Organometallic Dehydro[14]annulenes Containing Vollhardt's Cyclobutadiene: Are CpCo-Complexed Cyclobutadienes More Aromatic than Benzene?

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Pd-catalyzed coupling of 1,2-diethynyl-3,4-(bistrimethylsilyl)cyclobutadienecyclopentadienylcobalt to a series of 1-iodo-2-(trimethylsilylethynyl)benzenes and 1-chloro-4-trimethylsilylbut-1-ene-3-yne is followed by desilylation with potassium carbonate. $Cu(OAc)_2$-promoted oxidative ring closure leads to dehydro[14]annulenes and dehydro[14]benzoannulenes fused to a cyclobutadiene(cyclopentadienylcobalt) complex. Five of these fused dehydroannulenes were structurally characterized. ^{1}H NMR spectroscopy of the organometallic dehydro[14]annulenes incorporating the (bistrimethylsilyl)cyclobutadiene(cyclopentadienylcobalt) unit suggested that the aromaticity of the fused cyclobutadiene complex might be stronger than that of benzene according to the ring-current criterion.

Introduction

We describe the synthesis and structural characterization of novel CpCo(cyclobutadieno)-fused dehydroannulenes and dehydrobenzoannulenes and show by analysis of their ^{1}H NMR spectra that the cyclobutadiene in cyclobutadiene(cyclopentadienylcobalt) could be more aromatic than benzene.

Dehydroannulenes and dehydrobenzoannulenes have experienced an explosive renaissance, and representatives of different topologies have been prepared recently.[1−5] These macrocycles are fascinating structures in their own right *and* can serve as precursors to polydiacetylenes, carbon-onions, -ropes, and -tubes, and fullerene-60. The original interest in dehydroannulenes, first synthesized in the 1960s, was the quest for their aromaticity. Are macrocycles, made of benzene and alkyne units, aromatic even though they do show bond alternation between single and triple bonds? According to recent theoretical and experimental work by Vollhardt and Matzger[6] and Haley,[7] dehydrobenzoannulenes *are* aromatic and follow Hückel's $[4n+2]$ rule the very same way benzene does.

While a large number of purely organic dehydroannulenes have been made, much less is known about fused organometallic dehydroannulenes and derivatives of organometallic benzocyclynes.[8] This may be due to a misconception about their stability and the laborious access to suitable organometallic modules. Organometallic dehydroannulenes (a) are attractive as aesthetically pleasing synthetic targets, (b) can divulge the degree of aromaticity of the fused organometallic complex according to Mitchell,[9] (c) may display NLO activity, and (d) their pyrolysis could lead to metal-containing nanostructures. Herein we describe the synthesis, spectroscopic and structural characterization of a series of organometallic cyclobutadieno-fused dehydroannulenes utilizing a [6+4+4] annulation strategy originally developed by Vollhardt and Youngs[10] to access [14]benzocyclynes.

Results and Discussion

Syntheses. Reaction of Vollhardt's cyclobutadiene[11] (**1**) with a series of 1-iodo-2-(trialkylsilylethynyl)benzenes **2a**−**d** or **5a,b** under Pd/Cu catalysis in piperidine as

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[1] (a) Haley, M. M.; Pak, J. J.; Brand, S. C. *Top. Curr. Chem.* **1999**, *201*, 81. (b) Diederich, F. *J. Chem. Soc., Chem. Commun.* **2001**, 219. (c) Diederich, F.; Gobbi, L. *Top. Curr. Chem.* **1999**, *201*, 43. (d) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2633. (e) Faust, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2825. (f) For novel aromatics, see an excellent "Symposium in Print": *Tetrahedron* **2001**, *57*, 3507−3808.

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[5] Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81.

[6] Matzger, A. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1998**, *39*, 6791.

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[8] Altmann, M.; Friedrich, J.; Reuter, R.; Enkelmann, V.; Bunz, U. H. F. *J. Am. Chem. Soc.* **1997**, *119*, 1472. Bunz, U. H. F.; Roidl, G.; Altmann, M.; Enkelmann, V.; Shimizu, K. D. *J. Am. Chem. Soc.* **1999**, *121*, 10719. Bunz, U. H. F. *Top. Curr. Chem.* **1999**, *201*, 131. Bunz, U. H. F. *Synlett* **1997**, 1117.

[9] (a) Mitchell, R. H.; Chen, Y. S.; Khalifa, N.; Zhou, P. Z. *J. Am. Chem. Soc.* **1998**, *120*, 1785. (b) Schleyer, P. v. R.; Kiran, B.; Simion, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **2000**, *122*, 510. (c) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301. (d) For a discussion of the connection of aromaticity and vinylic $^3J_{HH}$ coupling constants see: Scott, L. T.; Kirms, M. A.; Günther, H.; Puttkammer, H. *J. Am. Chem. Soc.* **1983**, *105*, 1372.

[10] Baldwin, K. P.; Matzger, A. J.; Scheiman, D. A.; Tessier, C. A.; Vollhardt, K. P. C.; Youngs, W. J. *Synlett* **1995**, 1215. Dosa, P. I.; Erben, C.; Iyer, V. S.; Vollhardt, K. P. C.; Wasser, I. M. *J. Am. Chem. Soc.* **1999**, *121*, 10430.

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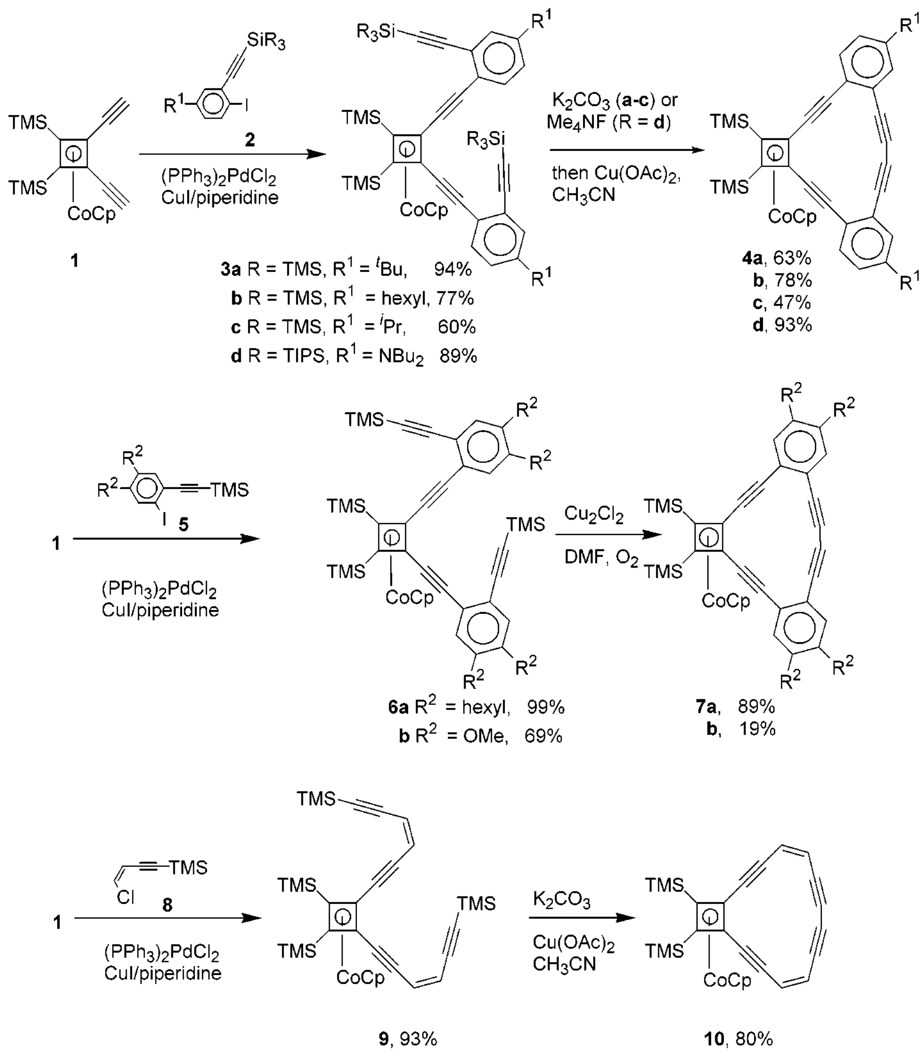
Scheme 1



