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Synthesis and redox behavior of 1,3,5- and 1,2,4-tri(6-azulenyl)benzene derivatives

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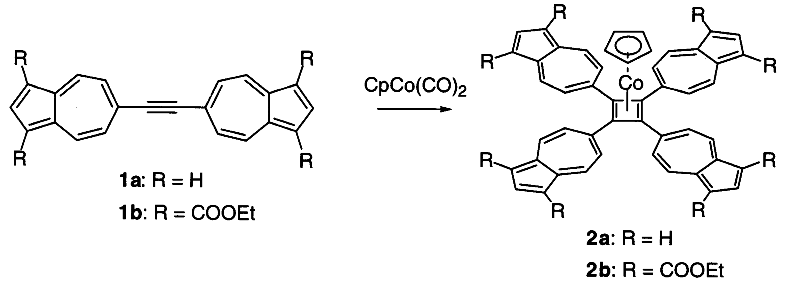
Abstract—Described herein is a cobalt-mediated cyclooligomerization of mono- and di(6-azulenyl)acetylenes to afford 1,3,5- and 1,2,4-tri(6-azulenyl)benzene derivatives and (η^5-cyclopentadienyl)[tetra- and di(6-azulenyl)cyclobutadiene]cobalt complexes. The redox behavior of these novel tri(6-azulenyl)benzene derivatives and [tetra- and di(6-azulenyl)cyclobutadiene]cobalt complexes examined by cyclic voltammetry is also described. © 2001 Elsevier Science Ltd. All rights reserved.

Recently, much attention has been focused on aromatic compounds with extended π-electron systems because of their special optical and electrical properties.[1] However, to date, molecules with potentially useful electronic properties constructed by azulene derivatives are fairly scarce. The azulene system has a tendency to stabilize cations as well as anions owing to its remarkable polarized properties,[2] which could be utilized to construct advanced materials for electronic and photonic applications. Recently, Hafner et al. reported the $CpCo(CO)_2$-mediated cyclooligomerization of (1-azulenyl)acetylenes to give (1-azulenyl)benzene derivatives and (cyclobutadiene)cobalt complexes in low yields.[3] We have reported the ethynylation of azulenes in a seven-membered ring utilizing Pd-catalyzed cross-coupling reaction of bromoazulenes with acetylenes and the transformation of the (6-azulenyl)acetylenes into mono- and 1,2-di(6-azulenyl)benzene derivatives by Diels–Alder reaction with tetraphenylcyclopentadienone.[4]

Herein we report our recent results on the metal-mediated cyclooligomerization of mono- and di(6-azulenyl)acetylenes to give 1,3,5- and 1,2,4-tri(6-azulenyl)benzene derivatives and [(6-azulenyl)cyclobutadiene]cobalt complexes,[5] which are expected to have a different character from that of 1-azulenyl derivatives. According to the polarized properties of the azulene systems, these compounds would exhibit the formation of a stabilized anionic species by electrochemical reduction. Although there are many reports concerning carbocations stabilized by 1-azulenyl substituents, little



1a: R = H
1b: R = COOEt

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

Scheme 1.

Keywords: ethynylazulenes; Co-mediated reaction; cyclotrimerization; redox potentials.

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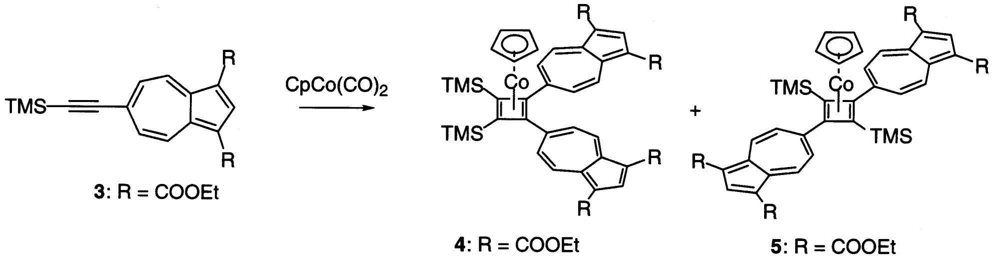
is known about carbanions stabilized by 6-azulenyl substituents because of the synthetic difficulty of the functionalization in a seven-membered ring. Thus, we also report here the redox behavior of these novel tri(6-azulenyl)benzene derivatives and [(6-azulenyl)cyclobutadiene]cobalt complexes examined by cyclic voltammetry (CV).

