 133.4 ($C_{5',7'}$), 117.8 ($C_{1',3'}$), 87.6 ($C_{1,4}$), 78.4 ($C_{2,3}$), 60.3 (t, 1′,3′-COOEt), 14.5 (q, 1′,3′-COOEt). Anal. Calcd for $C_{36}H_{30}O_8\cdot 2H_2O$: C, 69.00; H, 5.47. Found: C, 69.21; H, 5.55.

1,2-Di(6-azulenyl)tetraphenylbenzene (2a). A solution of **16a** (277 mg, 1.00 mmol) and **18** (2.70 g, 7.02 mmol) in diphenyl ether (30 mL) was stirred at 160 °C for 41 h under an Ar atmosphere. Column chromatography on silica gel with hexane, followed with 80% CH_2Cl_2/hexane, and GPC with $CHCl_3$ afforded **2a** (80 mg, 13%): blue crystals; mp >300 °C (toluene/hexane); MS (FAB) *m/z* 634 (M^+); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.76), 283 (5.02), 352 (4.14), 578 (2.81); ^1H NMR (600 MHz, $CDCl_3$) $\delta = 7.82$ (d, $J = 10.4$ Hz, 4H, $H_{4',8'}$), 7.64 (t, $J = 3.7$ Hz, 2H, $H_{2'}$), 7.05 (d, $J = 3.7$ Hz, 4H, $H_{1',3'}$), 7.00 (d, $J = 10.4$ Hz, 4H, $H_{5',7'}$), 6.88−6.83 (m, 10H, $H_{2'''-6'''}$), 6.80 (d, $J = 7.1$ Hz, 4H, $H_{2'',6''}$), 6.78 (dd, $J = 7.3$, 7.1 Hz, 4H, $H_{3'',5''}$), 6.74 (t, $J = 7.3$ Hz, 2H, $H_{4''}$); ^{13}C NMR (150 MHz, $CDCl_3$) $\delta = 149.9$ ($C_{6'}$), 142.5 ($C_{1,2}$), 140.9 ($C_{3,6}$, $C_{4,5}$, or $C_{1'''}$), 140.2 ($C_{3,6}$, $C_{4,5}$, or $C_{1'''}$), 140.0 ($C_{3,6}$, $C_{4,5}$, or $C_{1'''}$), 139.8 ($C_{1''}$), 138.8 ($C_{3'a,8'a}$), 136.3 ($C_{2'}$), 134.2 ($C_{4',8'}$), 131.3 ($C_{2''',6'''}$), 131.2 ($C_{2'',6''}$), 127.4 ($C_{5',7'}$), 126.8 ($C_{3'',5''}$), 126.7 ($C_{3''',5'''}$), 125.6 ($C_{4''}$), 125.4 ($C_{4'''}$), 117.5 ($C_{1',3'}$). Anal. Calcd for $C_{34}H_{30}$: C, 94.60; H, 5.40. Found: C, 94.19; H, 5.58.

1,2-Bis(1,3-diethoxycarbonyl-6-azulenyl)tetraphenylbenzene (2b). A solution of **16b** (802 mg, 1.42 mmol) and **18** (3.80 g, 9.88 mmol) in diphenyl ether (30 mL) was stirred at 160 °C for 24 h under an Ar atmosphere. Column chromatography on silica gel with hexane, followed with 5% ethyl acetate/CH_2Cl_2, and GPC with $CHCl_3$ afforded **2b** (1.18 g, 90%): pink crystals; mp >300 °C (toluene/hexane); MS (FAB) *m/z* 922 (M^+); IR (KBr disk) ν_{max} 1690 (C═O) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 234 (4.97), 272 (4.72), 302 (4.87), 510 (3.13); ^1H NMR (600 MHz, $CDCl_3$) $\delta = 9.23$ (d, $J = 11.1$ Hz, 4H, $H_{4',8'}$), 8.60 (s, 2H, $H_{2'}$), 7.52 (d, $J = 11.1$ Hz, 4H, $H_{5',7'}$), 6.91−6.85 (m, 10H, $H_{2'''-6'''}$), 6.84 (d, $J = 7.1$ Hz, 4H, $H_{2'',6''}$), 6.79 (dd, $J =$ 7.2, 7.1 Hz, 4H, $H_{3'',5''}$), 6.75 (t, $J = 7.2$ Hz, 2H, $H_{4''}$), 4.36−4.28 (m, 8H, 1′,3′-COOEt), 1.36 (t, $J = 7.1$ Hz, 12H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, $CDCl_3$) $\delta = 164.9$ (s, 1′,3′-COOEt), 153.4 ($C_{6'}$), 143.3 ($C_{2'}$), 142.6 ($C_{3'a,8'a}$), 141.9 ($C_{4,5}$), 140.9 ($C_{1,2}$), 140.2 ($C_{3,6}$), 139.5 ($C_{1'''}$), 138.8 ($C_{1''}$), 136.7 ($C_{4',8'}$), 134.4 ($C_{5',7'}$), 131.2 ($C_{2'',6''}$), 131.1 ($C_{2''',6'''}$), 127.2 ($C_{3'',5''}$), 126.8 ($C_{3''',5'''}$), 126.1 ($C_{4''}$), 125.7 ($C_{4'''}$), 116.2 ($C_{1',3'}$), 59.9 (t, 1′,3′-COOEt), 14.5 (q, 1′,3′-COOEt). Anal. Calcd for $C_{62}H_{50}O_8$: C, 80.67; H, 5.46. Found: C, 80.31; H, 5.93.

