ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 600 (2000) 56–62

Journal of Organometallic Chemistry

A novel weakly diatropic dehydroannulene containing the cyclobutadiene(cyclopentadienyl)cobalt unit. An organometallic dehydroannulene that obeys Hückel's rule

Uwe H.F. Bunz [a,*], Gaby Roidl [a,b], Richard D. Adams [a]

[a] *Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, SC 29208, USA*
[b] *Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55021 Mainz, Germany*

Received 11 September 1999; received in revised form 4 November 1999

Abstract

This contribution describes the synthesis of novel dehydrobenzannulenes containing CpCo-stabilized cyclobutadiene complexes. These dehydrobenzannulenes were made in two different ways. The first access involves a shotgun approach in which 1,2-diethynyl-3,4-bistrimethylsilylcyclobutadiene(cyclopentadienyl)cobalt and 1,2-diiodobenzene are reacted under Heck-type conditions utilizing $(PPh_3)_2PdCl_2$ as catalyst. The formation of a dimeric dehydrobenzannulene containing two benzene rings, two cyclobutadiene units and four alkyne units — even though in low yield — was observed. The second approach to organometallic dehydroannulenes involves the construction of a precursor by coupling 1,2-diethynyl-3,4-bistrimethylsilylcyclobutadiene(cyclopentadienyl)cobalt to 1-bromo-2-trimethylsilylethynylbenzene under Pd catalysis, deprotection and Vögtle coupling of the formed precursor to furnish the corresponding monomeric cycle in high yield. This cycle has been characterized by X-ray single-crystal analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organometallic dehydroannulenes; Cyclobutadiene complexes; Carbon-rich materials

1. Introduction

We have a strong interest in the field of CpCo- and $Fe(CO)_3$-stabilized cyclobutadiene complexes, and we have been successful in the synthesis and evaluation of the materials properties of the structures **1**–**7** [1–3] (Scheme 1). The targets were built by a combination of palladium- and copper-based couplings and represent an ongoing effort towards organometallic all-carbon networks. The cyclobutadiene–CpCo and $-Fe(CO)_3$ complexes display rare tetragonal symmetry, which is almost unavailable in organic chemistry and thus allows the synthesis of rectangular or square topologies otherwise difficult to realize. Cyclobutadiene complexes are now established modules in materials/polymer [4] science and construction-kits for larger organometallic objects [1–3]. During the last 6 years, crosses, stars, dumb-bells, rods, and rings have been realized. Cycle **4** is the first example of a cyclic fullerenyne segment and one of the few reported organometallic dehydroannulenes [5]. The progress in this area is documented in several review articles [1–3]. A new development includes the synthesis of the perethynylated cycles **5**, which represent substantial cyclic segments out of an organometallic all-carbon network [5]. At the same time **5** is the first known perethynylated organometallic dehydroannulene. Herein we wish to report the synthesis and structural characterization of novel organometallic dehydroannulenes based on CpCo-stabilized cyclobutadiene complexes, ethyne, and phenylene groups.

2. Results and discussion

2.1. Syntheses

To obtain large dehydroannulenes, we investigated the reaction of the diethynylcyclobutadiene complex **8**

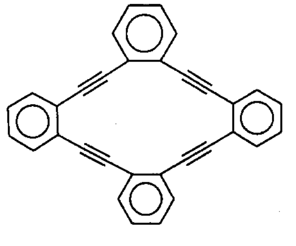
---

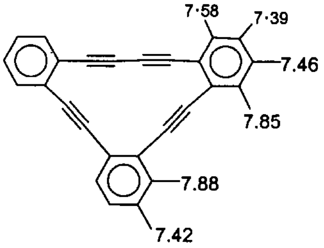
* Corresponding author. Tel.: +1-803-7778436; fax: +1-803-7779521.
E-mail address: bunz@mail.chem.sc.edu (U.H.F. Bunz)