Attempts for the cyclooligomerization of di(6-azulenyl)acetylenes **1a** and **1b**[4] in the presence of $CpCo(CO)_2$ in refluxing 1,4-dioxane did not yield the hexa(6-azulenyl)benzene derivatives but exclusively gave (η^5-cyclopentadienyl)[tetra(6-azulenyl)cyclobutadiene]cobalt complexes (**2a** and **2b**) in 43 and 81% yields, respectively (Scheme 1).[6] The spectral features of **2a** and **2b** are in agreement with the structure of these products.[7] Attempts for the cyclooligomerization of **1a** and **1b** in the presence of cobalt carbonyl[8] and dichlorobis(benzonitrile)palladium[9] following literature procedures did not afford satisfactory results.

Similarly, the reaction of 6-(trimethylsiliylethynyl)-azulene **3**[4] in the presence of $CpCo(CO)_2$ afforded a mixture (1:4.1) of *cis*- and *trans*-(η^5-cyclopentadienyl)[bis(1,3-diethoxycarbonyl-6-azulenyl)bis(trimethylsilyl)cyclobutadiene]cobalt complexes (**4** and **5**) in 82% yields,[7] which were separable by gel permeation chromatography with chloroform (Scheme 2). In these two reactions (6-azulenyl)benzene derivatives could not be obtained even in trace amount. Exclusive formation of the (cyclobutadiene)cobalt complexes **2a**, **2b**, **4**, and **5** is attributable to the steric hindrance among the azulene rings and/or trimethylsilyl groups. The regiochemistry of the *cis*- and *trans*-[di(6-azulenyl)cyclobutadiene]-cobalt complexes **4** and **5** could not be determined by the NMR spectroscopy. Suitable crystals of the major isomer **5** were obtained for X-ray structure determination. Thus, the relative stereochemistry of the major isomer **5** was established, as shown in Fig. 1.

In contrast to the results obtained by Hafner et al. using 1-ethynylazulenes,[3b] the cyclooligomerization of 6-ethynylazulene **6**[4,10] using $CpCo(CO)_2$ afforded a mixture (2.5:1) of 1,3,5- and 1,2,4-tri(6-azulenyl)benzene derivatives **7** and **8** in 21% yields along with (η^5-cyclopentadienyl)[1,2-bis(1,3-diethoxycarbonyl-6-azulenyl)cyclobutadiene]cobalt **9** in 47% yield (Scheme 3).[7] The benzene derivatives **7** and **8** were separable by silica gel preparative TLC with ethyl acetate/hexane.

The regiochemistry of the *cis*-cobalt complex **9** was confirmed by the ^{13}C satellite signals in the ^1H NMR spectrum,[11] which were definitely identified by the 2D HMQC spectrum measured under non-decoupling conditions. The negligibly small coupling constant (<1 Hz) between the cyclobutadiene protons clearly shows the presence of the 1,2-disubstitution pattern in the cyclobutadiene ring.[12] The *cis*-configuration of **9** was also confirmed by the preparation of *trans*-isomer **10**. The deprotection of the trimethylsilyl groups of *trans*-cobalt complex **5** was furnished by the treatment of **5** with tetrabutylammonium fluoride in tetrahydrofuran in 53% yield (Scheme 4). The ^{13}C satellite signals in the ^1H NMR spectrum of **10** showed that the coupling



3: R = COOEt

4: R = COOEt

5: R = COOEt

Scheme 2.

