was also reflected in its visible absorption spectrum, which exhibits a single band at 500 nm in DMF. Most interestingly, no tendency toward dimerization or aggregation was observed, and this suggests a different molecular structure for the magnesium complex. Magnesium ion analysis of the isolated solid pigment using atomic absorption indicated the presence of 3.2% magnesium. This indicates that the material exists predominantly in the 1:2 structure.

It is quite possible that the water of hydration was not totally removed from the magnesium chloride salt and prevented the formation of two six-membered ring system as shown for structure II in Scheme I. Instead, the magnesium intermolecularly binds two pigment molecules.

A comparison of the experimentally determined diffusion coefficient, D, of the various azo pigment–metal complexes with that calculated from the Stokes–Einstein equation is given in Table VII. The agreement is generally good with the exception of the magnesium complex, where the observed diffusion coefficient is much less than that calculated for the intramolecular complex. However, the calculated D for the structure (azo pigment)$_2$:Mg^{2+} is in excellent agreement with the observed value, which supports the validity of the proposed structures.

Conclusion

The polarographic technique was utilized not only to determine the absolute energy levels of molecules in solution, but also to provide insight into the azo pigment–metal ion complex formation, and subsequent molecular association in nonaqueous media.

The sodium salt of azo pigment **3** showed a tendency toward the formation of high molecular weight aggregates. This aggregation occurs in plane via hydrogen bonding without the participation of the delocalized electrons of the azo molecules. This is generally true for sodium sulfoarylazo-2-naphthols. However, the calcium salt of the azo pigment exhibited a definite tendency toward dimerization in DMF. The visible absorption spectrum of the dimer was found to be shifted to the red and has a higher extinction coefficient than that of the monomer. These results indicate that the delocalized electrons of the azo molecules are involved in the dimerization, i.e., the dimer has a parallel plane structure.

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Substituted Benzocyclobutenes, Indans, and Tetralins via Cobalt-Catalyzed Cooligomerization of α,ω-Diynes with Substituted Acetylenes. Formation and Synthetic Utility of Trimethylsilylated Benzocycloalkenes[1]

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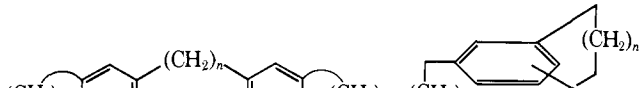
Abstract: A new synthesis of substituted benzocyclobutenes, indans, tetralins and two model anthraquinones is described which utilizes the catalytic ability of η^5-cyclopentadienyldicarbonylcobalt to cooligomerize α,ω-diynes with substituted monoacetylenes. Yields are best when bis(trimethylsilyl)acetylene (BTMSA) is used as one of the reactants to give the ortho-bistrimethylsilylated derivatives **8a, 14a–16a,** and **18a.** Reaction of monosubstituted diynes with unsymmetrical monoacetylenes yields the sterically more hindered aromatic products **8d** and **8f.** Catalytically inert cyclobutadiene cyclopentadienyl cobalt complexes are formed in side reactions when BTMSA is cooligomerized with α,ω-diynes. These include complexes derived from reaction of one (**19**) or both (**20, 21**) ends of the diyne molecule. The synthetic utility of the *o*-bis(trimethylsilyl)benzene unit in electrophilic substitutions is demonstrated. Selective and stepwise displacement of the trimethylsilyl groups by electrophiles results in a variety of new derivatized benzocycloalkenes. Some mechanistic considerations are presented.

Cyclization reactions comprise an important class of synthetic transformations at the disposal of the organic chemist. In the majority of cases these reactions lead to saturated or partially unsaturated five- or six-membered rings, whereas benzene rings are formed only on rare occasions. Synthetic strategy to complex molecules of interest containing benzene

rings (e.g., steroids, tetrahydroisoquinolines, anthracyclines, etc.) usually starts from a readily available and stable benzenoid precursor around which the rest of the molecule is built. One of the drawbacks of this procedure is the relative difficulty of introducing substituents at specific positions of the benzene ring, which can often only be achieved by relatively tedious aromatic substitution sequences. Multiple substitution, position selectivity, and substrate compatibility with electrophile are the major problems encountered in this approach.[3]

An alternative methodology involves in the crucial step cyclization of a suitable precursor or precursors to a molecule containing a newly formed benzene ring. Advantages of such a method are (a) the presumably high exothermicity of such a cyclization reaction which might provide a sufficient driving force for successful completion of the reaction even in sterically unfavorable cases, and (b) the possibility of extensive control of substitution of the aromatic ring to be formed if the appropriate precursors were readily available. We suggest that acetylenes might be such suitable precursors[4] and will describe a general synthesis of benzocycloalkenes based on the cooligomerization of α,ω-diynes with substituted monoacetylenes catalyzed by η^5-cyclopentadienyldicarbonylcobalt ($CpCo(CO)_2$).