solvent furnishes the appended complexes **3** and **6** in yields ranging from 60 to 99%. Deprotection of **3a**−**d** is followed by treatment with Cu(OAc)$_2$ in acetonitrile utilizing a procedure by Vögtle[12] to afford **4a**−**d** in fair to excellent yields (47−93%) as sole products after silica gel chromatography and crystallization from hexanes. In the case of **6**, deprotection was not necessary. Reaction with Cu$_2$Cl$_2$ in DMF at 60 °C led to an in situ loss of the trimethylsilyl groups that was followed by oxidative ring closure under formation of the butadiyne bridge. While **7a** forms in an 89% yield, the yield for the dimethoxycycle **7b** (19%) was disappointingly low. No side products were detected, but some unreacted starting material **6b** was recovered in addition to copious amounts of a dark and insoluble material, which stuck to the chromatography support. The decomposition probably arises from uncontrolled oxidation of the electron-rich conjugated starting material/intermediate(s).

Pd-catalyzed coupling of **1** to *cis*-1-chloro-4-trimethylsilylbut-1-en-3-yne (**8**)[13] leads to the tetrayne **9** in almost quantitative yield. Removal of the silyl protecting group and ring closure with Cu(OAc)$_2$ in acetonitrile furnishes **10** in an 80% yield after chromatography. The cyclic products **4**, **7**, and **10** are stable crystalline or microcrystalline compounds under ambient conditions. They can be stored for extended periods of time and melt without decomposition. The ^{1}H NMR spectroscopic properties of **4** and **7** suggest that the fused cyclobutadiene complex is aromatic. More instructive are the ^{1}H NMR spectra of **9** and **10** and their congeners **11**−**14** and **16**, specifically the resonance of the vinyl protons that are part of the dehydro[14]annulene (see Scheme 2).[14b,d]

NMR Spectroscopy and Aromaticity of 10. Mitchell[9a] has recently developed a model for the determination of the aromaticity of organometallic half-sandwich π-complexes by annelating them to dimethyldihydropyrene. The ^{1}H NMR shifts of the methyl groups placed above or below the plane of the aromatic perimeter are sensitive measures of the aromaticity (or the lack thereof) of the annelated, cyclically conjugated species. The external protons of the dimethyldihydropyrene perimeter are likewise useful in that regard; while the effects are smaller in size, they match the results from the analysis of the shift information of the methyl

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[12] Vögtle, F.; Berscheid, R. *Synthesis* **1992**, 58.

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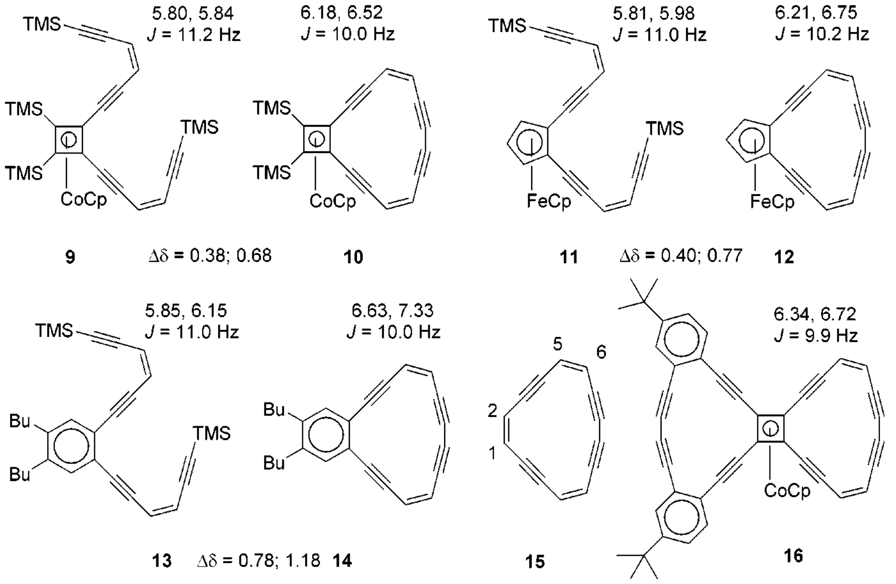
Scheme 2[a]



[a] Compounds **11**–**14**[14b] and **16**[14d] are reported in the literature. The Δδ values are determined between the open and the closed forms (i.e., between **9** and **10**, **11** and **12**, and **13** and **14**). The larger the Δδ values are, the more aromatic the annelated dehydro[14]annulene is. Consequently, the bond-fixing ability of the annelated moiety on the dehydroannulene is decreased. The coupling constant of **14** was redetermined at higher resolution and changed from 10.2[14b] to 10.0 Hz.

protons. The same concept of evaluating the aromaticity of fused π-perimeters can be used for the (hitherto unknown) [14]dehydroannulene **15**, which must be aromatic according to Hückel's $[4n+2]$ rule with $n = 3$. As a consequence, protons attached to the 5,6-positions will experience a downfield shift caused by the deshielding effect of the ring current. The fusion of *any* aromatic unit to the 1,2-double bond should weaken the ring current of the central dehydro[14]annulene as a consequence of bond fixing, which leads to an upfield shift of the protons attached to C5 and C6.