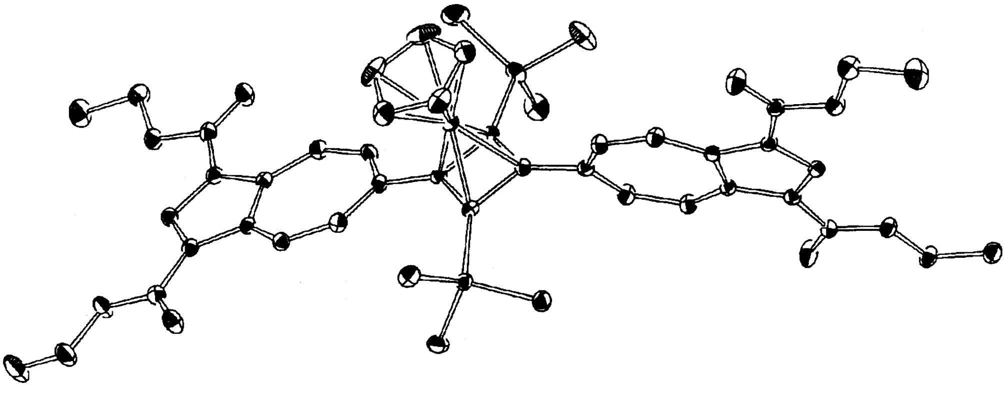
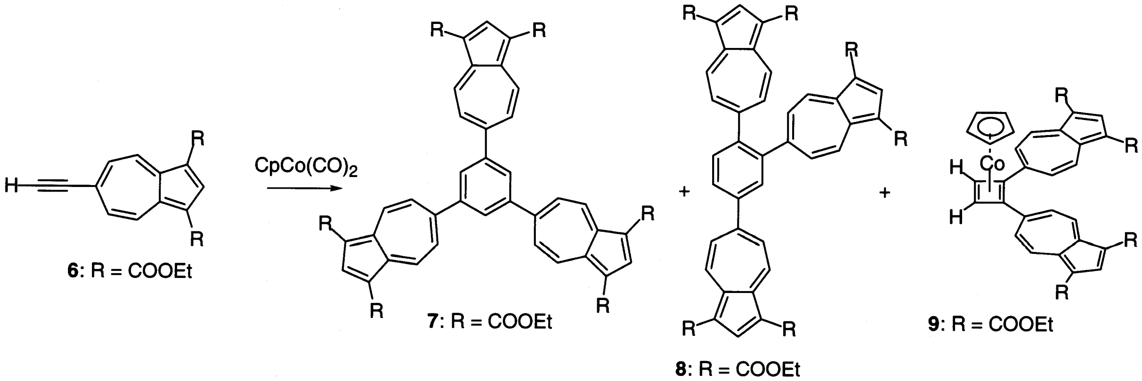


Figure 1. ORTEP plot (30% probability ellipsoids) of the molecular structure of **5**.



Scheme 3.

constant between the cyclobutadiene protons was 8.1 Hz, which is consistent with 1,3-disubstitution of the cyclobutadiene ring.[12]

The formation of both **7** and **8** could not be explained by the single intermediate **11** in this reaction, because the intermediate **11** could not afford the benzene derivative **7** by the further reaction with **6**. Formation of both benzene derivatives **7** and **8** is assumed by the existence of **12** as an intermediate in this reaction.[13] Exclusive formation of the *cis*-cobalt complex **9** in this reaction exhibits the existence of **11** as an intermediate and the relatively high reactivity of intermediate **12** toward **6** compared with the reductive elimination to give *trans*-cobalt complex **10** (Fig. 2).

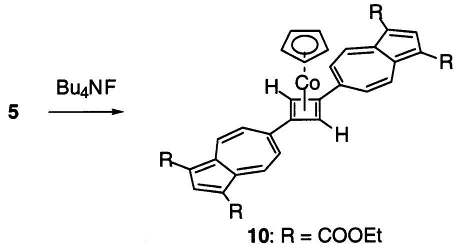
Redox potentials (V versus Ag/Ag$^+$) of these tri(6-azulenyl)benzene derivatives and [(6-azulenyl)cyclobutadiene]cobalt complexes measured by CV are summarized in Table 1. 1,3,5-Tri(6-azulenyl)benzene **7** in tetrahydrofuran exhibited an irreversible broad reduction wave centered at around −1.50 V upon CV. The wave was identified as barely separated three waves at −1.38, −1.46, and −1.55 V by differential pulse voltammetry (DPV). 1,2,4-Tri(6-azulenyl)benzene **8** showed a two-electron reduction wave at −1.31 V and a one-electron one at −1.63 V. In contrast to the reduction of **7**, the waves of **8** exhibited good reversibility at the scan rate of 100 mV s^{-1}. Therefore, the three 6-azulenyl substituents on benzene in a 1,2,4 relationship increased its electron-accepting properties because of the formation of a closed-shell dianionic structure.