6-(Phenylethynyl)azulene (19a). Phenylacetylene (2.30 g, 22.5 mmol) was added to a solution of **13a** (3.10 g, 15.0 mmol), PPh_3 (392 mg, 1.49 mmol), CuI (286 mg, 1.50 mmol), and $PdCl_2(PPh_3)_2$ (528 mg, 0.752 mmol) in triethylamine (40 mL) and toluene (40 mL). The resulting mixture was stirred at room temperature for 5 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with toluene. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to afford **19a** (3.07 g, 90%): blue plates; mp 174−175 °C (toluene); MS (70 eV) *m/z* (relative intensity) 228 (M^+, 100); IR (KBr disk) ν_{max} 2203 ($C{\equiv}C$) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 302 (4.67), 388 (4.44), 447 (2.03), 617 (2.58); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, J = 10.4 Hz, 2H, $H_{4',8'}$), 7.88 (t, J = 3.5 Hz, 1H, $H_{2'}$), 7.57 (m, 2H, $H_{2'',6''}$), 7.42 (d, J = 3.5 Hz, 2H, $H_{5',7'}$), 7.38 (d, J = 10.4 Hz, 2H, $H_{1',3'}$), 7.38−7.36 (m, 3H, $H_{3'',4'',5''}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.7 ($C_{3'a,8'a}$), 137.6 ($C_{2'}$), 135.0 ($C_{4',8'}$), 132.3 ($C_{6'}$), 131.9 ($C_{2'',6''}$), 128.8 ($C_{4''}$), 128.5 ($C_{3'',5''}$), 125.9 ($C_{5',7'}$), 122.8 ($C_{1''}$), 119.0 ($C_{1',3'}$), 93.9 (C_1), 91.9 (s, C_2). Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.73; H, 5.35.

Diethyl 6-(Phenylethynyl)azulene-1,3-dicarboxylate (19b). The same procedure as was used for the preparation of **19a** was adopted. The reaction of **13b** (9.19 g, 26.2 mmol) with phenylacetylene (3.99 g, 39.1 mmol), $PdCl_2(PPh_3)_2$ (912 mg, 1.30 mmol), PPh_3 (688 mg, 2.62 mmol), and CuI (497 mg, 2.61 mmol) in triethylamine (100 mL) and toluene (100 mL) for 20 h followed by column chromatography on silica gel with CH_2Cl_2 afforded **19b** (8.34 g, 86%): purple needles; mp 160 °C (toluene); MS (70 eV) *m/z* (relative intensity) 372 (M^+, 100); IR (KBr disk) ν_{max} 1693 ($C{=}O$) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.54), 270 (4.13), 313 (4.40), 350 (4.68), 392 (4.47), 458 (2.57), 536 (2.91); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.69 (d, J = 10.3 Hz, 2H, $H_{4',8'}$), 8.79 (s, 1H, $H_{2'}$), 7.92 (d, J = 10.3 Hz, 2H, $H_{5',7'}$), 7.63−7.61 (m, 2H, $H_{2'',6''}$), 7.43−7.42 (m, 3H, $H_{3'',4'',5''}$), 4.44 (q, J = 7.1 Hz, 4H, 1′,3′-COOEt), 1.46 (t, J = 7.1 Hz, 6H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 164.8 (s, 1′,3′-COOEt), 143.5 ($C_{2'}$), 143.2 ($C_{3'a,8'a}$), 137.4 ($C_{4',8'}$), 136.4 ($C_{6'}$), 133.2 ($C_{5',7'}$), 132.1 ($C_{3'',5''}$), 129.5 ($C_{4''}$), 128.6 ($C_{2'',6''}$), 122.0 ($C_{1''}$), 116.9 ($C_{1',3'}$), 95.4 (C_2), 92.7 (C_1), 60.1 (t, 1′,3′-COOEt), 14.5 (q, 1′,3′-COOEt). Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.10; H, 5.20.