The vinylic protons located on C5 and C6 are thus "sensors" for the bond-fixing ability and indicative of the relative aromaticity of the fused unit. One has to evaluate the shifts of the 5,6-protons in **10**, **12**, and **14** as well as their $^3J_{\mathrm{HH}}$ coupling constants[9c,d] to compare the aromaticity of cyclobutadiene(cyclopentadienylcobalt) to that of ferrocene and benzene. The cycle in which the vinylic 5,6-protons of the dehydro[14]annulene are shifted most upfield (cf. **10, 12,** and **14**) would, in a first approximation, feature the annelated ring with the highest bond-fixing ability, which in turn should be the most aromatic (Scheme 2), if other structural effects on the chemical shift of these protons can be excluded. According to this model, cyclobutadiene(cyclopentadienylcobalt) is the most "aromatic", closely followed by ferrocene, and interestingly enough, the least aromatic structure in this series would be benzene.

One may argue that the observed effects are not due to the aromaticity of ferrocene or CpCo(cyclobutadiene) but have to be ascribed instead to the local magnetic effect of the organometallic species. To exclude this possibility, the open, nonaromatic (with respect to the dehydro[14]annulene) precursors **9**, **11**, and **13** can be compared to their closed, aromatic dehydro[14]annulene analogues. As a consequence, the most aromatic entity in this series fused to the dehydro[14]annulene (either ferrocene, (CpCo)cyclobutadiene, or benzene) should display *the smallest downfield shift (Δδ) of the respective 5,6-H's upon ring closure* because the gain of aromaticity for the newly formed dehydro[14]annulene would be the least. If we apply this criterion, the cyclobutadiene complex still is the most aromatic species but only minutely more so than ferrocene. The dehydroannulene **14** containing the benzene ring shows the greatest shift of its 5,6-protons to lower-field values when compared to its precursor **13**, suggesting that benzene is *less* aromatic than either ferrocene or cyclobutadiene(cyclopentadienylcobalt). An important criterion for aromaticity, introduced by Scott and Günther,[9c] is the magnitude of the $^3J_{\mathrm{HH}}$ coupling constant of the vinylic protons (5,6-positions) in the open precursors (**9**, **11**, and **13**) and as the closed rings. In the open precursors, there is perfect bond alternation, and the $^3J_{\mathrm{HH}}$ coupling constant is large, ranging from 11.0 to 11.2 Hz. Upon ring closure, the bond order of the double bond decreases by the aromatic delocalization and the coupling constant is diminished to 10.2 Hz in **12**, 10.0 Hz in **14**, and 10.0 Hz in **10**, suggesting that the cyclobutadiene complex has less of a localizing power than ferrocene. We know[14d] that (a) the CpCo part is kinked away from the dehydro[14]annulene and (b) the geometry of the dehydroannulene part must be slightly different for **10**, **12**, and **14**. The angle at which the two alkyne groups protrude from benzene and ferrocene toward cyclobutadieneCpCo increases from 60° to 90°, changing the gross geometry of the annelated dehydro[14]annulene. Rehybridization and the concurrent geometric change affect the vinylic $^3J_{\mathrm{HH}}$ coupling constant. As an example, $^3J_{\mathrm{HH}}$ increases in cycloalkenes with ring size (cyclopropene, 1.3 Hz; cyclohexene, 8.8 Hz).[15] While geometric rearrangements in the fused dehydroannulenes **10**, **12**, and **14** are certainly small, so are the differences in the coupling constants, which vary by <0.2 Hz. Reliable information about molecular geometries is not available due to the lack of single-crystal

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(15) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*, 5th ed.; Thieme: New York, 1995; p 108.

Table 1. Electronic Spectra of 4, 7, and 10 in Solution and in Thin Films

	4a	**4b**	**4c**	**5d**	**7a**	**7b**	**10**
UV/vis ($CHCl_3$)	274, 337	275, 336	275, 337	321	275, 337	282, 346	262, 356
UV/vis (film)	218, 275, 338	225, 280, 343	223, 278, 339	221, 325	234, 290, 356	224, 287, 353	202, 265, 364

Table 2. Details of the Single-Crystal Structure Solution of 4a–d and 7b

compd	**4a**	**4b**	**4c**	**4d**	**7b**
	$C_{43}H_{47}CoSi_2$	$C_{47}H_{55}CoSi_2$	$C_{41}H_{43}CoSi_2$	$C_{51}H_{65}CoN_2Si_2$	$C_{43}H_{47}CoO_4Si_2$
a	19.377	9.792	9.542	16.081	9.604
b	12.225	11.254	28.183	15.562	13.677
c	33.876	20.833	14.258	20.108	15.010
α	90	100.029	90	90	113.181
β	90	103.301	106.021	99.181	93.442
γ	90	98.495	90	90	100.639
Z	8	2	4	4	2
V	8025.0	2157.3	3685.0	4967.2	1760.6
ρ_{calcd}	1.124	1.132	1.173	1.098	1.296
space group	Pn_a2_1	P-1	$P2_1/n$	$P2_1/c$	P-1
absorption correction	semiempirical	none	none	semiempirical	semiempirical
no. of reflections collected	45 269	12 884	21 742	24 659	11 468
no. of reflections observed	13 094	7646	6526	7158	6207
weighing scheme	$I > 2\delta(I)$	$I > 2\delta(I)$	$I > 2\delta(I)$	$I > 2\delta(I)$	$I > 2\delta(I)$
R	0.0694	0.0617	0.0527	0.0881	0.0518
absorption coefficient	0.514	0.483	0.557	0.426	0.594
crystal system	orthorhombic	triclinic	monoclinic	monoclinic	triclinic
λ (nm)	0.71073	0.71073	0.71073	0.71073	0.71073

structure analyses, and one should be careful not to overinterpret the $^3J_{HH}$ coupling constants as being reliable *numeric* measures for the relative aromaticity of cyclcobutadiene(cyclopentadienylcobalt).

Optical Spectroscopy, Thermal Behavior, and Single-Crystal Structure Determination of the Organometallic Dehydroannulenes 4a–d and 7a,b. The main optical transitions of **4**, **7**, and **10** in solution and in the solid state are listed in Table 1. None of the organometallic dehydroannulenes are fluorescent or solvatochromic besides **7a**, in which $\lambda_{max}(CHCl_3)$ is significantly different from λ_{max}(film), probably due to the overlap of the benzene rings in the solid state. All of the organometallic dehydroannulenes melt undecomposed and do not undergo any solid-state reaction, with the exception of **4a**.

Crystallization of **4a**–**d** and of **7b** from dichloromethane furnished suitable and well-developed specimen. Their packing diagrams are shown in Figures 1–5. Bond lengths and bond angles are in excellent agreement with reported values and are almost identical to those obtained for the parent **4e** (R = H).[14a] The packing of the cycles, particularly that of **4a**, is of interest. Noticeably, all of the cycles crystallize in different space groups with exceptions of **4b** and **7b**, which crystallize in P-1. Consequently, the substituents on the dehydroannulene part of the molecules have a decisive influence on the packing behavior.

Cycle **4a** shows a noncentrosymmetric packing and undergoes a solid-state reaction at >189 °C despite the absence of any close contacts between the butadiyne groups of different molecules. This finding almost certainly rules out polydiacetylene formation. However, the amorphous nature of the formed material makes its characterization difficult.