0022-328X/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(00)00029-2

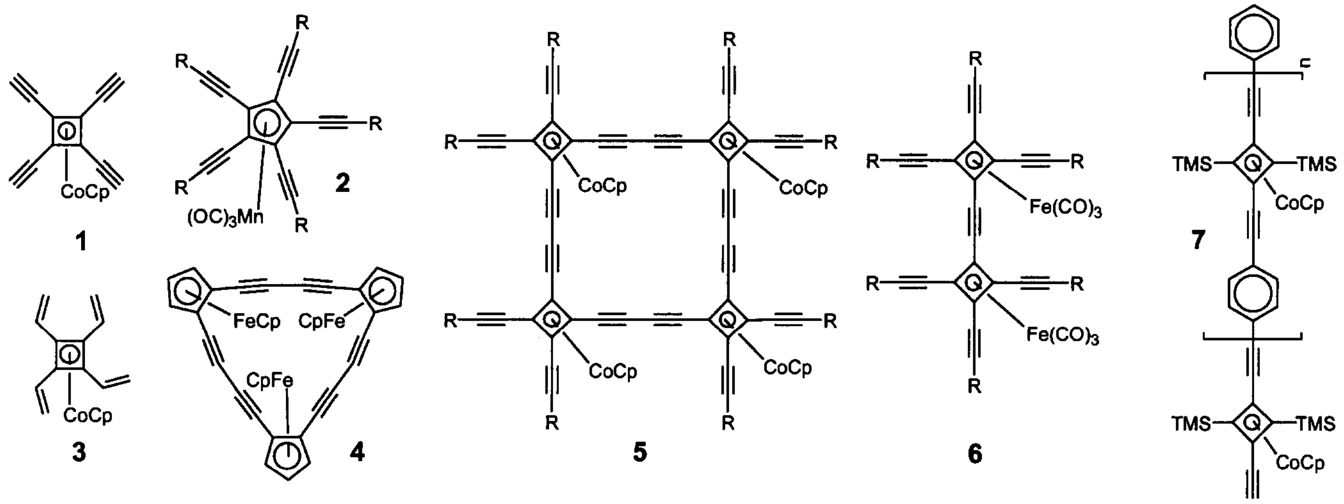
[6] with 1,4-diiodobenzene. This experiment furnished the bis-substitution product **9** in a 24% yield. Chromatographic separation revealed that a second product displaying a lower R_f had formed. It was identified by its NMR spectra and its mass spectrum to be the dimer **10**. While we assume that **10** forms as a mixture of two diastereomers, they were not separable and evidently possess identical shifts in their proton and carbon NMR spectra. However, we were not able to detect any cyclic oligomers, which would have represented molecular boxes (Scheme 2).

In order to obtain cycles, **8** was reacted with 1,2-diiodobenzene under Pd catalysis in piperidine [4]. Workup furnished two products, which were identified by their NMR and mass spectra after chromatography over flash silica gel. The first product was **11** (15% yield) and as second fraction a mixture of the two organometallic dehydrobenzannulenes **12** could be obtained, but in low yield (1.3%). In a second experiment we carefully balanced the stoichiometry of diiodide and diethynyl **8** and as a consequence the isolated yield of the cycles **12** increased to 10% (Scheme 3). The cycles **12** form as a mixture of two diastereomers (*syn*/*anti*). Careful separation by repeated thick-layer chromatography enabled the isolation of the corresponding diastereomers as brown oils. Molecular modelling shows that none of the isomers is planar, but that both assume a distinctly saddle-shaped conformation to accommodate their topology. A single-crystalline specimen could not be obtained, and a secure decision on which of the two isolated compounds would represent the *anti* and which the *syn* isomer of **12** was not possible with only the NMR data in hand.