(6-Azulenyl)pentaphenylbenzene (3a). A solution of **19a** (685 mg, 3.00 mmol) and **18** (8.01 g, 20.8 mmol) in diphenyl ether (30 mL) was stirred at 140 °C for 5 d under an Ar atmosphere. Column chromatography on silica gel with hexane, followed with CH_2Cl_2/hexane (1:1), and GPC with $CHCl_3$ afforded **3a** (559 mg, 32%): blue crystals; mp >300 °C (toluene); MS (70 eV) *m/z* (relative intensity) 584 (M^+, 100); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 239 (4.68), 299 (4.68), 335 (3.84), 351 (3.88), 368 (3.42), 578 (3.50), 618 (3.43), 686 (2.96); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 (d, J = 10.5 Hz, 2H, $H_{4',8'}$), 7.70 (t, J = 3.7 Hz, 1H, $H_{2'}$), 7.12 (d, J = 3.7 Hz, 2H, $H_{1',3'}$), 6.94 (d, J = 10.5 Hz, 2H, $H_{5',7'}$), 6.88 (d, J = 7.2 Hz, 4H, $H_{2'',6''}$), 6.87−6.83 (m, 15H, $H_{2'''-6'''}$ and $H_{2''''-6''''}$), 6.78 (dd, J = 7.2, 7.2 Hz, 4H, $H_{3'',5''}$), 6.73 (t, J = 7.2 Hz, 2H, $H_{4''}$); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 150.7 ($C_{6'}$), 143.2 (C_1), 140.7 (C_4 or $C_{1''''}$), 140.5 ($C_{3,5}$ or $C_{1'''}$), 140.4 (C_4 or $C_{1''''}$), 140.3 ($C_{3,5}$ or $C_{1'''}$), 140.0 ($C_{1''}$), 139.7 ($C_{2,6}$), 138.8 ($C_{3'a,8'a}$), 136.0 ($C_{2'}$), 134.2 ($C_{4',8'}$), 131.4 ($C_{2''',6'''}$), 131.3 ($C_{2'',6''}$ and $C_{2'''',6''''}$), 127.6 ($C_{5',7'}$), 126.7 ($C_{3'',5''}$), 126.6 ($C_{3''',5'''}$ and $C_{3'''',5''''}$), 125.5 ($C_{4''}$), 125.3 ($C_{4'''}$ and $C_{4''''}$), 117.2 ($C_{1',3'}$). Anal. Calcd for $C_{46}H_{32}$: C, 94.48; H, 5.52. Found: C, 93.88; H, 5.84.

(1,3-Diethoxycarbonyl-6-azulenyl)pentaphenylbenzene (3b). A solution of **19b** (729 mg, 1.96 mmol) and **18** (5.28 g, 13.7 mmol) in diphenyl ether (40 mL) was stirred at 160 °C for 5 d under an Ar atmosphere. Column chromatography on silica gel with hexane, followed with CH_2Cl_2/hexane (1:1), and GPC with $CHCl_3$ afforded **3b** (1.32 g, 93%): pink needles; mp >300 °C (CH_2Cl_2/hexane); MS (FAB) *m/z* 728 (M^+); IR (KBr disk) ν_{max} 1694 ($C{=}O$) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 236 (4.85), 270 (4.55), 320 (4.56), 503 (2.90); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.27 (d, J = 11.1 Hz, 2H, $H_{4',8'}$), 8.64 (s, 1H, $H_{2'}$), 7.50 (d, J = 11.1 Hz, 2H, $H_{5',7'}$), 6.90−6.84 (m, 15H, $H_{2'''-6'''}$ and $H_{2''''-6''''}$), 6.83 (d, J = 7.0 Hz, 4H, $H_{2'',6''}$), 6.78 (dd, J = 7.2, 7.0 Hz, 4H, $H_{3'',5''}$), 6.74 (t, J = 7.2 Hz, 2H, $H_{4''}$), 4.35 (q, J = 7.1 Hz, 4H, 1′,3′-COOEt), 1.40 (t, J = 7.1 Hz, 6H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 165.1 (s, 1′,3′-COOEt), 155.3 ($C_{6'}$), 142.8 ($C_{3'a,8'a}$), 142.7 ($C_{2'}$), 141.7 (C_1), 141.5 (C_4), 140.8 ($C_{3,5}$), 140.1 ($C_{1''''}$), 139.9 ($C_{1'''}$), 139.6 ($C_{2,6}$), 139.3 ($C_{1''}$), 136.4 ($C_{4',8'}$), 135.1 ($C_{5',7'}$), 131.3 ($C_{2'',6''}$), 131.2 ($C_{2''',6'''}$ and $C_{2'''',6''''}$), 127.1 ($C_{3'',5''}$), 126.7 ($C_{3''',5'''}$ and $C_{3'''',5''''}$), 125.8 ($C_{4''}$), 125.5 ($C_{4'''}$), 125.4 ($C_{4''''}$), 115.5 ($C_{1',3'}$), 59.9 (t, 1′,3′-COOEt), 14.5 (q, 1′,3′-COOEt). Anal. Calcd for $C_{52}H_{40}O_4$: C, 85.69; H, 5.53. Found: C, 85.05; H, 6.06.

Reaction of 16a with $CpCo(CO)_2$. A solution of **16a** (558 mg, 2.00 mmol) and $CpCo(CO)_2$ (721 mg, 4.00 mmol) in 1,4-dioxane (170 mL) was refluxed for 30 h. Column chromatography on silica gel with 50% CH_2Cl_2/hexane afforded **6a** (296 mg, 43%): brown crystals; mp >300 °C (toluene/hexane); MS (FAB) *m/z* 680 (M^+); UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 246 (4.68), 307 (5.04), 395 (4.54); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, J = 10.5 Hz, 8H, $H_{4',8'}$), 7.91 (t, J = 3.8 Hz, 4H, $H_{2'}$), 7.46 (d, J = 10.4 Hz, 8H, $H_{5',7'}$), 7.33 (d, J = 3.8 Hz, 8H, $H_{1',3'}$), 4.78 (s, 5H, Cp); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.7 ($C_{6'}$), 139.0 ($C_{3'a,8'a}$), 136.9 ($C_{2'}$), 134.8 ($C_{4',8'}$), 124.7 ($C_{5',7'}$), 119.1 ($C_{1',3'}$), 84.9 (Cp), 82.1 ($C_{1,2,3,4}$). Anal. Calcd for $C_{49}H_{33}Co{\cdot}H_2O$: C, 84.23; H, 5.05. Found: C, 83.77; H, 5.03.