The voltammogram of [tetra(6-azulenyl)cyclobutadiene]cobalt complex **2a** was characterized by quasi reversible two waves at −1.61 and −1.79 V and the next two irreversible waves at −1.91 and −2.09 V. The cobalt complex **2b** exhibited a one-electron transfer at less negative potentials compared with those of **2a**, but the next two- or three-electron transfer blended into one broad wave centered at −1.42 V. The less negative reduction potential of **2b** is attributable to the stabilization of the dianion state by the ethoxycarbonyl groups substituted in the five-membered ring. The voltammetric behavior of the compounds indicates that the ions of higher charge of **2a** and **2b** are considerably less stable under the reduction conditions.

The electrochemical reduction of **4** exhibited 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}. Complexes **5**, **9**, and **10** also showed similar reversible two-electron transfer upon CV, as indicated in Table 1. Formally, the reduction of **4**, **5**, **9**, and **10** corresponds to the formation of 20-electron cobalt complexes.[14]

The electrochemical oxidation of the cobalt complex **2b** exhibited two irreversible waves at 1.19 and 1.52 V upon CV. The electrochemical oxidation of the cobalt complexes **4**, **5**, **9**, and **10** also exhibited two irreversible waves at 0.80–0.88 and 1.33–1.52 V upon CV. The first irreversible wave is probably due to the Co(I) oxidation.[6a] The second one is attributable to the redox reaction of 6-azulenyl groups, based on analogy with those of **2b** and those of **4**, **5**, **9**, and **10**. The relatively less positive E_2^{ox} value of **10** (1.33 V) could be rationalized by the contribution of the conjugation between two 6-azulenyl groups and cyclobutadiene ring due to the least steric hindrance among these compounds. The electrochemical oxidation of the cobalt complex **2a** showed irreversible waves at 0.71–1.13 V owing to the lower oxidation potentials of azulene.

We have demonstrated the cobalt-mediated cyclooligomerization of mono- and di(6-azulenyl)acetylenes to afford novel 1,3,5- and 1,2,4-tri(6-azulenyl)benzenes and (η^5-cyclopentadienyl)[tetra- and di(6-azulenyl)-cyclobutadiene]cobalt complexes with redox activities.



Scheme 4.

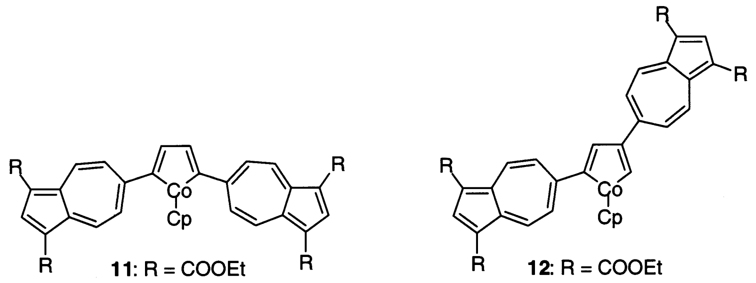


Figure 2.

Table 1. Redox potentials[a] of compounds **2a**, **2b**, **4**, **5**, and **7**–**10**

Sample	E_1^{ox}	E_2^{ox}	E_1^{red}	E_2^{red}	E_3^{red}
7[b]			(−1.38)[c]	(−1.46)[c]	(−1.55)[c]
8[b]			−1.31 (2e)	−1.63	
2a	(0.71)	(0.91), (1.13)[e]	−1.61	−1.79	(−1.91), (−2.09)[f]
2b	(1.19)	(1.52)	−1.24	(−1.42)[d]	
4	(0.88)	(1.48)	−1.37	−1.53	
5	(0.87)	(1.52)	−1.38	−1.53	
9	(0.82)	(1.45)	−1.34 (2e)		
10	(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 into one broad wave.

[e] E_3^{ox} value.

[f] E_4^{red} value.

These compounds represented the presumed multi-electron redox properties under the electrochemical conditions. Further studies of the metal-mediated cyclooligomerization of 6-azulenylacetylenes using other than $CpCo(CO)_2$ are now in progress.