Despite the fact that transition metal catalyzed trimerizations of monoacetylenes proceed with remarkable ease,[6] even in the presence of extensive functionality, little is known about oligomerizations and cooligomerizations of diacetylenes. α,ω-Diacetylenes $HC{\equiv}C(CH_2)_nC{\equiv}CH$ with Ziegler-type catalysts (trialkylaluminum–titanium tetrachloride) give only small amounts of trimers of the type **1** (n = 2–5) and **2** (n = 5–7).[7] Using bis(triphenylphosphine)dicarbonylnickel[8] even smaller amounts of **1** are formed (n = 3, 4) and bis(tetracarbonylcobalt)mercury gives compounds of type **3**.[7] The predominant by-product of all these reactions is reported to be insoluble polymeric material. Cooligomerizations of alkylacetylenes with α,ω-diynes (n = 3, 4) using $(P(C_6H_5)_3)_2Ni(CO)_2$ also result in difficultly separable mixtures containing **4**, other oligomers, and mainly polymer.[8] Macomber assigned structure **5** to a complex obtained from the reaction



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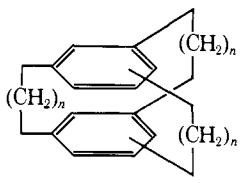

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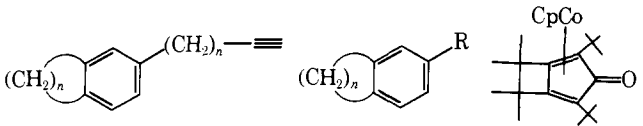


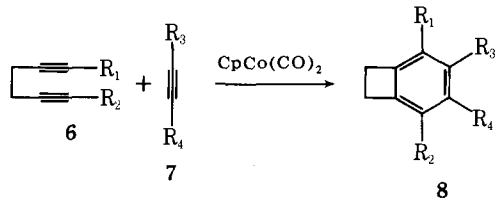
3 **4**, R = alkyl **5**, Cp = η^5-C_5H_5

of 1,6-di-*tert*-butyl-3,3,4,4-tetramethyl-1,5-hexadiyne with $CpCo(CO)_2$.[9] King et al. described reactions of transition metal compounds with macrocyclic alkadiynes. Thus, iron carbonyls, $CpCo(CO)_2$, and $CpRh(CO)_2$ result in cyclobutadiene complexes, ferroles (ferrocyclopentadienes), and other more complex clusters, depending on the conditions employed.[10-13] Simpler acetylene complexes are formed with $(CpNiCO)_2$ and $Co_2(CO)_8$.[14] Müller et al. have isolated a large variety of rhodacyclopentadienes from the reaction of (mainly phenyl-) substituted diketodiynes with tris(triphenylphosphine)rhodium(I) chloride. These metallocycles can be used as substrates in further transformations to give various aromatic systems.[15] Macrocyclic and long-chained α,ω-diynes have also been used in the preparation of complex cyclophane cage structures by acetylene cyclization.[16]

At the outset of our work, few efficient, catalytic, and synthetically useful cooligomerizations of acetylenes to cyclic products had been achieved. We now wish to give a full account of our first efforts at developing transition metal catalyzed acetylene cyclizations as a synthetic alternative in organic chemistry.[26g] The catalyst found most successful in these reactions is $CpCo(CO)_2$[20] and was used throughout.

Results

Silylated Benzocyclobutenes. Bis(trimethylsilyl)acetylene (BTMSA) does not trimerize when exposed to acetylene trimerization catalysts.[17] However, slow addition of 1,5-hexadiyne **6** ($R_1 = R_2 = H$) in BTMSA containing $CpCo(CO_2)$

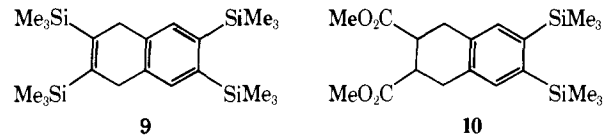


6 **7** **8**

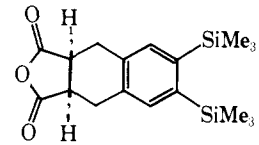
8a, $R_1 = R_2 = H$; $R_3 = R_4 = SiMe_3$
b, $R_1 = R_2 = H$; $R_3 = CH_2OMe$; $R_4 = SiMe_3$
c, $R_1 = R_2 = CH_2OMe$; $R_3 = SiMe_3$; $R_4 = H$
d, $R_1 = R_3 = SiMe_3$; $R_2 = R_4 = H$
e, $R_1 = R_2 = R_3 = SiMe_3$; $R_4 = H$
f, $R_1 = R_3 = SiMe_3$; $R_2 = H$; $R_4 = CH_2OMe$

catalyst to a refluxing solution of the same catalyst in BTMSA under air-free conditions using syringe pump techniques gave 4,5-bis(trimethylsilyl)benzocyclobutene (**8a**). Continuous addition of catalyst was found advantageous since it is slowly being depleted in a side reaction that leads to catalytically inert cyclobutadiene complexes (vide infra). Depending on the conditions employed (time of addition, scale, concentrations of catalyst and reagents, temperature) varying amounts of side products were obtained: trimer **1** (n = 2)[7] derived from 1,5-hexadiyne, cycloadduct **9**, formed by reaction of **8a** with solvent BTMSA, and cobalt complex **21b**. High-dilution conditions and a large excess of BTMSA are essential to the successful outcome of this reaction.

The spectral and chemical properties of **8a** are consistent with its structure (see Table I for selected spectral data in comparison with similar model compounds). Irradiation with a medium- or high-pressure Hg lamp led to recovered starting material.[18] Similarly, hydrogenation did not occur under atmospheric pressure at room temperature (PtO_2–ethanol). The isolation of **9** in the synthesis of **8a** indicated that it could be



9 **10**



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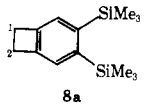
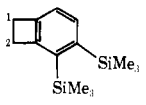
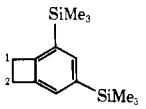
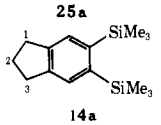
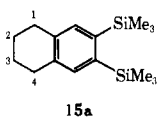
used as an *o*-xylylene precursor. Indeed, reaction of the benzocyclobutene **8a** with dimethyl maleate or maleic anhydride at 200°C gave **10** and **11**, respectively.