The other derivatives likewise pack in a fashion so that the butadiyne units avoid contacts. A good example is the hexyl-substituted **4b**, where all of the 14-dehydroannulene parts lie in the same plane, with the CpCo and the hexyl groups acting as insulators between neighboring planes. In this arrangement, the dehydroannulene portions and, as a consequence, the butadiyne groupings are effectively separated from each other, and no solid-state reactivity is observed. The other interesting case is that of **4d** in which the benzene groups are dibutylamino-substituted. The benzene rings in **4d** lie on top of each other but are completely coplanar. The interplanar distance between the two benzene rings is 3.63 Å, suggesting van der Waals contacts. The unusual coplanar positioning of the benzene rings is due to an effective cancellation of the dipole moments in this donor–acceptor

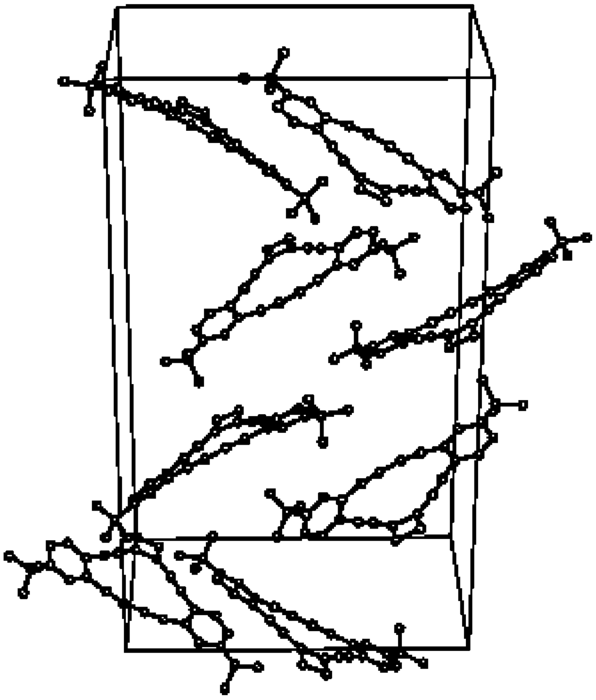

Figure 1. Herringbone-type packing of **4a** in the solid state; for clarity, the CpCo units and the trimethylsilyl substituents have been omitted.

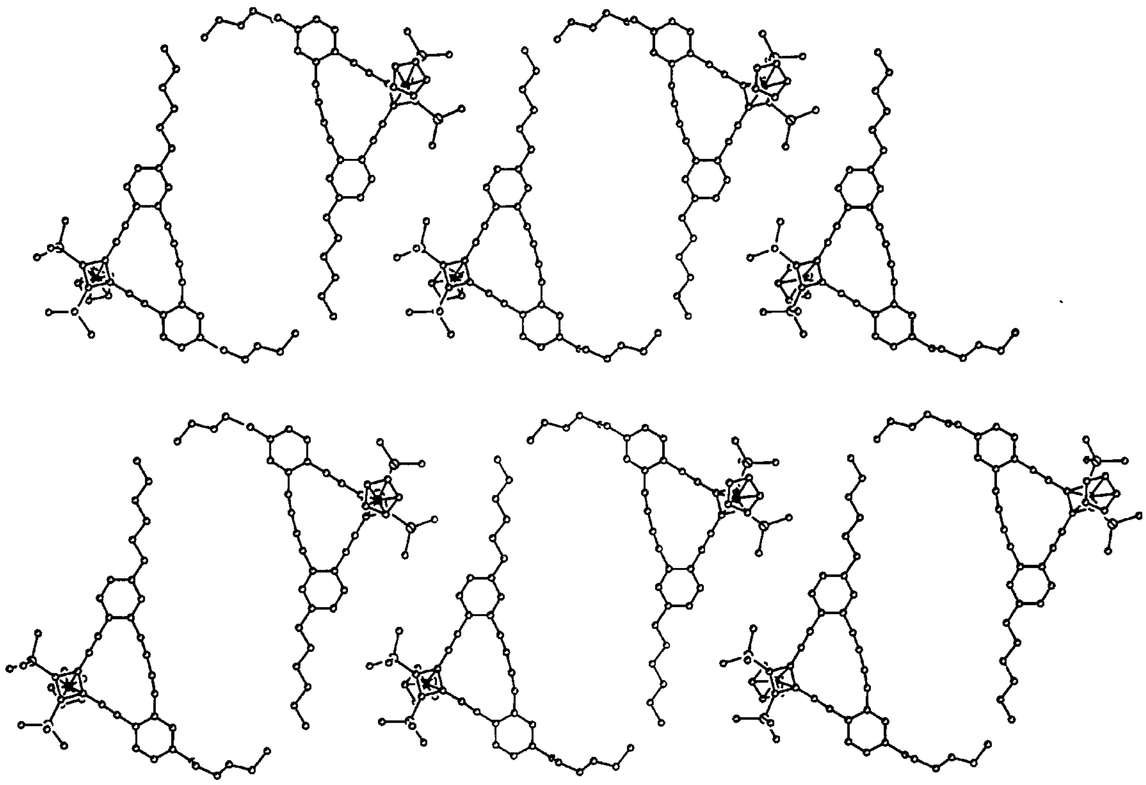

Figure 2. Bilayer-type packing of **4b** in the solid state.

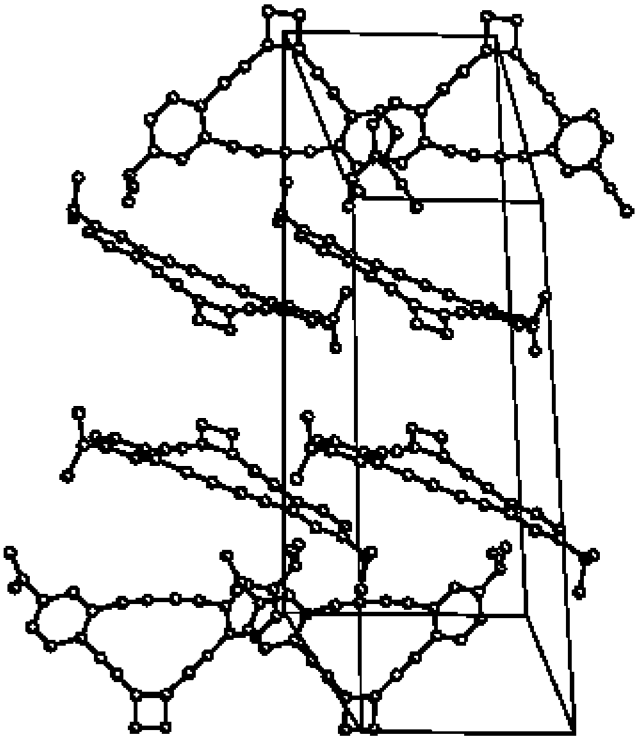

Figure 3. Herringbone-type packing of **4c** in the solid state; for clarity, the CpCo units and the trimethylsilyl substituents have been omitted.

substituted dehydroannulene as well as an attractive electrostatic force in the solid state.