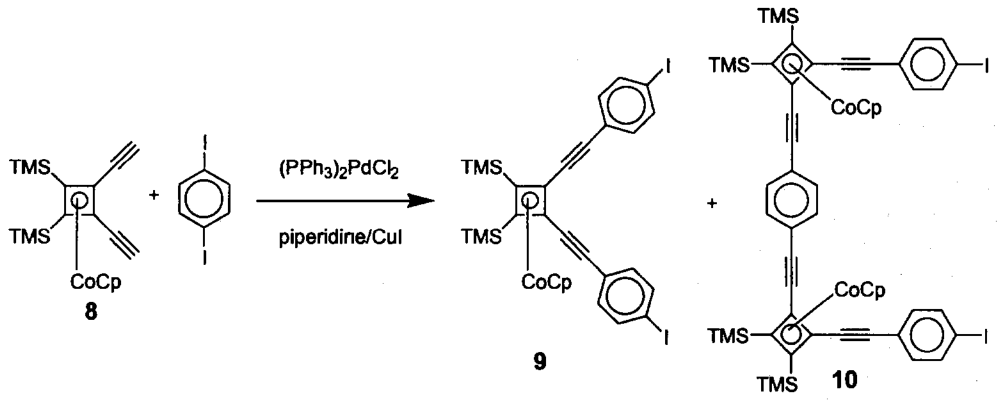

A



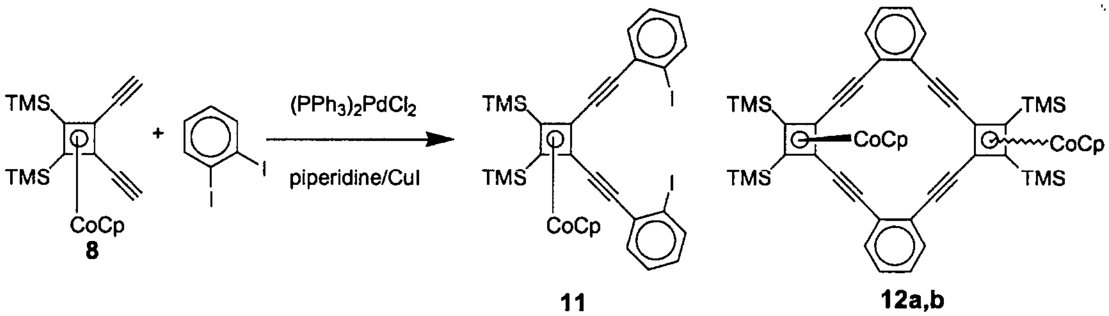
B



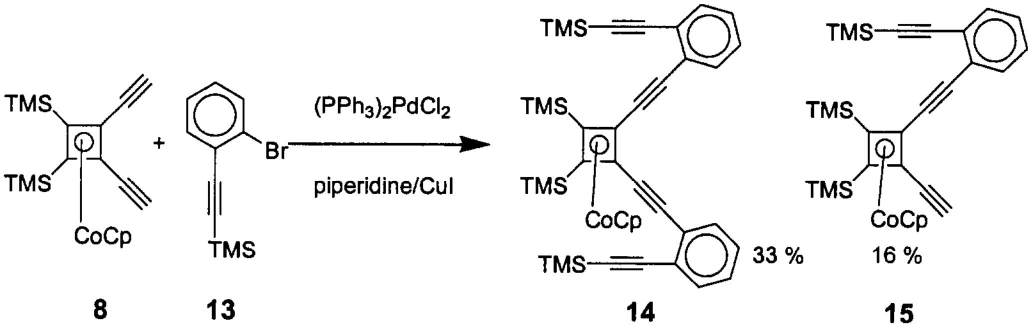
Scheme 1.



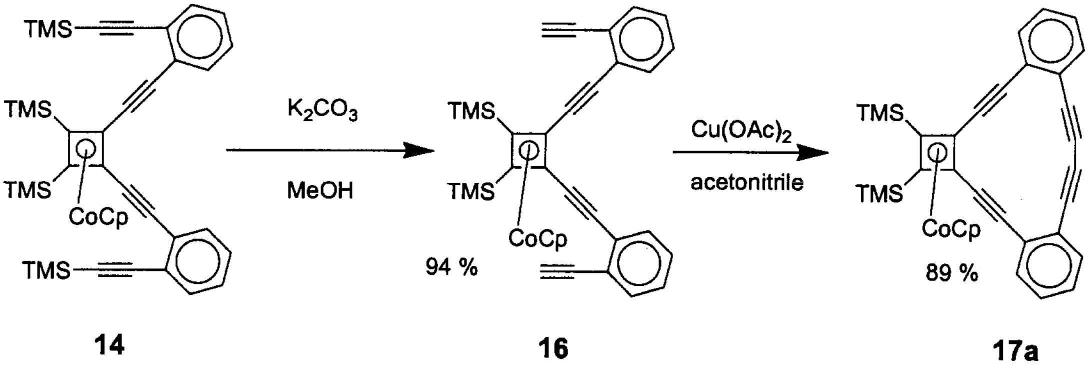
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

Youngs and co-workers [7] have shown that the dehydrobenzannulene **B** is capable of undergoing a solid-state polymerization to a novel conjugated polymer of tubular topology. With the necessary building blocks at hand, we decided to extend this concept to organometallic chemistry. Coupling of **8** to the bromide **13** (Scheme 4) furnished bis-substitution product **14** in a 33% yield. As a by-product we were able to separate a compound that displayed a higher R_f value in the chromatographic separation. Spectroscopic examination leads to the assignment of this compound to the mono substitution product **15**, in which only one of the two alkyne groups had been coupled to **8**. The tetrayne **14** was deprotected by K_2CO_3 in methanol and furnished **16** in 76% yield. Treatment of **16** with copper(II) acetate in acetonitrile, the conditions of the Vögtle [8] variant of the Eglinton coupling, leads to the desired crystalline cycle **17a** in a 84% yield. The cycle is the sole product; the formation of oligomers was not observed. We were pleasantly surprised by the high yield of this cyclization reaction and attribute it to the close proximity of the two alkyne groups in the precursor **16**, poised to close the ring (Scheme 5).