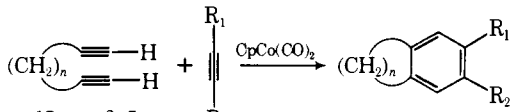
Other silylated benzocyclobutenes can be made by cooligomerization of appropriately substituted 1,5-hexadiynes and monoacetylenes, but the yields decrease with increasing substitution and/or when acetylenes capable of self-trimerization are employed. Thus, although **8b** and **8f** are prepared in relatively good yield from trimethylsilylpropargyl methyl ether

Table I. Relevant Spectral Characteristics of Bis(trimethylsilyl)butenealkenes

	^{1}H NMR, τ (CCl_4)	^{13}C NMR, ppm ($CDCl_3$)	^{29}Si NMR, ppm (0.3 M $Cr(acac)_3$)	UV, nm (log ϵ) (95% EtOH)
 **8a**	2.86 (s, 2 H), 6.86(s, 4 H), 9.67 (s, 18 H)	145.9 ($C_{7,8}$), 144.3 ($C_{4,5}$), 129.1 ($C_{3,6}$), 30.2 ($C_{1,2}$), 2.41 (Me_3Si)	−3.2	226 sh (4.00), 248 sh (3.04) 266 (2.79), 272.5 (2.91), 280.5 (2.81)
 **8d**	2.60 (d, J = 8 Hz, 1 H), 3.11 (d, J = 8 Hz, 1 H), 6.87 (m, 4 H), 9.67 (s, 18 H)	153.5 (C_8), 146.0 (C_7), 134.1 (C_5), 122.1 (C_6), 34.1, 28.7 ($C_{1,2}$), 2.6 (Me_3Si)		276 (3.52), 285 sh (3.46)
 **25a**	2.72 (bs, 1 H), 2.95 (bs, 1 H), 6.85 (bs, 4 H), 9.73 (s, 9 H), 9.77 (s, 9 H)			220 sh (4.09), 269 sh (3.13), 275.5 (3.32), 283 (3.33)
 **14a**	2.54 (s, 2 H), 7.15 (bt, J = 7 Hz, 4 H), 8.05 (quin, J = 7 Hz, 2 H), 9.58 (s, 18 H)	143.9 ($C_{8,9}$), 143.4 ($C_{5,6}$), 131.6 ($C_{4,7}$), 32.9 ($C_{1,3}$), 24.9 (C_2), 2.20 (Me_3Si)	−3.49	228 (4.01), 230.5 sh (4.01), 266 (2.72), 274 (2.74), 282 (2.59)
 **15a**	2.70 (s, 2 H), 7.30 (m, 4 H), 8.25 (m, 4 H), 9.63 (s, 18 H)	142.4 ($C_{6,7}$), 136.9 ($C_{9,10}$), 136.8 ($C_{5,8}$), 29.3 ($C_{1,4}$), 23.3 ($C_{2,3}$), 2.00 (Me_3Si)	−4.00	228 (4.08), 229 sh (4.08), 267 sh (2.57), 271 (2.60), 277 sh (2.48)

(**7**) (R_3 = $SiMe_3$, R_4 = CH_2OMe)[19] and the appropriate diyne, compounds **8c, 8d,** and **8e** are formed in lesser amounts. The corresponding substituted diynes were prepared by standard alkylation reactions of 1,6-dilithio-1,5-hexadiyne; e.g., **6** (R_1 = R_2 = CH_2OCH_3), **6** (R_1 = R_2 = $SiMe_3$). Reaction of this dianion with only 1 equiv of trimethylsilyl chloride yielded (after workup) a 1:1 mixture of 1,5-hexadiyne starting material and 1,6-bis(trimethylsilyl)-1,5-hexadiyne. The synthesis of the precursor to **8d, 6** (R_1 = $SiMe_3$; R_2 = H), was carried out by alkylation of 1-trimethylsilylpropargyllithium (generated with butyllithium–TMEDA) with propargyl bromide, or trimethylsilylation of 1,5-hexadiyne monomagnesium bromide. The structure of compounds **8b–f** was consistent with spectral and chemical data (see subsequent and Experimental Section). Some spectral properties of **8d** are shown in Table I. Attempts to prepare 3,4,5,6-tetrakis(trimethylsilyl)benzocyclobutene (**8**, R_1 = R_2 = R_3 = R_4 = $SiMe_3$) by acetylene cyclization failed.