Conclusions

We have synthesized a series of organometallic dehydroannulenes and dehydrobenzoannulenes through a combination of Pd- and Cu-catalyzed couplings utilizing Vollhardt's and Young's [6+4+4] annulation strategy.[10] The organometallic dehydrobenzoannulenes **4** and **7** display substituent-dependent packing behavior. Cycle **4a** shows a noncentrosymmetric packing motif and thus may be NLO active.[7,8] The organometallic dehydroannulene **10** was synthesized utilizing the same methodology. Comparison of the ^{1}H NMR spectra of **10** to those of **12** and **14** revealed that cyclobutadiene(cyclopentadienylcobalt) may be more aromatic than benzene according to the ring-current criterion. We are currently preparing organometallic dehydro[12]- and -[18]annulenes to further corroborate the highly aromatic character of (cyclopentadienylcobalt)-stabilized cyclobutadiene complexes.

Experimental Section

General. All reagents were of commercial grade and used as obtained. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 300 or a Varian Mercury 400 spectrometer. Coupling constants are accurate to ±0.2 Hz. To determine the vinylic coupling constant in **10**, the resolution was enhanced to 50 data points/Hz giving an accuracy of ±0.03 Hz. The mass spectra were measured on a VG 70SQ spectrometer. IR spectra were obtained using a Perkin-Elmer FTIR 1600 spectrometer on NaCl plates. X-ray structure analyses were obtained at 293 K using a Bruker SMART APEX CCD-based diffractometer system equipped with a Mo-target X-ray tube.

Synthesis of 3a. A round-bottom flask was charged with **1** (190 mg, 0.520 mmol), 4-iodo-3-(trimethylsilylethynyl)-*tert*-butylbenzene[16] (390 mg, 1.10 mmol), $(PPh_3)_2PdCl_2$ (0.01 equiv), CuI (0.03 equiv), and piperidine (10 mL). After purging the reaction vessel with N_2, we stirred the reaction mixture at room temperature for 18 h. After aqueous workup with dichloromethane, the brown mixtures were chromatographed on silica gel with 8:2 hexanes:EtOAc to give **3a** (340 mg, 94%) as a red oil. IR (neat): ν 2955, 2333, 2266, 1244, 822 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 18H), 0.11 (s, 18H), 1.27 (s, 9H), 4.97 (s, 5H), 7.21 (dd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.9$ Hz,

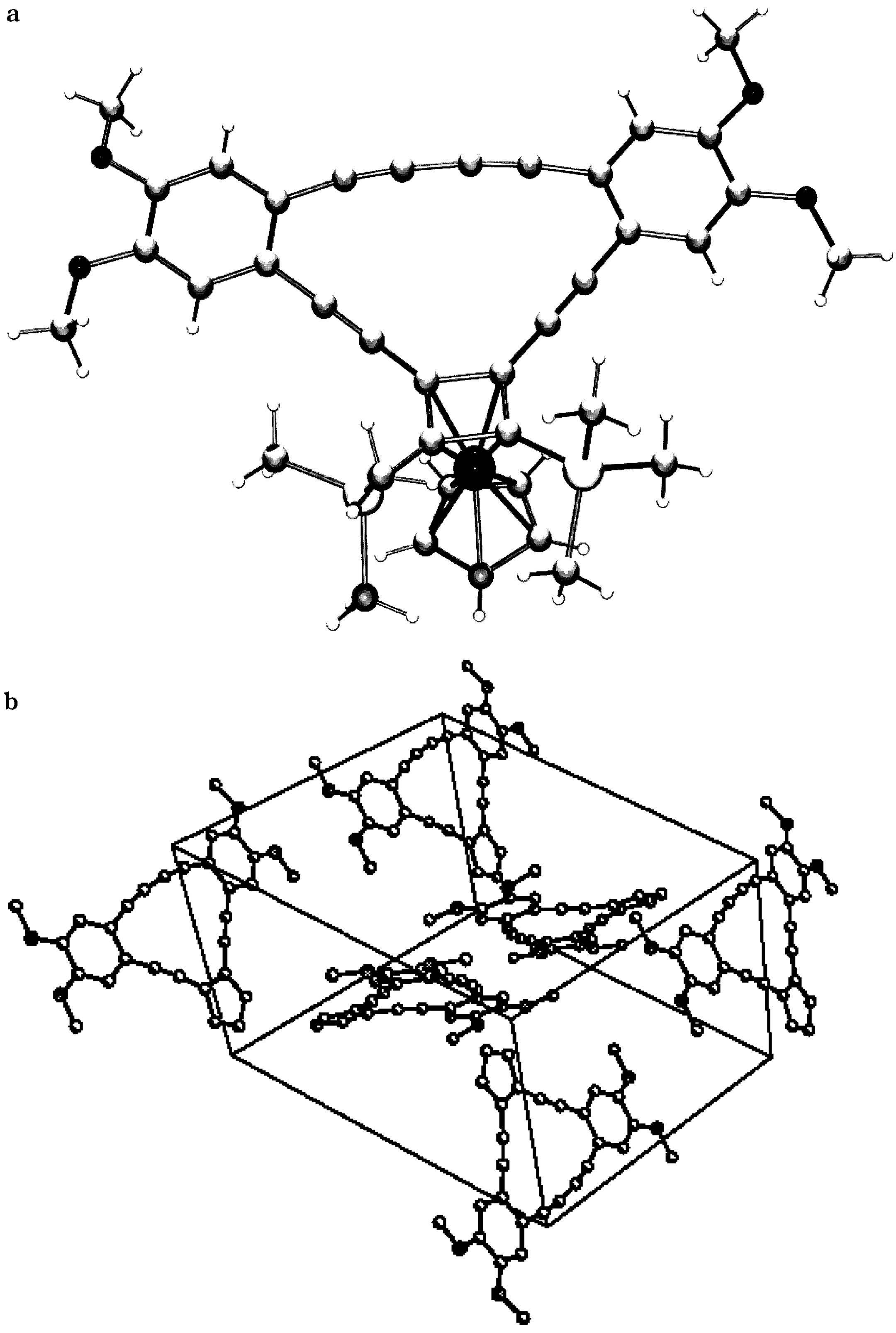

Figure 4. (a) Molecular structure of **7b**. (b) Packing of **7b** in the solid state; for clarity, the CpCo units and the trimethylsilyl substituents have been omitted.

2H), 7.32 (d, $^3J_{HH} = 8.2$ Hz, 2H), 7.42 (d, $^4J_{HH} = 1.9$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.16, 0.51, 30.96, 34.60, 68.22, 72.50, 81.51, 89.95, 90.12, 97.27, 104.48, 123.81, 123.93, 125.46, 132.02, 150.46. MS (EI) *m*/*z*: M^+ calcd for $C_{49}H_{65}CoSi_4$, 824.3495; found, 824.3499 ($E = 0.5$ ppm).