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7. All new compounds were fully characterized by physical and spectral methods, selected spectral data for **2a**, **2b**, **4**, **5**, and **7**–**10** are given below. Compound **2a**: brown crystals; mp >300°C; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 246 (4.68), 307 (5.04), 395 (4.54); ^1H NMR ($CDCl_3$) $\delta=8.05$ (d, $J=10.5$ Hz, 8H), 7.91 (t, $J=3.8$ Hz, 4H), 7.46 (d, $J=10.4$ Hz, 8H), 7.33 (d, $J=3.8$ Hz, 8H), 4.78 (s, 5H). Compound **2b**: brown crystals; mp >300°C; 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); ^1H NMR ($CDCl_3$) $\delta=9.52$ (d, $J=10.9$ Hz, 8H), 8.86 (s, 4H), 7.90 (d, $J=10.9$ Hz, 8H), 4.91 (s, 5H), 4.42 (q, $J=7.1$ Hz, 16H), 1.44 (t, $J=7.1$ Hz, 24H). Compound **4**: reddish brown crystals; mp 161–167°C; 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); ^1H NMR ($CDCl_3$) $\delta=9.48$ (d, $J=11.3$ Hz, 4H), 8.77 (s, 2H), 7.76 (d, $J=11.3$ Hz, 4H), 4.88 (s, 5H), 4.41 (q, $J=7.2$ Hz, 8H), 1.43 (t, $J=7.2$ Hz, 12H), 0.30 (s, 18H). Compound **5**: reddish brown prisms; mp 286–288°C; 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); ^1H NMR ($CDCl_3$) $\delta=9.56$ (d, $J=11.1$ Hz, 4H), 8.75 (s, 2H), 7.82 (d, $J=11.1$ Hz, 4H), 4.88 (s, 5H), 4.44 (q, $J=7.1$ Hz, 8H), 1.46 (t, $J=7.1$ Hz, 12H), 0.29 (s, 18H). Compound **7**: pink crystals; mp >300°C; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 237 (4.94), 273 (4.68), 333 (5.18), 517 (3.36); ^1H NMR ($CDCl_3$) $\delta=9.88$ (d, $J=11.0$ Hz, 6H), 8.87 (s, 3H), 8.06 (d, $J=11.0$ Hz, 6H), 8.05 (s, 3H), 4.45 (q, $J=7.1$ Hz, 12H), 1.46 (t, $J=7.1$ Hz, 18H). Compound **8**: pink crystals; mp 150–153°C; UV–vis

(CH_2Cl_2) λ_{max}, nm (log ε) 237 (4.97), 271 (4.75), 337 (5.02), 515 (3.40); ^{1}H NMR ($CDCl_3$) $\delta=9.88$ (d, $J=11.0$ Hz, 2H), 9.59 (d, $J=11.0$ Hz, 2H), 9.58 (d, $J=11.0$ Hz, 2H), 8.87 (s, 1H), 8.79 (s, 2H), 8.05 (d, $J=11.0$ Hz, 2H), 7.92 (dd, $J=7.9$, 1.9 Hz, 1H), 7.91 (d, $J=1.9$ Hz, 1H), 7.77 (d, $J=7.9$ Hz, 1H), 7.70 (d, $J=11.0$ Hz, 2H), 7.68 (d, $J=11.0$ Hz, 2H), 4.46 (q, $J=7.1$ Hz, 4H), 4.39 (q, $J=7.1$ Hz, 8H), 1.48 (t, $J=7.1$ Hz, 6H), 1.42 (t, $J=7.1$ Hz, 6H), 1.41 (t, $J=7.1$ Hz, 6H). Compound **9**: brown crystals; mp 254°C; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 240 (4.83), 265 (4.63), 313 (4.61), 361 (4.72), 377 (4.69); ^{1}H NMR ($CDCl_3$) $\delta=9.51$ (d, $J=11.1$ Hz, 4H), 8.76 (s, 2H), 7.80 (d, $J=11.1$ Hz, 4H), 4.92 (s, 2H), 4.80 (s, 5H), 4.43 (q, $J=7.1$ Hz, 8H), 1.45 (t, $J=7.1$ Hz, 12H). Compound **10**: brown crystals; mp >300°C; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 240 (4.81), 268 (4.64), 341 (4.61), 362 (4.64), 465 (4.71); ^{1}H NMR ($CDCl_3$) $\delta=9.50$ (d, $J=11.1$ Hz, 4H), 8.72 (s, 2H), 7.53 (d, $J=11.1$ Hz, 4H), 5.56 (s, 2H), 4.65 (s, 5H), 4.43 (q, $J=7.1$ Hz, 8H), 1.45 (t, $J=7.1$ Hz, 12H).

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