Reaction of 16b with $CpCo(CO)_2$. A solution of **16b** (900 mg, 1.59 mmol) and $CpCo(CO)_2$ (491 mg, 2.73 mmol) in 1,4-dioxane (700 mL) was refluxed for 40 h. To the mixture, additional $CpCo(CO)_2$ (286 mg, 1.59 mmol) was added, and the mixture was further refluxed for 43 h. Column chromatography on silica gel with 3% ethyl acetate/CH_2Cl_2 afforded **6b** (804 mg, 81%): brown crystals; mp >300 °C (toluene/hexane); MS (FAB) *m/z* 1256 (M^+); IR (KBr disk) ν_{max} 1694 ($C{=}O$) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (5.04), 268 (4.84), 337 (4.95), 365 (4.95), 383 (4.94), 418 (4.65); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.52 (d, J = 10.9 Hz, 8H, $H_{4',8'}$), 8.86 (s, 4H, $H_{2'}$), 7.90 (d, J = 10.9 Hz, 8H, $H_{5',7'}$), 4.91 (s, 5H, Cp), 4.42 (q, J = 7.1 Hz, 16H, 1′,3′-COOEt), 1.44 (t, J = 7.1 Hz, 24H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 164.8 (s, 1′,3′-COOEt), 148.7 ($C_{6'}$), 143.6 ($C_{2'}$), 142.7 ($C_{3'a,8'a}$), 137.3 ($C_{4',8'}$), 131.0 ($C_{5',7'}$), 117.6 ($C_{1',3'}$), 85.5 (Cp), 81.6 ($C_{1,2,3,4}$), 60.2 (t, 1′,3′-COOEt), 14.6 (q, 1′,3′-COOEt). Anal. Calcd for $C_{73}H_{65}O_{16}Co{\cdot}H_2O$: C, 68.75; H, 5.30. Found: C, 69.08; H, 5.26.

Reaction of 14b with $CpCo(CO)_2$. A solution of **14b** (478 mg, 1.30 mmol) and $CpCo(CO)_2$ (402 mg, 2.23 mmol) in 1,4-dioxane (130 mL) was refluxed for 24 h. To the mixture, additional $CpCo(CO)_2$ (400 mg, 2.22 mmol) was added, and the mixture was further refluxed for 40 h. Column chromatography on silica gel with $CHCl_3$ afforded a mixture (1:4.1) of **7** and **8** (456 mg, 82%). The products **7** and **8** were separated by GPC with $CHCl_3$. **7**: reddish brown crystals; mp 161−167 °C (hexane); MS (70 eV) *m/z* (relative intensity) 860 (M^+, 100); IR (KBr disk) ν_{max} 1694 ($C{=}O$) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.81), 271 (4.72), 314 (4.73), 363 (4.66), 378 (4.64), 434 (4.30); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.48 (d, J = 11.3 Hz, 4H, $H_{4',8'}$), 8.77 (s, 2H, $H_{2'}$), 7.76 (d, J = 11.3 Hz, 4H, $H_{5',7'}$), 4.88 (s, 5H, Cp), 4.41 (q, J = 7.2 Hz, 8H, 1′,3′-COOEt), 1.43 (t, J = 7.2 Hz, 12H, 1′,3′-COOEt), 0.30 (s, 18H, 1,2-TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.1 (s, 1′,3′-COOEt), 152.6 ($C_{6'}$), 142.4 ($C_{4',8'}$ and $C_{3'a,8'a}$), 136.9 ($C_{2'}$), 131.4 ($C_{5',7'}$), 116.8 ($C_{1',3'}$), 91.6 ($C_{3,4}$), 82.4 (Cp), 72.5 ($C_{1,2}$), 60.0 (t, 1′,3′-COOEt), 14.6 (q, 1′,3′-COOEt), 2.0 (1,2-TMS). Anal. Calcd for $C_{47}H_{53}O_8Si_2Co{\cdot}H_2O$: C, 64.22; H 6.31. Found: C, 64.38; H, 6.07. **8**: reddish brown prisms; mp 286−288 °C (CH_2Cl_2/hexane); MS (70 eV) *m/z* (relative intensity) 860 (M^+, 100); IR (KBr disk) ν_{max} 1692 ($C{=}O$) cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.80), 271 (4.67), 317 (4.67), 366 (4.61), 378 (4.62), 455 (4.51); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.56 (d, J = 11.1 Hz, 4H, $H_{4',8'}$), 8.75 (s, 2H, $H_{2'}$), 7.82 (d, J = 11.1 Hz, 4H, $H_{5',7'}$), 4.88 (s, 5H, Cp), 4.44 (q, J = 7.1 Hz, 8H, 1′,3′-COOEt), 1.46 (t, J = 7.1 Hz, 12H, 1′,3′-COOEt), 0.29 (s, 18H, 1,3-TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.2 (s, 1′,3′-COOEt), 155.2 ($C_{6'}$), 142.5 ($C_{3'a,8'a}$), 142.1 ($C_{2'}$), 136.5 ($C_{4',8'}$), 131.3 ($C_{5',7'}$), 116.6 ($C_{1',3'}$), 92.7 ($C_{2,4}$), 82.4 (Cp), 72.8 ($C_{1,3}$), 60.0 (t, 1′,3′-COOEt), 14.6 (q, 1′,3′-COOEt), 1.7 (1,3-TMS). Anal. Calcd for $C_{47}H_{53}O_8Si_2Co{\cdot}H_2O$: C, 64.22; H, 6.31. Found: C, 64.06; H, 6.26.