Synthesis of 3b. In a procedure analogous to that described in the synthesis of **3a**, **1** (300 mg, 0.820 mmol) and 4-iodo-3-(trimethylsilylethynyl)hexylbenzene[16] (660 mg, 1.72 mmol) were reacted. Chromatography on silica gel with hexanes gives **3b** (540 mg, 77%) as a red oil. IR (neat): ν 2955, 2922, 2844, 2155, 1244, 842 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 18H), 0.23 (s, 18H), 0.84−0.87 (m, 6H), 1.24−1.27 (m, 12H), 1.53−1.57 (m, 4H), 2.51 (t, $^3J_{HH} = 7.6$ Hz, 4H), 4.96 (s, 5H), 7.00 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.7$ Hz, 2H), 7.25 (d, $^4J_{HH} = 1.7$ Hz, 2H), 7.31 (d, $^3J_{HH} = 8.0$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.14, 0.52, 14.09, 22.58, 28.82, 31.04, 31.67, 35.61,

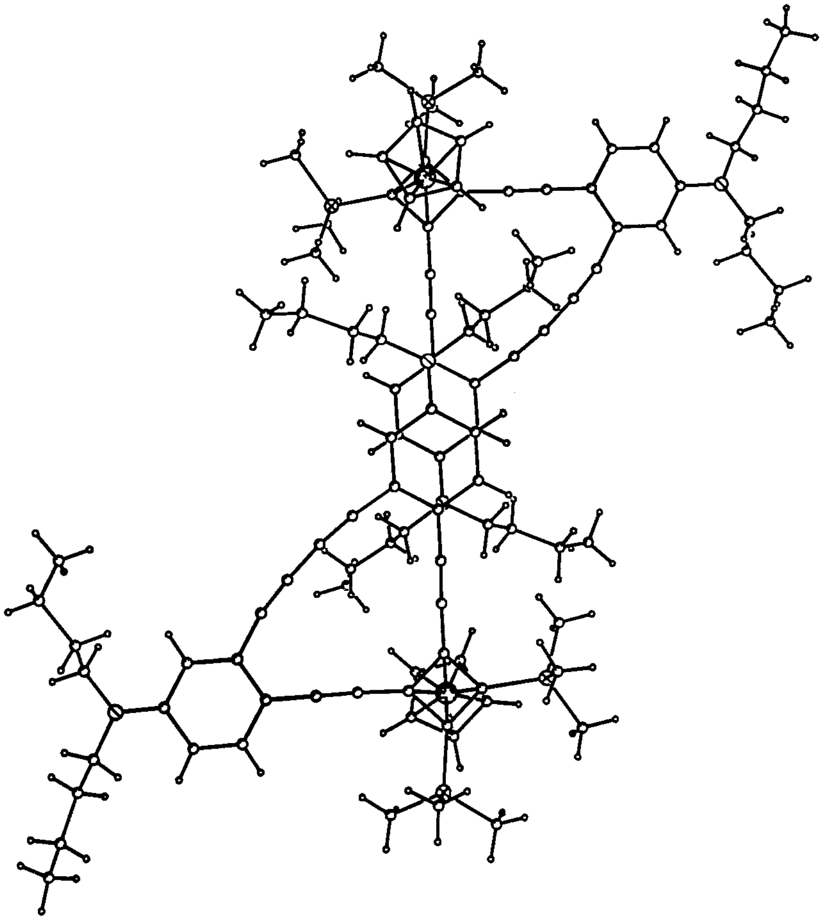

Figure 5. Face-to-face packing of **4d** in the solid state.

68.24, 72.53, 81.62, 89.99, 90.16, 97.60, 104.25, 123.98, 124.22, 128.47, 132.17, 132.91, 142.35. MS (EI) *m*/*z*: M^+ calcd for $C_{53}H_{73}CoSi_4$, 880.4121; found, 880.4161 (E = 4.5 ppm).

Synthesis of 3c. In a procedure analogous to the that described in the synthesis of **3a**, **1** (200 mg, 0.540 mmol) and 4-iodo-3-(trimethylsilylethynyl)isopropylbenzene[16] (389 mg, 1.13 mmol) were reacted. Chromatography on silica gel with hexanes gives **3c** (270 mg, 60%) as a red oil. IR (neat): ν 2904, 2155, 1244, 843 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 18H), 0.23 (s, 18H), 1.20 (d, $^3J_{HH} = 7.0$ Hz, 12H), 2.83 (sept, $^3J_{HH} = 7.0$ Hz, 2H), 4.96 (s, 5H), 7.06 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.7$ Hz, 2H), 7.29 (d, $^4J_{HH} = 1.7$ Hz, 2H), 7.33 (d, $^3J_{HH} = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.16, 0.52, 23.61, 33.90, 68.68, 72.36, 81.62, 89.93, 90.17, 97.53, 104.31, 124.13, 124.24, 126.59, 130.98, 132.30, 148.24. MS (EI) *m*/*z*: M^+ calcd for $C_{47}H_{61}CoSi_4$, 796.3182; found, 796.3176 (E = 0.8 ppm).

Synthesis of 3d. In a procedure analogous to that described in the synthesis of **3a**, **1** (200 mg, 0.540 mmol) and 4-iodo-3-(trimethylsilylethynyl)dibutylaminobenzene[7b] (700 mg, 1.37 mmol) were reacted. Chromatography on silica gel with hexanes gives **3d** (548 mg, 89%) as a red oil. IR (neat): ν 2944, 2867, 2144, 1594, 1500, 1461, 1367, 1227, 1094, 844 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 18H), 0.92 (t, $^3J_{HH} = 7.3$ Hz, 6H), 1.07 (s, 21H), 1.28−1.35 (m, 4H), 1.47−1.55 (m, 4H), 3.22 (t, $^3J_{HH} = 7.9$ Hz, 4H), 4.91 (s, 5H), 6.47 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 2.6$ Hz, 2H), 6.66 (d, $^4J_{HH} = 2.6$ Hz, 2H), 7.22 (d, $^3J_{HH} = 8.1$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.46, 11.36, 13.92, 29.27, 50.63, 18.80, 20.23, 69.43, 71.21, 81.28, 87.27, 90.99, 92.87, 107.08, 111.79, 113.01, 115.74, 125.71, 133.47, 146.80. MS (EI) *m*/*z*: M^+ calcd for $C_{69}H_{107}CoN_2Si_4$, 1135.91; found, 1135.59.