*2.2. X-ray crystal structure of **17a***

Due to the novel and appealing topology of **17a**, we decided to grow a single-crystalline specimen suitable for X-ray structure determination. A well-developed needle was obtained from dichloromethane. An ORTEP plot is shown in Fig. 1. The organic portion of this organometallic benzocyclyne, **17a**, is perfectly planar. The bond lengths and bond angles are in excellent agreement with values of similar alkyne-substituted cyclobutadiene complexes [9] (Tables 1 and 2). It is clearly visible from the ORTEP plot that this cycle is almost unstrained and there is only very slight bending observed in the butadiyne bridges of **17a**. The unstrained nature of the cycle **17a** must be the reason for its high yield of formation in the Vögtle-type coupling from the precursor **16**. Packing of **17a** in the solid state was examined. Contrary to Eglinton's hydrocarbon [10] and to the Vollhardt–Youngs' cyclyne [7], **17a** does not show any solid-state activity. No productive closest contacts exist in the solid state. However, when heating **17a** to above 245°C the material detonated explosively [11]. Currently we are investigating the products of this reaction; the carbonaceous residues may contain carbon nanotubes or multi-shelled carbon onions.

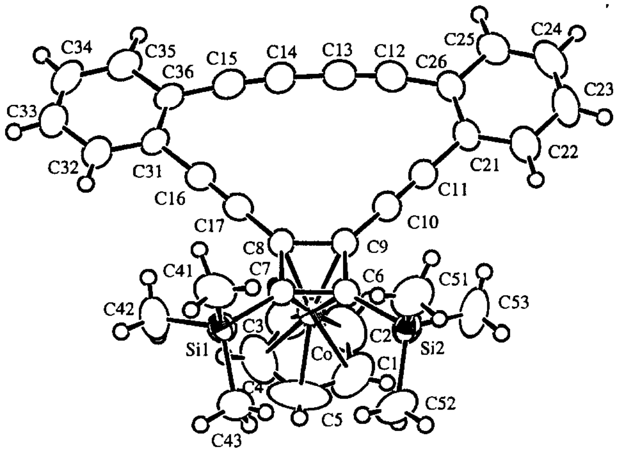


Fig. 1. An ORTEP diagram of $C_{35}H_{31}Si_2Co$, **17a**, showing 40% probability thermal ellipsoids.

Table 1
Selected bond lengths of **17a**

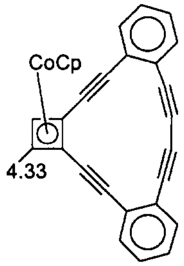
Atoms	Bond lengths (Å)	Atoms	Bond lengths (Å)
C(1)–C(2)	1.35(1)	C(1)–C(5)	1.37(1)
C(2)–C(3)	1.35(1)	C(3)–C(4)	1.37(1)
C(4)–C(5)	1.39(1)	C(6)–C(7)	1.484(6)
C(6)–C(9)	1.482(6)	C(7)–C(8)	1.469(6)
C(8)–C(9)	1.470(6)	C(8)–C(17)	1.406(7)
C(9)–C(10)	1.413(6)	C(10)–C(11)	1.197(6)
C(11)–C(21)	1.440(6)	C(12)–C(13)	1.203(7)
C(12)–C(26)	1.413(7)	C(13)–C(14)	1.386(8)
C(14)–C(15)	1.191(7)	C(15)–C(36)	1.426(7)
C(16)–C(17)	1.196(6)	C(16)–C(31)	1.446(7)
C(21)–C(22)	1.393(7)	C(21)–C(26)	1.412(6)
C(22)–C(23)	1.392(7)	C(23)–C(24)	1.356(9)
C(24)–C(25)	1.376(8)	C(25)–C(26)	1.410(6)