Reaction of 19b with $CpCo(CO)_2$. A solution of **19b** (745 mg, 2.00 mmol) and $CpCo(CO)_2$ (720 mg, 4.00 mmol) in 1,4-dioxane (170 mL) was refluxed for 18 h. Column chromatography on silica gel with ethyl acetate/$CHCl_3$ afforded a mixture (1:1.1) of **9** and **10** (817 mg, 94%). The products **9** and **10** were separated by GPC with CHCl$_3$. **9**: reddish brown crystals; mp 290−296 °C (1,4-dioxane); MS (FAB) m/z 868 (M$^+$); IR (KBr disk) ν_{max} 1688 (C=O) cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max}, nm (log ϵ) 239 (4.89), 271 (4.69), 319 (4.78), 365 (4.63), 380 (4.63), 414 (4.37), 458 (4.32); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 9.47 (d, J = 11.1 Hz, 4H, H$_{4',8'}$), 8.80 (s, 2H, H$_{2'}$), 7.94 (d, J = 11.1 Hz, 4H, H$_{5',7'}$), 7.45 (d, J = 7.1 Hz, 4H, H$_{2'',6''}$), 7.35 (t, J = 7.5 Hz, 2H, H$_{4''}$), 7.29 (dd, J = 7.5, 7.1 Hz, 4H, H$_{3'',5''}$), 4.75 (s, 5H, Cp), 4.42 (q, J = 7.1 Hz, 8H, 1′,3′-COOEt), 1.44 (t, J = 7.1 Hz, 12H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 165.1 (s, 1′,3′-COOEt), 152.8 (C$_{6'}$), 142.5 (C$_{2'}$ and C$_{3'a,8'a}$), 137.2 (C$_{4',8'}$), 133.6 (C$_{1''}$), 130.9 (C$_{5',7'}$), 129.4 (C$_{2'',6''}$), 128.5 (C$_{3'',5''}$), 127.6 (C$_{4''}$), 117.0 (C$_{1',3'}$), 84.4 (Cp), 80.3 (C$_{3,4}$), 77.6 (C$_{1,2}$), 60.1 (t, 1′,3′-COOEt), 14.6 (q, 1′,3′-COOEt). Anal. Calcd for $C_{53}H_{45}O_8Co\cdot 2H_2O$: C, 70.35; H, 5.46. Found: C, 70.51; H, 5.24. **10**: reddish brown crystals; mp >300 °C (ethyl acetate/hexane); MS (FAB) m/z 868 (M$^+$); IR (KBr disk) ν_{max} 1690 (C=O) cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max}, nm (log ϵ) 240 (4.92), 267 (4.73), 333 (4.71), 362 (4.69), 378 (4.68), 448 (4.58); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 9.36 (d, J = 11.1 Hz, 4H, H$_{4',8'}$), 8.73 (s, 2H, H$_{2'}$), 7.76 (d, J = 11.1 Hz, 4H, H$_{5',7'}$), 7.65 (d, J = 6.9 Hz, 4H, H$_{2'',6''}$), 7.45 (t, J = 7.5 Hz, 2H, H$_{4''}$), 7.41 (dd, J = 7.5, 6.9 Hz, 4H, H$_{3'',5''}$), 4.76 (s, 5H, Cp), 4.40 (q, J = 7.1 Hz, 8H, 1′,3′-COOEt), 1.43 (t, J = 7.1 Hz, 12H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 165.1 (s, 1′,3′-COOEt), 153.5 (C$_{6'}$), 142.5 (C$_{3'a,8'a}$), 142.1 (C$_{2'}$), 137.1 (C$_{4',8'}$), 133.1 (C$_{1''}$), 130.6 (C$_{2'',6''}$), 129.8 (C$_{5',7'}$), 128.9 (C$_{3'',5''}$), 128.2 (C$_{4''}$), 116.6 (C$_{1',3'}$), 84.2 (Cp), 80.3 (C$_{2,4}$), 77.8 (C$_{1,3}$), 60.0 (t, 1′,3′-COOEt), 14.6 (q, 1′,3′-COOEt). Anal. Calcd for $C_{53}H_{45}O_8Co$: C, 73.27; H, 5.22. Found: C, 72.95; H, 5.33.