Indans, Tetralins, Benzocycloheptenes, and Anthraquinones. Benzocycloalkenes **14–16** were prepared by cooligomerization of 1,6-hepta-, 1,7-octa-, and 1,8-nonadiyne with suitable monoacetylenes. Again, BTMSA proved to be the most efficient cyclization reagent when used as solvent to give 5,6-bis(trimethylsilyl)indan (**14a**) and 6,7-bis(trimethylsilyl)tetralin (**15a**). Some comparative spectral data are shown in Table I. Formation of the seven-membered ring in **16a** is, however,

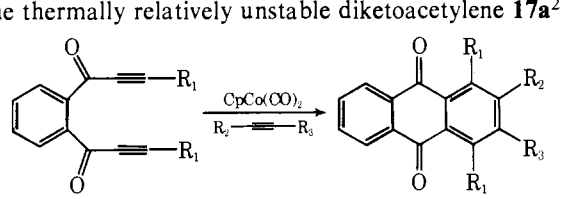


12, n = 3–5 + **13** ($CpCo(CO)_2$)

n = 3; **14a**, R_1 = R_2 = $SiMe_3$
b, R_1 = R_2 = CO_2Me
c, R_1 = C_6H_5; R_2 = H
d, R_1 = R_2 = C_6H_5
e, R_1 = n-Hex; R_2 = H
n = 4; **15a**, R_1 = R_2 = $SiMe_3$
b, R_1 = R_2 = CO_2Me
c, R_1 = C_6H_5; R_2 = H
d, R_1 = R_2 = C_6H_5
e, R_1 = n-Hex; R_2 = H
f, R_1 = $SiMe_3$; R_2 = Me
n = 5; **16a**, R_1 = R_2 = $SiMe_3$

considerably less favored owing to depletion of catalyst to inactive cyclobutadiene complexes **19b** and **20c** (vide infra), and only traces of the benzocycloheptene are observed. When monoacetylenes capable of catalyzed self-trimerization were employed, 1:1 ratios of reagents had to be used in hydrocarbon (n-octane) or aromatic (toluene, o-xylene) solvents. High-dilution conditions were maintained with syringe pump techniques. Yields of the corresponding indans and tetralins were moderate, the major side products being individually trimerized starting materials and complex cooligomers. Products could usually be easily separated by column chromatography.

Two examples of the potential of a catalytic anthraquinone synthesis were tested in the preparation of **18a**, starting with the thermally relatively unstable diketoacetylene **17a**[21] and

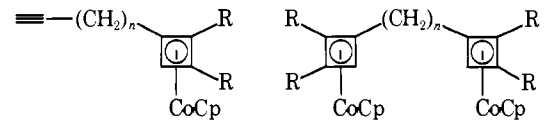


17a, R_1 = H
b, R_1 = $SiMe_3$

18a, R_1 = H; R_2 = R_3 = $SiMe_3$
b, R_1 = $SiMe_3$; R_2 = n-Hex; R_3 = H

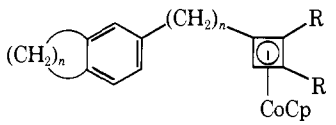
BTMSA, and **18b**, from **17b** and 1-octyne, in low yield. The low yield of **18a** is probably due to extensive decomposition of **17a** under the reaction conditions. In the case of **18b**, the catalyst was slowly converted to inactive cyclobutadiene complex **22**, again accounting for the lower yield observed.

Silylcyclobutadienecyclopentadienylcobalt Complexes. Although in most runs the catalytic efficiency of the catalyst did not seem to decrease during the course of the reaction, cooligomerizations of α,ω-diynes with silylacetylenes, particularly BTMSA, resulted in varying amounts of catalytically inert cyclobutadienecyclopentadienylcobalt sandwich complexes. Similar results were obtained with di-*tert*-butylacetylene. These side reactions led to a significant decrease in the production of organic product in the syntheses of **16a** and **18b**. The cobalt complexes were separated by column chromatography under nitrogen (when necessary) and purified by recrystallization, sublimation, or microdistillation. Three

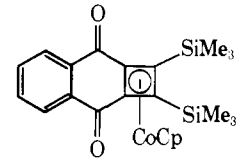


19a, n = 2; R = t-Bu
b, n = 5; R = $SiMe_3$

20a, n = 2; R = t-Bu
b, n = 4; R = $SiMe_3$
c, n = 5; R = $SiMe_3$



21a, n = 2; R = t-Bu
b, n = 2, R = $SiMe_3$
c, n = 3; R = $SiMe_3$
d, n = 4; R = $SiMe_3$



22

classes of compounds were obtained: monocyclobutadiene complexes **19**, in which one end of the diyne had remained unreacted, biscyclobutadiene sandwiches **20**, in which both acetylene units of the diyne had cyclized, and compounds **21**, in which one diyne acetylene moiety had cotrimerized with another molecule of diyne and the other had formed a cyclobutadiene ring. Two isomers of **20a** (denoted α and β) could be separated by careful chromatography. Attempts to distinguish the meso from the *dl* diastereomers in NMR experiments using chiral solvents[22] were unsuccessful. To our knowledge there are only few not completely substituted cyclobutadiene-CpCo complexes known.[17b,23] We have therefore tabulated some spectral information on these compounds (Table II), including mass spectral data, in response to some current interest in the fragmentation processes of cyclobutadiene-metal complexes on electron impact.[24]

The potential catalytic activity of the cyclobutadienecobalt complexes was tested as follows. Exposure of 1,5-hexadiyne to catalytic amounts of **21b** in refluxing, partially degassed *n*-octane for 6 days gave 11% of trimer **1** (n = 2) and 20% recovered cobalt complex. Repetition of this reaction with 1,6-dideuterio-1,5-hexadiyne gave the appropriately deuterated trimer **1**, but *no* significant deuterium incorporation into the complex. A repeat of the same experiment with 1,7-octadiyne under rigorously air-free conditions (evacuated, sealed tube) gave no trimer but a product that appeared to be derived from cycloaddition of one acetylene moiety to the benzocyclobutene unit in **21b**.