Table 2
Selected bond angles of **17a**

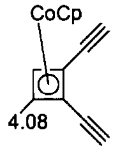
Atoms	Bond angles (°)	Atoms	Bond angles (°)
Co–C(1)–C(2)	70.9(5)	C(2)–C(1)–C(5)	108.4(8)
C(1)–C(2)–C(3)	109.1(8)	C(2)–C(3)–C(4)	108.2(8)
C(3)–C(4)–C(5)	107.5(8)	C(1)–C(5)–C(4)	106.8(7)
C(7)–C(6)–C(9)	89.2(3)	C(6)–C(7)–C(8)	90.2(3)
C(7)–C(8)–C(9)	90.2(3)	C(7)–C(8)–C(17)	134.9(4)
C(9)–C(8)–C(17)	134.7(4)	C(6)–C(9)–C(8)	90.3(3)
C(6)–C(9)–C(10)	134.4(4)	C(8)–C(9)–C(10)	134.8(4)
C(9)–C(10)–C(11)	176.7(5)	C(10)–C(11)–C(21)	178.6(5)
C(13)–C(12)–C(26)	171.6(5)	C(12)–C(13)–C(14)	173.9(5)
C(13)–C(14)–C(15)	174.1(5)	C(14)–C(15)–C(36)	171.1(5)
C(17)–C(16)–C(31)	176.7(5)	C(8)–C(17)–C(16)	177.8(5)
C(11)–C(21)–C(22)	121.2(5)	C(11)–C(21)–C(26)	120.0(4)
C(22)–C(21)–C(26)	118.8(4)	C(21)–C(22)–C(23)	120.4(6)
C(22)–C(23)–C(24)	120.2(6)	C(23)–C(24)–C(25)	121.8(6)
C(24)–C(25)–C(26)	119.1(5)	C(12)–C(26)–C(21)	118.5(4)
C(12)–C(26)–C(25)	121.8(5)	(21)–C(26)–C(25)	119.7(5)
C(16)–C(31)–C(32)	120.1(5)	C(16)–C(31)–C(36)	119.6(4)
C(32)–C(31)–C(36)	120.3(5)	C(31)–C(32)–C(33)	120.1(6)
C(32)–C(33)–C(34)	119.6(6)	C(33)–C(34)–C(35)	121.5(6)
C(34)–C(35)–C(36)	120.0(6)	C(15)–C(36)–C(31)	118.9(4)
C(15)–C(36)–C(35)	122.4(5)	C(31)–C(36)–C(35)	118.6(5)

2.3. NMR spectra of the organometallic dehydroannulenes

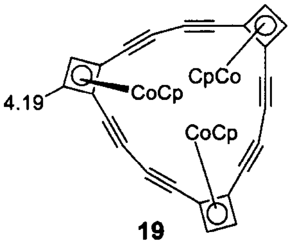
Planar benzodehydroannulenes [12] adhere to Hückel's rule, as was recently demonstrated by Matzger and Vollhardt [13]. While **A** is saddle-shaped-atropic, i.e. non-aromatic, the planar benzocyclyne **B** is a $4n+2$ system and shows weakly diatropic, i.e. aromatic, character.



17b



18



19

The organometallic dehydroannulene **17a** is planar as was demonstrated by single-crystal X-ray diffraction and may display diatropicity as a $4n+2$ π-system. While the signal cluster at lower field experiences a shielding of 0.02 ppm when closing the ring, a deshielding effect is more pronounced for the signal cluster centred at higher field. This cluster shifts from 7.22 to 7.30 ppm upon ring closure. Deprotection of **17a** leads to **17b** in which the cyclobutadiene protons are observed as a singlet at 4.33 ppm. Thus, the protons of the cyclobutadiene nucleus are downfield shifted by 0.25 ppm when incorporated into a dehydroannulene structure. The parent **18** shows a shift of 4.08 ppm for its cyclobutadiene protons. The organometallic dehydroannulene **19**, a planar $4n + 2$ system, likewise shows a small downfield shift when compared with **18**. The shift suggests that it is also slightly diatropic. However, the diatropicity in the *smaller* cyclyne **17** is enhanced in comparison with **19**, exactly as is observed in organic benzocyclynes.

2.4. Conclusions

We have demonstrated that cyclobutadiene complexes can be incorporated into benzocyclynes by either the Pd-catalysed coupling of Heck type [4] or by a combination of Heck chemistry and Eglinton couplings [8]. Dehydroannulenes **17a,b** display weak diatropicity. An excellent indicator for this conclusion is the ^{1}H-NMR spectroscopic shift of the protons attached to the cyclobutadiene nucleus in **17b**. While the shift-difference is slightly smaller for the cyclobutadiene complex than for benzene units when going from the open monomer **18** to the closed dehydroannulenes, it is nevertheless clearly observable and we can conclude that Hückel's rule is in effect for organometallic dehydroannulenes **17a,b** and **19**. We plan to make smaller organometallic cyclynes with $4n$ π-electrons and compare their properties with those of **17a,b**–**19**.

3. Experimental

3.1. General procedures

THF was freshly distilled from sodium benzophenone, hexane was distilled over a Vigreux column prior to use. All other reagents were commercial grade and used as obtained. Literature methods were employed for the preparation of 1-bromo-2-(trimethylsilylethynyl)benzene. ^{1}H- and ^{13}C-NMR spectra in $CDCl_3$ were recorded on a Bruker AM 300 or a Varian Mercury 400 spectrometer. The mass spectra were measured on a VG 70SQ. IR spectra were obtained with a Perkin–Elmer FTIR 1600 on NaCl plates. Elemental analysis of **17a** was carried out by the Elementaranalytisches Laboratorium der Universität Mainz.