***tert*-Butyldehydroannulene 4a.** A round-bottom flask was charged with **3a** (283 mg, 0.420 mmol), K_2CO_3 (160 mg, 1.16 mmol), and methanol (10 mL). The resulting mixture was stirred at ambient temperature for 18 h. Aqueous workup followed by removal of the solvent gives a dark red oil. To the flask were added $Cu(OAc)_2$ (2.00 g, 11.0 mmol) and acetonitrile (50 mL). The reaction mixture was heated to 80 °C for 6 h after which the mixture was washed with water and extracted with ethyl ether. Chromatography on silica gel with hexanes yields **4a** (177 mg, 63%) as a red-brown solid. Mp: 189 °C dec. IR (neat): ν 2956, 2355, 2177, 1477, 1244, 844 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.26 (s, 18H), 1.31 (s, 18H), 4.91 (s, 5H), 7.34 (dd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.9$ Hz, 2H), 7.40 (d, $^3J_{HH} = 8.2$ Hz, 2H), 7.43 (d, $^4J_{HH} = 1.9$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.45, 31.05, 34.88, 68.40, 73.60, 79.00, 84.43, 90.33, 91.85, 81.31, 123.09, 126.25, 127.02, 127.40, 130.09, 150.37. MS (EI) *m*/*z*: M^+ calcd for $C_{43}H_{47}CoSi_2$, 678.2548; found, 678.2554 (E = 0.9 ppm). UV/vis ($CHCl_3$): λ 274.1 (ϵ = 12 598 cm^{-1} M^{-1}), 337 (ϵ = 11 527 cm^{-1} M^{-1}). UV/vis (film): λ 218, 275, 338. Elemental analysis, calcd: C, 76.07; H, 6.98. Found: C, 75.92; H, 7.07.

Hexyldehydroannulene 4b. In a procedure analogous to that described in the synthesis of **4a**, **3b** (280 mg, 0.380 mmol), K_2CO_3 (170 mg, 1.23 mmol), and $Cu(OAc)_2$ (2.00 g, 11.0 mmol) were reacted to give **4b** (217 mg, 78%) as a red-brown solid. Mp: 175 °C. IR (neat): ν 2924, 2855, 2366, 2177, 1405, 1244, 1200, 849 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.27 (s, 18H), 0.85−0.89 (m, 6H), 1.26−1.29 (m, 12H), 1.52−1.60 (m, 4H), 2.56 (t, $^3J_{HH} = 7.5$ Hz, 4H), 4.92 (s, 5H), 7.12 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.8$ Hz, 2H), 7.25 (d, $^4J_{HH} = 1.8$ Hz, 2H), 7.36 (d, $_3J_{HH} = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.39, 14.07, 22.56, 28.82, 30.97, 31.65, 35.73, 68.31, 73.47, 79.11, 84.19, 90.31, 91.80, 81.22, 123.19, 127.52, 129.15, 129.90, 130.15, 142.16. MS (EI) *m*/*z*: M^+ calcd for $C_{47}H_{55}CoSi_2$, 734.3174; found, 734.3172 (E = 0.3 ppm). UV/vis ($CHCl_3$): λ 275.1 (ϵ = 11 302 cm^{-1} M^{-1}), 336 (ϵ = 10 553 cm^{-1} M^{-1}). UV/vis (film): λ 225, 280, 343. Elemental analysis, calcd: C, 76.80; H, 7.54. Found: C, 76.71; H, 7.41.

Isopropyldehydroannulene 4c. In a procedure analogous to that described in the synthesis of **4a**, **3c** (170 mg, 0.260 mmol), K_2CO_3 (110 mg, 0.80 mmol), and $Cu(OAc)_2$ (1.20 g, 6.61 mmol) were reacted to give **4c** (80 mg, 47%) as a red-brown solid. Mp: 188 °C. IR (neat): ν 2956, 2344, 2178, 1405, 1244, 833 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.25 (s, 18H), 1.23 (d, $^3J_{HH} = 6.9$ Hz, 12H), 2.89 (sept, $^3J_{HH} = 6.9$ Hz, 2H), 4.97 (s, 5H), 7.20 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.6$ Hz, 2H), 7.32 (d, $^4J_{HH} = 1.6$ Hz, 2H), 7.41 (d, $^3J_{HH} = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.39, 23.60, 34.00, 68.20, 73.81, 79.01, 84.23, 90.29, 91.73, 81.23, 123.24, 127.31, 127.67, 128.01, 130.27, 148.03. MS (EI) m/z: M$^+$ calcd for $C_{47}H_{55}CoSi_2$, 734.3174; found, 734.3172 ($E = 0.3$ ppm). UV/vis ($CHCl_3$): λ 275 (ϵ = 13 671 cm^{-1} M^{-1}), 337 (ϵ = 12 842 cm^{-1} M^{-1}). UV/vis (film): λ 223, 278, 339. Elemental analysis, calcd: C, 75.66; H, 6.66. Found: C, 75.53; H, 6.76.

Dibutylaminedehydroannulene 4d. A round-bottom flask was charged with **3d** (0.240 g, 0.212 mmol), Me_4NF (300 mg, 3.23 mmol), diethyl ether (10 mL), and DMSO (10 mL). The resulting mixture was stirred at ambient temperature for 18 h. Aqueous workup followed by removal of the solvent gives a dark red oil. To the flask were added $Cu(OAc)_2$ (0.780 g, 4.29 mmol) and acetonitrile (50 mL). The reaction mixture was heated to 80 °C for 10 h after which the mixture was washed with water and extracted with hexanes. Chromatography on silica gel with hexanes yields **4d** (149 mg, 93%) as an orange, crystalline solid. Mp: 148 °C. IR (neat): ν 2930, 2866, 2355, 1595, 1494, 1361, 1239, 1088, 838 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.25 (s, 18H), 0.95 (t, $^3J_{HH} = 5.8$ Hz, 6H), 1.29−1.37 (m, 4H), 1.49−1.57 (m, 4H), 3.24 (t, $^3J_{HH} = 7.4$ Hz, 4H), 4.89 (s, 5H), 6.57 (dd, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 2.5$ Hz, 2H), 6.63 (d, $^4J_{HH} = 2.5$ Hz, 2H), 7.28 (d, $^3J_{HH} = 8.8$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.38, 13.95, 17.84, 29.23, 50.71, 69.30, 71.41, 81.03, 78.29, 84.66, 89.31, 90.92, 112.25, 112.41, 116.52, 124.35, 131.41, 146.70. UV/vis ($CHCl_3$): λ 321 (ϵ = 40 557 cm^{-1} M^{-1}). UV/vis (film): λ 221, 325. MS (EI) m/z: M$^+$ calcd for $C_{51}H_{65}CoN_2Si_2$, 820.40; found, 820.38.

Synthesis of 6a. In a procedure analogous to that described in the synthesis of **3a**, **1** (200 mg, 0.540 mmol) and 1,2-dihexyl-4-trimethylsilylethynyl-5-iodobenzene (551 mg, 1.14 mmol) were reacted. Chromatography on silica gel with 8:2 hexanes: EtOAc gives **6a** (567 mg, 99%) as a red oil. IR (neat): ν 2956, 2911, 2844, 2155, 1238, 839 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 18H), 0.23 (s, 18H), 0.85−0.90 (m, 6H), 1.27−1.33 (m, 12H), 1.49−1.52 (m, 4H), 2.47−2.54 (m, 4H), 4.97 (s, 5H), 7.18 (s, 2H), 7.21 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.21, 0.53, 14.08, 22.60, 29.28, 29.33, 30.92, 30.97, 31.70, 31.71, 32.41, 68.37, 72.42, 81.63, 89.50, 90.37, 96.71, 104.43, 121.74, 123.91, 132.90, 133.65, 140.44, 141.17. MS (EI) m/z: M$^+$ calcd for $C_{65}H_{97}CoSi_4$, 1048.60; found, 1048.63.