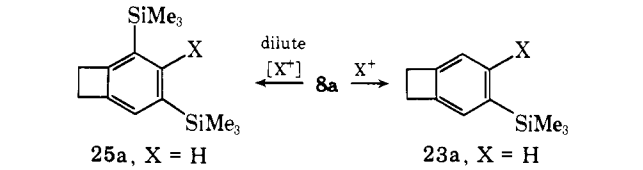
Bisnoranthraquinone complex **22** was obtained from reaction of **17b** with $CpCo(CO)_2$ and was also shown to be catalytically inert in acetylene trimerizations.

Electrophilic Substitution Chemistry of Silylbenzocycloalkenes. Treatment of 4,5-bis(trimethylsilyl)benzocyclobutene (**8a**) with excess trifluoroacetic acid led to clean protodesilylation resulting in benzocyclobutene (**24a**).[25a] Similarly, reaction with deuteriotrifluoroacetic acid gave 4,5-dideuteriobenzocyclobutene (**24b**). A mixture of deuterated and undeuterated acid produced partially deuterated benzocyclobutene, the NMR spectrum of which shows a decreased intensity of the lower half of the AA'BB' pattern for the benzenic protons, confirming the chemical shift assignments of Adcock et al.[25b] in benzocyclobutene. Relative rates of deuteriodesilylation of **8a** in CF_3COOD-CD_3COOD-CCl_4 were measured under pseudo-first-order conditions. The rate of deuteriodesilylation of the first relative to the second trimethylsilyl group was found to be k_1/k_2 = 38 for **8a**. Similar measurements were carried out for **14a** (k_1/k_2 = 36), **15a** (k_1/k_2 = 42), and **8d** (k_1/k_2 = 500). These experiments revealed that dilute acid solutions (CCl_4) caused significant rearrangement of one of the silyl groups to the meta position to give, for example, **25a** and **25b**. Similar migrations were observed in other electrophilic substitution reactions but can apparently be suppressed by either using a higher concentra-

Table II. Spectral Characteristics of Cyclobutadienecyclopentadienylcobalt Complexes

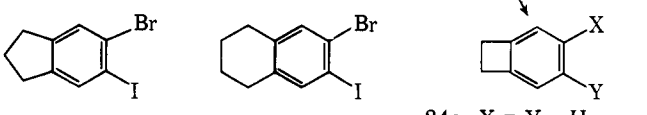
Compd	NMR, τ (CCl_4)	Mass spectrum,[a] *m/e* (rel intensity)
19a	5.25 (s, 5 H), 6.27 (s, 1 H), 7.78 (bs, 4 H), 8.20 (narrow m, 1 H), 8.80 (s, 9 H), 8.92 (s, 9 H)	340 (M^+, 100), 325 (16), 301 (33), 244 (22), 124 (53), 99 (26), 59 (41), 57 (33)
19b	5.26 (s, 5 H), 5.90 (s, 1 H), 7.86 (m, 2 H), 8.17 (m, 2 H), 8.23 (bt, 1 H), 8.57 (m, 6 H), 9.90 (s, 9 H), 9.95 (s, 9 H)	414 (M^+, 100), 294 (43), 243 (13), 155 (11), 124 (20), 97 (11), 83 (15), 73 (45)
20aα	5.26 (s, 10 H), 6.33 (s, 2 H), 8.00 (bs, 4 H), 8.80 (s, 18 H), 8.90 (s, 18 H)	602 (M^+, 12), 302 (21), 301 (100), 57 (21)
20aβ	5.26 (s, 10 H), 6.37 (s, 2 H), 8.00 (bs, 4 H), 8.80 (s, 18 H), 8.90 (s, 18 H)	602 (M^+, 11), 302 (13), 301 (59), 57 (100)
20b	5.25 (s, 10 H), 5.90 (s, 2 H), 8.17 (m, 4 H), 8.70 (m, 4 H), 9.87 (s, 18 H), 9.93 (s, 18 H)	694 (M^+, 100), 294 (42), 207 (19), 189 (23), 155 (26), 109 (98), 73 (57)
20c	5.27 (s, 10 H), 5.92 (s, 2 H), 8.20 (m, 4 H), 8.87 (m, 6 H), 9.90 (s, 18 H), 9.95 (s, 18 H)	708 (M^+, 34), 600 (15), 360 (28), 294 (52), 196 (19), 189 (28), 182 (16), 124 (33), 73 (100)
21a	3.25 (m, 3 H), 5.30 (s, 5 H), 6.38 (s, 1 H), 6.92 (bs, 4 H), 7.46 (m, 2 H), 7.76 (m, 2 H), 8.82 (s, 9 H), 8.94 (s, 9 H)	418 (M^+, 100), 301 (75), 271 (17), 217 (34)
21b	3.20 (m, 3 H), 5.24 (s, 5 H), 5.92 (s, 1 H), 6.90 (bs, 4 H), 7.33 (m, 2 H, 7.85 (m, 2 H), 9.88 (s, 9 H), 9.94 (s, 9 H)	450 (M^+, 93), 333 (100), 294 (50), 163 (74), 73 (78)
21c	3.13 (m, 3 H), 5.30 (s, 5 H), 5.93 (s, 1 H), 6.8-7.6 (m, 6 H), 7.6-8.3 (m, 6 H), 9.92 (s, 9 H), 9.97 (s, 9 H)	478 (M^+, 11), 294 (12), 226 (13), 73 (100)
21d	3.22 (bs, 3 H), 5.32 (s, 5 H), 5.93 (s, 1 H), 7.13-7.70 (m, 6 H), 7.95-8.65 (m, 10 H), 9.93 (s, 9 H), 9.97 (s, 9 H)	506 (M^+, 24), 434 (46), 294 (12), 73 (100)

[a] Only parent and important fragmentation peaks are reported. The corresponding silicon isotope peaks were also observed, but are not listed.