3.2. Details of structure solution of *17a*

X-ray structure analysis was carried out by Professor Dr R.D. Adams, USC, Columbia, SC, on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo–K_α radiation. The structure was solved by heavy atom methods (Patterson) and a unit cell $a = 13.865(2)$, $b = 13.907(3)$, $c = 16.588(3)$ Å, $\alpha = \beta = 90$, $\gamma = 103.71°$; $V = 3107.4$ (8) Å^3 was obtained. $D_x = 1.211$ g cm^{-3}; $Z = 4$, $P2_1/c$, reflections collected = 3774, reflections observed 2497, $R = 0.0382$, $R_w = 0.0488$, temperature of data collection = 293.2 K.

3.3. Pd-catalysed reaction of *8* with 1,4-diiodobenzene

1,4-Diiodobenzene (1.95 g, 59.0 mmol), **8** (218 mg, 0.590 mmol), $PdCl_2(PPh_3)_2$ (20.7 mg, 0.029 mmol), and CuI (6 mg, 0.032 mmol) were dissolved in piperidine (30 ml) and stirred for 18 h under nitrogen. Chromatography (flash silica gel–hexanes) furnishes **9** (110 mg, 24%, oil) as a first fraction and **10** (45 mg, 6%, oil) as a second fraction. **9**: IR (KBr): $\nu = 2958$, 2188, 1484, 1389, 1260, 1247, 1005, 863, 815, 698. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.24 (s, 18H, TMS–H); 4.97 (s, 5H, Cp–H); 7.15–7.64 (dd, 8H, $J = 8.06$ Hz). ^{13}C-NMR (300 MHz, CD_2Cl_2): δ 1.4 (6C, TMS–C); 68.5, 74.2 (4C, cyclobutadiene C); 82.6 (5C, Cp-C); 89.7, 91.7 (4C, alkyne-C); 94.4 (2C); 124.8, 133.5, 138.7 (10C). FDMS $m/z = 772.0$ (Calc. $C_{31}H_{31}CoSi_2I_2$: 771.8). **10**: IR (KBr): $\nu = 2955$, 2924, 2854, 2188, 1488, 1246, 1005, 857, 836, 812, 753, 692. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 0.23, 0.24 (s, 36H, TMS–H); 5.00 (s, 10H, Cp–H); 7.40 (s, 4H, H-a); 7.20–7.69 (dd, 8H, $J = 8.6$ Hz). ^{13}C-NMR (300 MHz, CD_2Cl_2): δ 0.46 (12C, TMS–C); 67.6, 67.8, 73.3 (8C); 81.6 (10C, Cp-C); 88.7, 89.2, 90.7, 91.7 (8C); 93.4 (2C); 123.6, 123.9, 131.0, 132.6, 137.8 (16C). FDMS $m/z = 1214.4$ (Calc. $C_{56}H_{40}Co_2Si_4I_2$: 1213.8).

3.4. Pd-catalysed reaction of *8* with 1,2-diiodobenzene (10:1)

1,2-Diiodobenzene (9.20 g, 27.9 mmol), **8** (1.05 g, 2.85 mmol), $PdCl_2(PPh_3)_2$ (100 mg, 0.14 mmol), and CuI (30 mg, 0.14 mmol) were dissolved in piperidine (30 ml) and stirred for 18 h under nitrogen. Chromatography (flash silica gel–hexanes then hexanes–1% dichloromethane) furnishes **11** (331 mg, 15%, oil) as a first fraction and **12** (35 mg, 1.3%) as a second fraction. Repeated thick-layer chromatography (hexanes–1% dichloromethane) separates **12a** (5 mg) and **12b** (7 mg) as pure diastereomers. **11**: IR (KBr): $\nu = 2953$, 2188, 1468, 1246, 1015, 840, 751. ^{1}H-NMR (400 MHz, Acetone-d_6): δ 0.29 (s, 18H, TMS–H); 5.07 (s, 5H, Cp–H); 7.12 (t, 2H, $J = 7.7$ Hz); 7.40 (t, 2H, $J = 7.7$ Hz); 7.51–7.93 (dd, 4H, $J = 7.7$ Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 0.67 (6C, TMS–C); 67.7, 73.1 (4C, cyclobutadiene C); 90.8, 93.0 (8C, alkyne C); 81.5 (5C, Cp–C); 99.8 (2C); 127.6, 128.6, 130.7, 132.2, 138.6 (10C). EIMS: $m/z = 772.0$ (Calc. $C_{31}H_{31}CoSi_2I_2$: 771.8). **12a**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.28 (s, 36H, TMS–H); 5.04 (s, 10H, Cp–H); 7.29–7.42 (dd, 8H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 0.7 (12C, TMS–C); 67.8, 73.5 (8C, cyclobutadiene C); 81.7 (10C, Cp–C); 90.5, 91.3 (8C, alkyne C); 125.2, 127.3, 131.9 (12C). EIMS: $m/z = 884.0$ (Calc. $C_{31}H_{31}Co_2Si_4$: 884.20). **12b**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.28 (s, 36H, TMS–H); 5.04 (s, 10H, Cp–H); 7.26–7.44 (m, 8H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 0.6 (12C, TMS–C); 67.8, 72.8 (8C, cyclobutadiene C); 81.7 (10C, Cp–C); 89.8, 90.5 (8C, alkyne C); 126.1, 127.3, 131.3 (12C). EIMS: $m/z = 884.0$ (Calc. $C_{31}H_{31}Co_2Si_4$: 884.20).