Reaction of 15a with CpCo(CO)$_2$. A solution of **15a** (1.00 g, 6.57 mmol) and CpCo(CO)$_2$ (1.22 g, 6.78 mmol) in 1,4-dioxane (400 mL) was refluxed for 43 h. Column chromatography on silica gel with 50% CH$_2$Cl$_2$/hexane and GPC with CHCl$_3$ afforded **4a** (5 mg, 0.5%), **5a** (3 mg, 0.3%), and **11a** (274 mg, 19%). **4a**: MS (70 eV) m/z (relative intensity) 456 (M$^+$, 100); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 8.46 (d, J = 10.4 Hz, 6H, H$_{4',8'}$), 7.96 (s, 3H, H$_{2,4,6}$), 7.95 (t, J = 3.7 Hz, 3H, H$_{2'}$), 7.53 (d, J = 10.4 Hz, 6H, H$_{5',7'}$), 7.46 (d, J = 3.7 Hz, 6H, H$_{1',3'}$); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 150.1 (C$_{6'}$), 146.4 (C$_{1,3,5}$), 139.1 (C$_{3'a,8'a}$), 137.4 (C$_{2'}$), 135.9 (C$_{4',8'}$), 128.3 (C$_{2,4,6}$), 123.4 (C$_{5',7'}$), 118.8 (C$_{1',3'}$). HRMS calcd for $C_{36}H_{24}$ 456.1878, found 456.1880. **5a**: MS (70 eV) m/z (relative intensity) 456 (M$^+$, 90); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 8.44 (d, J = 10.5 Hz, 2H, H$_{4''',8'''}$), 8.16 (d, J = 10.5 Hz, 4H, H$_{4',8'}$ and H$_{4'',8''}$), 7.93 (t, J = 3.7 Hz, 1H, H$_{2'''}$), 7.84 (d, J = 2.0 Hz, 1H, H$_3$), 7.84 (t, J = 3.7 Hz, 2H, H$_{2'}$ and H$_{2''}$), 7.79 (dd, J = 8.0, 2.0 Hz, 1H, H$_5$), 7.67 (d, J = 8.0 Hz, 1H, H$_6$), 7.51 (d, J = 10.5 Hz, 2H, H$_{5''',7'''}$), 7.45 (d, J = 3.7 Hz, 2H, H$_{1''',3'''}$), 7.30 (d, J = 3.7 Hz, 4H, H$_{1',3'}$ and H$_{1'',3''}$), 7.20 (d, J = 10.5 Hz, 2H, H$_{5'',7''}$), 7.18 (d, J = 10.5 Hz, 2H, H$_{5',7'}$); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 150.3 (C$_{6'}$ or C$_{6''}$), 150.1 (C$_{6'}$ or C$_{6''}$), 149.7 (C$_{6'''}$), 144.9 (C$_4$), 144.5 (C$_2$), 143.7 (C$_1$), 139.1 (C$_{3a''',8a'''}$), 139.0 (C$_{3a'',8a''}$), 138.9 (C$_{3a',8a'}$), 137.3 (C$_{2'''}$), 137.2 (C$_{2'}$ and C$_{2''}$), 135.9 (C$_{4''',8'''}$), 135.4 (C$_{4',8'}$ and C$_{4'',8''}$), 131.5 (C$_6$), 131.2 (C$_3$), 128.0 (C$_5$), 125.6 (C$_{5'',7''}$), 125.5 (C$_{5',7'}$), 123.2 (C$_{5''',7'''}$), 118.7 (C$_{1''',3'''}$), 118.5 (C$_{1',3'}$ or C$_{1'',3''}$), 118.4 (C$_{1',3'}$ or C$_{1'',3''}$). HRMS calcd for $C_{36}H_{24}$ 456.1878, found 456.1888. **11a**: brown crystals; mp 175−180 °C (hexane); MS (FAB) m/z 428 (M$^+$, 100); UV−vis (CH$_2$Cl$_2$) λ_{max}, nm (log ϵ) 237 (4.55), 295 (4.82), 329 (4.60), 394 (4.35); ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.12 (d, J = 10.5 Hz, 4H, H$_{4',8'}$), 7.84 (t, J = 3.7 Hz, 2H, H$_{2'}$), 7.37 (d, J = 10.5 Hz, 4H, H$_{5',7'}$), 7.29 (d, J = 3.7 Hz, 4H, H$_{1',3'}$), 4.77 (s, 5H, Cp), 4.73 (s, 2H, H$_{3,4}$); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 149.6 (C$_{6'}$), 138.5 (C$_{3'a,8'a}$), 135.7 (C$_{2'}$), 135.1 (C$_{4',8'}$), 121.9 (C$_{5',7'}$), 118.7 (C$_{1',3'}$), 81.5 (Cp), 80.3 (C$_{1,2}$), 59.9 (C$_{3,4}$). Anal. Calcd for $C_{29}H_{21}Co\cdot {}^1/_2H_2O$: C, 79.63; H, 5.07. Found: C, 80.04; H, 5.12.