25a, X = H
b, X = D
c, X = Br

23a, X = H
b, X = D
c, X = Br



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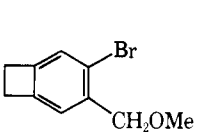
24a, X = Y = H
b, X = Y = D
c, X = Y = Br
d, X = Br; Y = I
e, X = Br; Y = Ac
f, X = Y = I

tion of electrophile or by adding base. Thus, bromination of **8a** (equimolar amounts), which yields significant amounts of **25c**, gave pure 4-bromo-5-trimethylsilylbenzocyclobutene (**23c**) when 2 equiv of bromine was added to a solution of **8a** containing 1 equiv of pyridine. Monobromide **23c** serves as starting material for the preparation of a variety of unknown substituted benzocyclobutenes **24c–e** by treatment with the appropriate electrophile (Br_2, ICl, CH_3COCl–$AlCl_3$, respectively). Diiodination of **8a** was effected directly by treatment with 2 equiv of ICl. Similar transformations were carried out on the bis(trimethylsilyl)indan **14a** and tetralin **15a**, as exemplified by the highly efficient two-step conversion to bromoiodides **26** and **27**, respectively. Not only **8a**, but also other silylated benzocyclobutenes can be transformed to the corresponding derivatives by electrophilic substitution, reactions that are synthetically useful and in addition serve as chemical structural proof for the substrate. For instance, **8b** gave bromide **28** on bromination, **8c** gave iodide **29** on iodination (ICl), **8d** and **8e** resulted in benzocyclobutene on treatment with acid, and **8f** hydrolyzed at the more reactive 4 position to the meta-substituted benzocyclobutene **30**. Further hydrolysis of **30** gave 3-methoxymethylbenzocyclobutene, identical with the ether obtained from **28** on treatment with butyllithium following by quenching.[26f]



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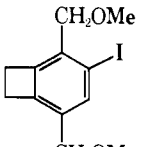

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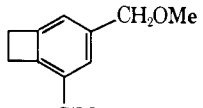

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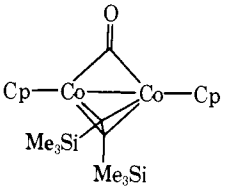
Discussion

Benzocyclobutenes, valuable precursors to molecules of theoretical interest,[26] are now gaining increasing importance as intermediates in the synthesis of natural products.[27] A versatile, high-yield synthetic entry into this class of compounds would therefore be desirable, particularly if some control of substitution were to be found. We had reported earlier[28] a one-step synthesis of substituted benzocyclobutenes involving cooligomerization of linear mono- and diacetylenes catalyzed by $CpCo(CO)_2$. Some aspects of the chemistry of the catalyst[29] were investigated in order to shed some light on the mechanism of this reaction.[30] The yields in these cyclizations were, however, low (ca. 15%), particularly in the case of synthetically desirable functionalized benzocyclobutenes (for example, 4,5-bis(carbomethoxy)benzocyclobutene). Moreover, we have found benzocyclobutenes substituted by electrophiles such as halogens to be inaccessible by this route owing to the instability of the corresponding acetylenic precursors and/or catalyst under the reaction conditions.[31] In order to improve the efficiency of the acetylene cocyclization reaction we sought an acetylene that would cooligomerize with an α,ω-diyne but not cyclotrimerize on its own. This might, in principle, be achieved by using a sterically hindered monoacetylene as exemplified by di-*tert*-butylacetylene. However, attempted cocyclization of this substance with 1,5-hexadiyne in the presence of $CpCo(CO)_2$ resulted in cyclobutadiene complexes **19a**, **20a**, and **21a** and none of the desired organic product. Moreover, since we desired an acetylene that would bear functionality that might easily be converted into a range of other functional groups once it had completed reaction, we turned to an investigation of the potential of silicon substituted acetylenes in cyclizations mediated by $CpCo(CO)_2$. The greater length of the silicon–carbon bond (ca. 1.9 Å)[32] when compared with the carbon–carbon bond in conjunction with the excellent leaving group capabilities of trialkylsilyl groups in electrophilic aromatic substitutions[33] made trimethylsilylated acetylenes the substrates of choice.