3.4.1. Second experiment (1:1)

1,2-Diiodobenzene (525 mg, 1.59 mmol), **8** (586 mg, 1.59 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.07 mmol), and CuI (15 mg, 0.07 mmol) were dissolved in piperidine (30 ml) and stirred for 18 h under nitrogen. Chromatography (flash silica gel–hexanes then hexanes–1% dichloromethane) furnishes **11** (108 mg, 8%, oil) as a first fraction and **12** (142 mg, 10%) as a second fraction.

3.5. Pd-catalysed reaction of *8* with 1-bromo-2-(trimethylsilylethynyl)benzene

1-Bromo-2-(trimethylsilylethynyl)benzene (0.831 g, 3.26 mmol), **8** (500 mg, 1.36 mmol), $PdCl_2(PPh_3)_2$ (114 mg, 0.160 mmol), PPh_3 (85.5 mg, 0.33 mmol), and CuI (30.9 mg, 0.160 mmol) were dissolved in triethylamine (30 ml) and refluxed for 18 h under nitrogen. Aqueous workup and chromatography (flash silica gel, hexanes–5% dichloromethane) leads to the isolation of **15** (120 mg, 16%, m.p. 66°C) and **14** (320 mg, 33%; oil). **15**: IR (KBr): $\nu = 3308$, 3061, 2956, 2191, 2156, 1482, 1251, 1207. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.24, 0.28, 0.33 (s, 27H, TMS–H); 3.16 (s, 1H, alkyne H); 4.98 (s, 5H, Cp–H); 7.33–7.36 (m, 4H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 0.4, 0.6 (s, 9C, TMS–C); 66.9, 67.9, 72.2, 72.8 (4C, cyclobutadiene C); 79.4, 80.8, 90.0, 90.5, 98.2, 103.7 (6C, alkyne C); 81.5 (5C, Cp–C); 124.2, 127.9, 128.3, 132.9, 133.5, 137.1 (6 C). EIMS: $m/z = 540$ (Calc. $C_{30}H_{37}CoSi_3$: 540.81). **14**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.26, 0.30 (s, 36H, TMS–H); 5.03 (s, 5H, Cp–H); 7.23–7.26 (m, 4H); 7.45–7.49 (m, 4H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 0.25, 0.68 (12C, TMS–C); 68.0, 72.9 (4C, cyclobutadiene C); 90.0, 90.8, 98.2, 103.9 (6C, alkyne C); 124.4, 126.5, 127.1, 127.9, 132.1, 132.9 (12C). EIMS: $m/z = 712$ (Calc. $C_{41}H_{49}CoSi_4$: 713.12).

3.6. Deprotection of *14* to *16*

A round-bottomed flask was charged with methanol (10 ml), potassium carbonate (approximately 50 mg), and **15** (300 mg, 0.422 mmol). Stirring for 18 h followed by aqueous workup and chromatography (flash silica gel, hexanes–2% dichloromethane) led to the isolation of **16** (181 mg, 76%). IR (KBr) $\nu = 3298$, 2955, 2188, 1590, 1483, 1247, 1206. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.29 (s, 18H, TMS–H); 3.30 (s, 2H, alkyne H); 5.01 (s, 5H, Cp–H); 7.26–7.29 (m, 4H); 7.47–7.51 (m, 4H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ 0.6 (6C, TMS–C); 68.0, 72.9 (4C, cyclobutadiene C); 81.2, 82.5, 89.7, 91.0 (8C, alkyne C); 81.6 (5C, Cp–C); 123.6, 127.1, 127.2, 128.3, 131.4, 132.5 (12 C). EIMS $m/z = 568.0$ (Calc. $C_{35}H_{33}CoSi_2$: 568.75).