Synthesis of 6b. In a procedure analogous to that described in the synthesis of **3a**, **1** (200 mg, 0.540 mmol) and 1,2-dimethoxy-4-trimethylsilylethynyl-5-iodobenzene (431 mg, 1.20 mmol) were reacted. Chromatography on silica gel with 8:2 hexanes:EtOAc gives **6b** (311 mg, 69%) as a red oil. IR (neat): ν 2955, 2844, 2144, 1594, 1505, 1244, 1216, 839 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 18H), 0.23 (s, 18H), 3.84 (s, 6H), 3.86 (s, 6H), 4.98 (s, 5H), 6.85 (s, 2H), 6.88 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.15, 0.44, 55.86, 55.90, 68.04, 72.42, 81.54, 89.23, 89.99, 96.49, 104.00, 114.22, 114.93, 117.36, 119.79, 148.39, 148.97. MS (EI) m/z: M$^+$ calcd for $C_{45}H_{57}CoO_4Si_4$, 832.27; found, 832.31.

Dihexyldehydroannulene 7a. A three-necked, round-bottom flask was charged with **6a** (250 mg, 0.280 mmol), Cu_2Cl_2 (24.0 mg, 0.121 mmol), and *N*,*N*-dimethylformamide (50 mL). The mixture was heated to 60 °C for 6 h under a constant flow of O_2. The resulting solution was neutralized with aq 1 M HCl and extracted with ethyl ether. After removal of the solvent in vacuo, the dark oil was chromatographed on silica gel with 9:1 hexanes:EtOAc to give **7a** (222 mg, 89%) as an orange powder. Mp: 137 °C. IR (neat): ν 2923, 2855, 2366, 1461, 1236, 855 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.28 (6C), 0.86−0.95 (m, 12H), 1.29−1.38 (m, 24H), 1.49−1.56 (m, 8H), 2.51−2.61 (m, 8H), 4.92 (s, 5H), 7.19 (s, 2H), 7.21 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.42, 14.07, 22.60, 22.61, 29.30, 30.79, 30.85, 31.65, 31.70, 32.50, 32.63, 68.48, 73.25, 78.71, 84.17, 90.46, 91.32, 81.22, 120.82, 127.46, 130.47, 130.75, 140.17, 142.00. MS (EI) m/z: M$^+$ calcd for $C_{59}H_{79}CoSi_2$, 686.1719; found, 686.1700 ($E = 2.8$ ppm). UV/vis ($CHCl_3$): λ 275 (ϵ = 81 325 cm^{-1} M^{-1}), 337 (ϵ = 77 192 cm^{-1} M^{-1}). UV/vis (film): λ 234, 290, 356. Elemental analysis, calcd: C, 78.44; H, 8.81. Found: C, 78.39; H, 8.71.

Dimethoxydehydroannulene 7b. In a procedure analogous to that described in the synthesis of **7a**, **6b** (232 mg, 0.280 mmol), Cu_2Cl_2 (30.0 mg, 0.152 mmol), and *N*,*N*-dimethylformamide (50 mL) were reacted. Chromatography on silica gel with 7:3 hexanes:EtOAc gives **7b** (35.0 mg, 19%) as an orange solid. Mp: 203 °C dec. IR (neat): ν 2922, 2333, 2166, 1594, 1400, 1255, 1211, 833 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.28 (s, 18H), 3.88 (s, 6H), 3.91 (s, 6H), 4.94 (s, 5H), 6.89 (s, 2H), 6.90 (s, 2H).^{13}C NMR (75 MHz, $CDCl_3$): δ 0.99, 55.92, 56.04, 68.40, 73.14, 78.50, 84.25, 90.18, 91.14, 81.19, 112.08, 112.58, 116.32, 123.78, 148.32, 149.84. MS (EI) m/z: M$^+$ calcd for $C_{39}H_{39}CoO_4Si_2$, 902.5052; found, 902.5057 ($E = 0.6$ ppm). UV/vis ($CHCl_3$): λ 282 (ϵ = 42 712 cm^{-1} M^{-1}), 346 (ϵ = 41 153 cm^{-1} M^{-1}). UV/vis (film): λ 224, 287, 353. Elemental analysis, calcd: C, 68.20; H, 5.72. Found: C, 68.05; H, 5.52.

Synthesis of 9. In a procedure analogous to that described in the synthesis of **3a**, **1** (200 mg, 0.540 mmol) and **8** (260 mg, 1.64 mmol)[13] were reacted. Chromatography on silica gel with hexanes gives **9** (320 mg, 93%) as a red oil. IR (neat): ν 2955, 2922, 2167, 2133, 1405, 1250, 840 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 18H), 0.21 (s, 18H), 4.92 (s, 5H), 5.80 (d, $^3J_{HH} = 11.2$ Hz, 2H). 5.84 (d, $^3J_{HH} = 11.2$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.04, 0.48, 67.57, 73.68, 81.62, 89.14, 95.32, 102.58, 102.73, 116.65, 120.80. MS (EI) m/z: M$^+$ calcd for $C_{33}H_{45}CoSi_4$, 612.1943; found, 612.1930 ($E = 0.8$ ppm).

Dehydroannulene 10. In a procedure analogous to that described in the synthesis of **4a**, **9** (108 mg, 0.176 mmol), K_2CO_3 (73 mg, 0.530 mmol), and $Cu(OAc)_2$ (0.710 g, 3.91 mmol) were reacted to give **10** (64 mg, 80%) as a red oil. IR (neat): ν 2944, 2122, 1400, 1244, 838 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.24 (s, 18H), 4.88 (s, 5H), 6.18 (d, $^3J_{HH} = 10.0$ Hz, 2H), 6.52 (d, $^3J_{HH} = 10.0$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.29, 69.56, 75.71, 80.97, 83.47, 88.00, 91.44, 99.07, 115.40, 126.51. UV/vis ($CHCl_3$): λ 262 (ϵ = 4451 cm^{-1} M^{-1}), 356 (ϵ = 3444 cm^{-1} M^{-1}). UV/vis (film): λ 202, 265, 364. MS (EI) m/z: M$^+$ calcd for $C_{27}H_{27}CoSi_2$, 466.0991; found, 466.0983 ($E = 1.7$ ppm). Elemental analysis, calcd: C, 69.50; H, 5.83. Found: C, 70.10; H, 5.95.

Crystal Structure Determination. See ref 17.

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(17) Details of the crystal structure determination of **4a**−**d** and **7a** are deposited at the Cambridge Crystallographic Database under the numbers CCD 16 0753−160757.