Bis(trimethylsilyl)acetylene (BTMSA) indeed cooligomerizes with α,ω-diynes to form bistrimethylsilylated benzocycloalkenes (**8a, 14a, 15a**) in good yield. BTMSA had been shown earlier[17] to form the dinuclear complex **31** on treatment



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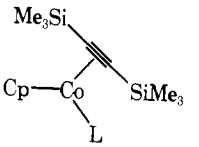


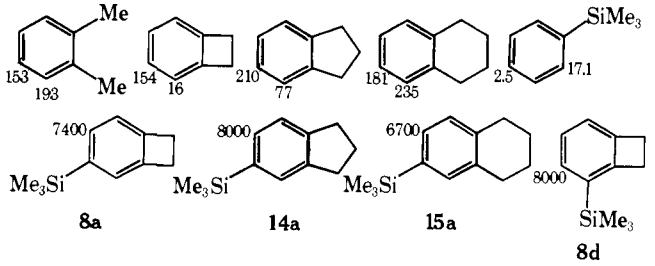
32

with $CpCo(CO)_2$. This complex was, however, never observed under our reaction conditions. Since BTMSA was used in large excess (solvent) in the synthesis of **8a, 14a–16a,** and **18a** it is conceivable that mononuclear complexes of the type **32** (L = CO, BTMSA) were formed and constituted first steps en route to cyclized organic structures. Although the yields decrease when other monoacetylenes are used (a notable exception is trimethylsilylpropargyl methyl ether **7**, R_1 = $SiMe_3$; R_2 = CH_2OMe) and when the synthesis of more highly substituted products is attempted, the cobalt-catalyzed cooligomerization method remains very useful for the synthesis of specifically substituted benzocycloalkenes inaccessible by other routes. In particular, we have employed this approach quite successfully in the synthesis of strained molecules of theoretical interest.[26d-f]

Ortho-bistrimethylsilylated benzocyclobutenes might be regarded as interesting structures in their own right since they represent molecules in which one might expect varying degrees of benzene ring distortion due to the cumulative effect of silyl group crowding and strained ring fusion. Compounds **8a** and **8d**, for example, are formally two of the most strained simple benzocyclobutenes known. Yet there is little dramatic spectroscopic (see Table I) or chemical evidence to illustrate any significant increase in strain when compared with model systems. The proton chemical shifts, for instance, are consistent with expectations based on anticipated perturbations caused by the silicon substituents.[25] Similarly, the ^{13}C NMR spectrum exhibits the expected decrease in chemical shift of the carbon α to the fused ring when going from **15a** to **14a** and **8a**, a phenomenon commonly associated with ring strain.[26d, 34,35] The electronic spectra do not reveal unusual trends and are normal for silylated benzocycloalkenes.[41]

Bond fixation arguments[36] would predict benzocyclobutene **8a** to be chemically activated both due to the bulky trimethylsilyl groups and cyclobutenoid ring strain contributions.[37] However, (a) ring opening occurs at rates comparable to benzocyclobutene; (b) hydrogenation, a popular indicator of cyclohexatrienic character,[26d,38] does not occur under the usual hydrogenation conditions; and (c) irradiation does not result in the corresponding cyclobutabenzvalene or other isomers, as observed for 1,2,4,5-tetrakis(trimethylsilyl)benzene.[18] Moreover, rate ratios of deuteriodesilylation of the silyl groups along the series **8a, 14a,** and **15a** indicate a fairly constant steric acceleration factor of ca. 40. Scheme I tabulates some of the literature values[39] for the rate of protodesilylation of various trimethylsilyl-substituted arenes (10^3k (min^{-1})) relative to phenyltrimethylsilane ($HClO_4$–MeOH–H_2O, H_2SO_4–AcOH–H_2O) in comparison with our data (CF_3COOD–CD_3COOD–CCl_4) on **8a, 8d, 14a,** and **15a**. The results are internally consistent and rule out unusual bond fixation contributions in **8a**. Minor discrepancies can be attributed to the difference in solvent systems used and possible deuterium isotope effects. It is interesting to note that our k_1/k_2 ratios are more than double the size reported for *o*-bis(trimethylsilyl)-

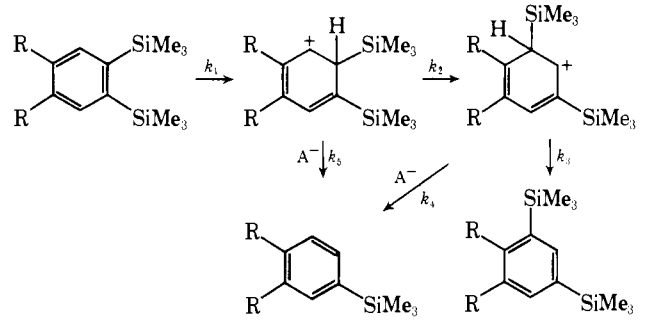
Scheme I



8a **14a** **15a** **8d**

k_1/k_2 38 36 42 500

Scheme II



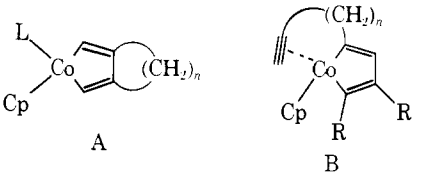
benzene[39] measured spectrophotometrically.[42] The lower values observed for the latter compound could be due to the interference of an undetected,[40] competing ortho → meta rearrangement[41] under the conditions employed. Similar rearrangements occur in **8a, 14a,** and **15a** under dilute acid conditions when the half-life of the first protodesilylation exceeds 4–5 min. The high k_1/k_2 ratio for 3,4-bis(trimethylsilyl)benzocyclobutene (**8d**) (500) is reasonable once the steric (and possibly electronic) effect of the *o*-silyl substituent (~40) is factored out. The resulting β:α position reactivity ratio (~12.5) compares favorably with the literature value (~10).[39]