3.7. Synthesis of the dehydroannulene *17a* by intramolecular Vögtle coupling of *16*

A Schlenk flask was charged with **16** (180 mg, 0.32 mmol), acetonitrile (30 ml), and copper(II) acetate (1.50 g, 8.23 mmol). The mixture was heated for 18 h to 80°C. Aqueous workup and chomatography (flash silica gel, hexanes) furnishes **17a** (152 mg, 84%, m.p. 245°C explosion) as the sole product. IR (KBr) $\nu = 2956$, 2180. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.28 (s, 18H, TMS–H); 4.95 (s, 5H, Cp–H); 7.28–7.33 (m, 4H); 7.44–7.47 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 0.5 (6C, TMS–C); 68.0, 74.0 (4C, cyclobutadiene C); 79.3, 84.1, 90.2, 92.6 (8C, alkyne C); 81.3 (5C, Cp–C); 123.1, 126.8, 128.6, 130.0, 130.1 (12 C). EIMS $m/z = 566.0$ (Calc. $C_{35}H_{31}CoSi_2$: 566.74). UV–vis ($CHCl_3$): $\lambda =$ 271.8 ($\varepsilon = 45100$), 338 ($\varepsilon = 45800$). Calc.: C, 74.18; H, 5.47; Found: C, 73.91; H, 5.62.

3.8. Deprotection of *17a* to *17b*

Dehydroannulene **17a** (52.0 mg, 91.9 μmol) in ethyl ether (10 ml) and tetramethylammoniumfluoride (400 mg, 4.32 mmol) in DMSO (5 ml) are mixed and stirred under nitrogen for 18 h at ambient temperature. Aqueous workup and chromatography (1:3 hexanes–dichloromethane) furnishes **17b** (15 mg, 30%, decomp. 178°C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.33 (s, 2H, cyclobutadiene H); 5.03 (s, 5H, Cp–H); 7.28–7.35 (m, 4H); 7.45–7.53 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 58.5, 63.0 (4C, cyclobutadiene C); 79.2, 84.0, 89.9, 91.9 (8C, alkyne C); 81.3 (5C, Cp–C); 123.3, 126.9, 128.7, 129.7, 130.1, 130.3 (12C).

Acknowledgements

This work was financed by the start-up funds provided by The University of South Carolina and the Petroleum Research Fund. U.H.F.B. is an NSF CAREER awardee (CHE 9981765, 2000-2003). We thank Willi Dindorf for elemental analysis of **17a**. G.R. and U.H.F.B. thank Professor Klaus Müllen for continued interest and support. We wish to thank Professor Bruce M. Foxman for helpful discussions with regard to the packing behaviour of **17a**. Professor Mike M. Haley is acknowledged for discussions with regard to the aromaticity of **17**.

References

[1] U.H.F. Bunz, Synlett (1997) 1117.
[2] U.H.F. Bunz, Y. Rubin, Y. Tobe, Chem. Soc. Rev. 28 (1999) 107.
[3] U.H.F Bunz, Top. Curr. Chem. 201 (1999) 131.
[4] M. Altmann, U.H.F. Bunz, Angew. Chem. 34 (1995) 569.
[5] (a) M. Altmann, R. Reuter, F. Beer, V. Enkelmann, J. Friedrich, U.H.F. Bunz, J. Am. Chem. Soc. 119 (1997) 1472. (b) G. Roidl, V. Enkelmann, U.H.F. Bunz, Organometallics 18 (1999) 4. (c) U.H.F. Bunz, G. Roidl, M. Altmann, V. Enkelmann, K.D. Shimizu, J. Am. Chem. Soc. 121 (1999) 10719.
[6] J.R. Fritch, K.P.C. Vollhardt, Organometallics 1 (1982) 590.
[7] K.P. Baldwin, A.J. Matzger, D.A. Scheiman, C.A. Tessier, K.P.C. Vollhardt, W.J. Youngs, Synlett (1995) 1215. For other benzocyclynes see (a) L. Guo, J.D. Bradshaw, C.A. Tessier, W.J. Youngs, Organometallics 14 (1995) 586. (b) L. Guo, J.D. Bradshaw, C.A. Tessier, W.J. Youngs, J. Chem. Soc. Chem. Commun. (1994) 243.
[8] R. Berscheid, F. Vögtle, Synthesis (1992) 58.
[9] (a) M. Altmann, G. Roidl, V. Enkelmann, U.H.F. Bunz, Angew. Chem. 36 (1997) 1107. (b) U.H.F. Bunz, V. Enkelmann, Organometallics 13 (1994) 3823. (c) U.H.F. Bunz, V. Enkelmann, Angew. Chem. 32 (1993) 1653.
[10] U.H.F. Bunz, V. Enkelmann, Chem. Eur. J. 5 (1999) 263.
[11] A.J. Matzger, K.P.C. Vollhardt, J. Am. Chem. Soc. 117 (1997) 2052.
[12] M.M. Haley, J.J. Pak, S.C. Brand, Top. Curr. Chem. 201 (1999) 81.
[13] A.J. Matzger, K.P.C. Vollhardt, Tetrahedron Lett. 39 (1998) 6791.