Reaction of 15b with CpCo(CO)$_2$. A solution of **15b** (593 mg, 2.00 mmol) and CpCo(CO)$_2$ (360 mg, 2.00 mmol) in 1,4-dioxane (170 mL) was refluxed for 44 h. Column chromatography on silica gel with 10% ethyl acetate/CH$_2$Cl$_2$ afforded a mixture (2.5:1) of **4b** and **5b** (125 mg, 21%) and **11b** (334 mg, 47%). The products **4b** and **5b** were separated by silica gel preparative TLC with 30% ethyl acetate/hexane. **4b**: pink crystals; mp >300 °C (ethyl acetate/hexane); MS (FAB) m/z 888 (M$^+$); IR (KBr disk) ν_{max} 1694 (C=O) cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max}, nm (log ϵ) 237 (4.94), 273 (4.68), 333 (5.18), 517 (3.36); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 9.88 (d, J = 11.0 Hz, 6H, H$_{4',8'}$), 8.87 (s, 3H, H$_{2'}$), 8.06 (d, J = 11.0 Hz, 6H, H$_{5',7'}$), 8.05 (s, 3H, H$_{2,4,6}$), 4.45 (q, J = 7.1 Hz, 12H, 1′,3′-COOEt), 1.46 (t, J = 7.1 Hz, 18H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 164.9 (s, 1′,3′-COOEt), 152.8 (C$_{6'}$), 145.6 (C$_{1,3,5}$), 144.0 (C$_{2'}$), 142.9 (C$_{3'a,8'a}$), 138.6 (C$_{4',8'}$), 130.6 (C$_{5',7'}$), 129.3 (C$_{2,4,6}$), 117.1 (C$_{1',3'}$), 30.2 (t, 1′,3′-COOEt), 14.6 (q, 1′,3′-COOEt). Anal. Calcd for $C_{54}H_{48}O_{12}\cdot H_2O$: C, 71.51; H, 5.56. Found: C, 71.39; H, 5.59. **5b**: pink crystals; mp 150−153 °C (ethyl acetate/hexane); MS (FAB) m/z 888 (M$^+$); IR (KBr disk) ν_{max} 1694 (C=O) cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max}, nm (log ϵ) 237 (4.97), 271 (4.75), 337 (5.02), 515 (3.40); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 9.88 (d, J = 11.0 Hz, 2H, H$_{4''',8'''}$), 9.59 (d, J = 11.0 Hz, 2H, H$_{4'',8''}$), 9.58 (d, J = 11.0 Hz, 2H, H$_{4',8'}$), 8.87 (s, 1H, H$_{2'''}$), 8.79 (s, 2H, H$_{2'}$ and H$_{2''}$), 8.05 (d, J = 11.0 Hz, 2H, H$_{5''',7'''}$), 7.92 (dd, J = 7.9, 1.9 Hz, 1H, H$_5$), 7.91 (d, J = 1.9 Hz, 1H, H$_3$), 7.77 (d, J = 7.9 Hz, 1H, H$_6$), 7.70 (d, J = 11.0 Hz, 2H, H$_{5'',7''}$), 7.68 (d, J = 11.0 Hz, 2H, H$_{5',7'}$), 4.46 (q, J = 7.1 Hz, 4H, 1‴,3‴-COOEt), 4.39 (q, J = 7.1 Hz, 8H, 1′,3′- and 1″,3″-COOEt), 1.48 (t, J = 7.1 Hz, 6H, 1‴,3‴-COOEt), 1.42 (t, J = 7.1 Hz, 6H, 1′,3′- or 1″,3″-COOEt), 1.41 (t, J = 7.1 Hz, 6H, 1′,3′- or 1″,3″-COOEt); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 164.9 (s, 1‴,3‴-COOEt), 164.8 (s, 1′,3′- and 1″,3″-COOEt), 152.7 (C$_{6''}$), 152.6 (C$_{6'}$), 152.5 (C$_{6'''}$), 144.3 (C$_4$), 144.0 (C$_{2'}$ or C$_{2''}$), 143.9 (C$_{2'}$ or C$_{2''}$), 143.8 (C$_{2'''}$), 143.5 (C$_2$), 143.1 (C$_1$), 142.9 (C$_{3'''a,8'''a}$), 142.8 (C$_{3'a,8'a}$ and C$_{3''a,8''a}$), 138.6 (C$_{4''',8'''}$), 138.0 (C$_{4',8'}$ and C$_{4'',8''}$), 132.6 (C$_{5',7'}$ and C$_{5'',7''}$), 132.1 (C$_6$), 131.5 (C$_3$), 130.5 (C$_{5''',7'''}$), 129.1 (C$_5$), 117.1 (C$_{1',3'}$ or C$_{1'',3''}$), 117.0 (C$_{1',3'}$, C$_{1'',3''}$, and/or C$_{1''',3'''}$), 60.2 (t, 1‴,3‴-COOEt), 60.1 (t, 1′,3′- and 1″,3″-COOEt), 14.6 (q, 1‴,3‴-COOEt), 14.5 (q, 1′,3′- and 1″,3″-COOEt). Anal. Calcd for $C_{54}H_{48}O_{12}\cdot {}^1/_2H_2O$: C, 72.23; H, 5.50. Found: C, 72.14; H, 5.48. **11b**: brown crystals; mp 254 °C (ethyl acetate/hexane); MS (FAB) m/z 716 (M$^+$); IR (KBr disk) ν_{max} 1686 (C=O) cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max}, nm (log ϵ) 240 (4.83), 265 (4.63), 313 (4.61), 361 (4.72), 377 (4.69); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 9.51 (d, J = 11.1 Hz, 4H, H$_{4',8'}$), 8.76 (s, 2H, H$_{2'}$), 7.80 (d, J = 11.1 Hz, 4H, H$_{5',7'}$), 4.92 (s, 2H, H$_{3,4}$), 4.80 (s, 5H, Cp), 4.43 (q, J = 7.1 Hz, 8H, 1′,3′-COOEt), 1.45 (t, J = 7.1 Hz, 12H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 165.0 (s, 1′,3′-COOEt), 154.2 (C$_{6'}$), 142.1 (C$_{2'}$ and C$_{3'a,8'a}$), 137.4 (C$_{4',8'}$), 128.5 (C$_{5',7'}$), 117.0 (C$_{1',3'}$), 81.9 (Cp), 78.9 (C$_{1,2}$), 61.9 (C$_{3,4}$), 60.0 (t, 1′,3′-COOEt), 14.6 (q, 1′,3′-COOEt). Anal. Calcd for $C_{41}H_{37}O_8Co\cdot {}^1/_2H_2O$: C, 67.86; H, 5.28. Found: C, 67.60; H, 5.32.

(η^5-Cyclopentadienyl)[1,3-bis(1,3-diethoxycarbonyl-6-azulenyl)cyclobutadiene]cobalt (12). A solution of n-Bu$_4$NF (1.0 M, 0.8 mL) in THF was added to a solution of **8** (69 mg, 0.080 mmol) in the same solvent (2 mL). The mixture was stirred at room temperature for 30 min. The reaction mixture was poured into water and extracted with CH$_2$Cl$_2$. The organic layer was washed with water, dried over MgSO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 5% ethyl acetate/CH$_2$Cl$_2$ to afford **12** (30 mg, 53%): brown crystals; mp >300 °C (ethyl acetate); MS (70 eV) m/z (relative intensity) 716 (M$^+$, 100); IR (KBr disk) ν_{max} 1688 (C=O) cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max}, nm (log ϵ) 240 (4.81), 268 (4.64), 341 (4.61), 362 (4.64), 465 (4.71); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 9.50 (d, J = 11.1 Hz, 4H, H$_{4',8'}$), 8.72 (s, 2H, H$_{2'}$), 7.53 (d, J = 11.1 Hz, 4H, H$_{5',7'}$), 5.56 (s, 2H, H$_{2,4}$), 4.65 (s, 5H, Cp), 4.43 (q, J = 7.1 Hz, 8H, 1′,3′-COOEt), 1.45 (t, J = 7.1 Hz, 12H, 1′,3′-COOEt); ^{13}C NMR (150 MHz, CDCl$_3$) δ = 165.1 (s, 1′,3′-COOEt), 153.8 (C$_{6'}$), 142.0 (C$_{3'a,8'a}$), 141.6 (C$_{2'}$), 137.6 (C$_{4',8'}$), 125.7 (C$_{5',7'}$), 116.9 (C$_{1',3'}$), 81.8 (Cp), a signal in CDCl$_3$ region (C$_{1,3}$) confirmed by a 2D heteronuclear multiple-bond correlation (HMBC) spectrum, 60.0 (t, 1′,3′-COOEt), 57.9 (C$_{2,4}$), 14.6 (q, 1′,3′-COOEt). Anal. Calcd for $C_{41}H_{37}O_8Co\cdot H_2O$: C, 67.03; H, 5.35. Found: C, 67.09; H, 5.26.

X-ray Crystallographic Data for 8. Data and diffraction parameters were obtained for a crystal with dimensions of 0.07 × 0.15 × 0.20 mm using a Rigaku/MSC mercury CCD diffractometer with Mo Kα radiation (λ = 0.710 6$\underline{9}$ Å) at −103 °C. Crystal system: triclinic. Space group: $P\bar{1}$. Unit cell dimensions: a = 9.634(3) Å, b = 10.536(2) Å, c = 22.457(4) Å, α = 91.034(8)°, β = 90.12(1)°, γ = 106.414(2)°, V = 2186.3(9) Å^3, and Z = 2. D_{calcd} = 1.308 g cm^{-3}. μ (Mo Kα) = 5.00 cm^{-1}.

$F(000) = 908$. 2θ range for data collection = 0.0−55.0°. Number of measured reflections = 15 735. Independent reflections = 8675 ($R_{\mathrm{int}} = 0.027$). Final $R = 0.056$, $R_w = 0.169$ for 5956 observed reflections ($I_0 > 2\sigma(I_0)$). Parameters = 523. GOF = 1.10. $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ are 0.37 and −0.43 $e^- Å^{-3}$, respectively. Refinement method: full matrix least-squares. All calculations were performed using the software package of Molecular Structure Corporation (Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1999).

JO010540U