A possible mechanism that accounts for the results is suggested in Scheme II. Protonation of starting material occurs as the rate-determining step.[33] The protonated intermediate can either rearrange in a unimolecular[41] fashion (k_2) to the protonated meta isomer or lose a trimethylsilyl group by nucleophilic attack of counterion A on silicon (k_5). The meta intermediate might deprotonate at low concentrations of A (k_3) to give the observed meta-substituted arenes. At higher concentrations of A nucleophilic displacement on silicon occurs to give desilylated products (k_4). The last two reactions are possibly competitive even under very dilute conditions. Rate k_2, however, has to be faster than k_5 under the latter conditions. Evidence for this hypothesis was obtained not only from the acid hydrolysis experiments described above, but also from other electrophilic substitution experiments. For example, bromination of **8a** under dilute conditions gave significant amounts of 3,5-bis(trimethylsilyl)-4-bromobenzocyclobutene (**25c**). However, on addition of bromine to a pyridine containing solution of **8a** (conditions under which pyridine perbromide is generated[43]) clean bromodesilylation to **23c** was observed, presumably owing to more efficient attack on silicon by the additional base.

From a preparative viewpoint the utility of ortho-silylated arenes for the synthesis of specifically substituted benzene derivatives is easily demonstrated by the preparation of compounds **23–27.** Steric acceleration of the first trimethylsilyl group allows for mild, selective, and stepwise introduction of two different electrophiles. Structures **28–30** are further examples of such electrophilic displacements.[33,39]

The synthesis of the sterically more hindered benzocyclobutenes **8d** and **8f** (small amounts of the other possible isomer can be detected spectroscopically in the case of **8f**) by cooligomerization of monotrimethylsilylated 1,5-hexadiyne with unsymmetrical acetylenes is a potentially very useful reaction, the scope and limitations of which are currently being explored. In addition, it offers some insight into the mechanism of the cooligomerization reaction.

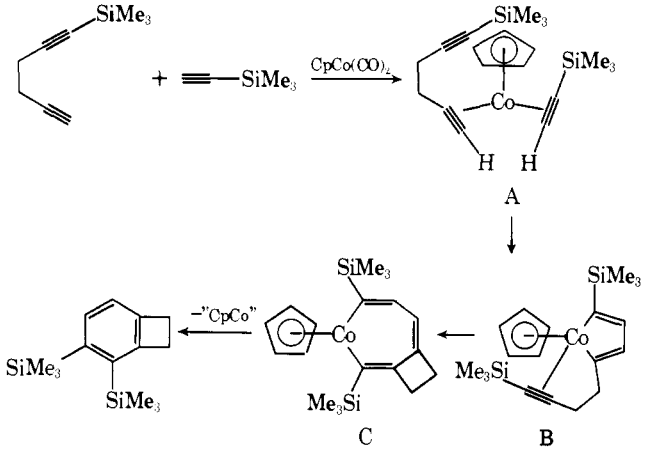
Investigations in various laboratories[44] have elucidated some of the basic steps involved in the cyclotrimerization of acetylenes catalyzed by low-valent group 8 transition metal complexes. Although a "zipper" mechanism,[44i] in which three acetylene units cyclize in the coordination sphere of the metal, cannot be ruled out, isolated intermediates point to the occurrence of metallocyclic cobaltacyclopentadienes. In cooligomerizations of α,ω-diynes with monoacetylenes two alternative "coboles", A and B, respectively, can be envisaged.



Structure A is formed by intramolecular oxidative coupling of the two acetylene moieties of a diyne; B arises via intermolecular reaction of one end of a diyne with a monoacetylene. To give final product, A would react with a molecule of monoacetylene (possibly via an intermediate complex, L = R—≡—R) either by insertion or a Diels–Alder type process followed by extrusion of cobalt. On the other hand, B would undergo these processes intramolecularly to give the same benzenic products. It is difficult to distinguish between these mechanistic possibilities and indeed different systems might arrive at the cyclized product by different or more than one distinct pathways. For instance, 2,7-nona- and 2,8-decadiyne have been shown to rapidly form observable intramolecular coboles when treated with $CpCo[P(C_6H_5)_3]_2$.[30] On the other hand, 2,6-octadiyne, which would form a cobole fused to a four ring, does not. This suggests that indans and tetralins may be formed by the intramolecular cobole route, but benzocyclobutenes by the intermolecular path. Variations in the yields of analogous substituted benzocycloalkenes obtained by cooligomerization reactions[29] parallel each other quite strikingly, indicating that the size of the developing fused ring has no product-determining influence. Further interesting evidence is provided by the isolation of cyclobutadiene complexes **19–21** from cooligomerizations with BTMSA and di-*tert*-butylacetylene, respectively. These complexes could possibly be derived by rearrangement of coboles B to give first **19** which reacts further to either **20** or **21**.

If B is descriptive of the mechanism of benzocyclobutene formation, then an attractive explanation for the preferred formation of sterically more hindered products (**8d, 8f**) could be proposed as shown in Scheme III. The crucial feature of this scheme is the intermediacy of complexes in which steric hindrance is minimized before the benzene-forming step when the full gain of resonance overrides steric considerations. Thus, it might be assumed that oxidative coupling to an intermolecular cobole would occur from A (drawn in the appropriate, but possibly less stable, conformation) such as to give the 2-trimethylsilylated metallocycle B (one trimethylsilyl–hydrogen interaction) rather than the presumably more hindered 3 derivative (two trimethylsilyl–hydrogen interactions). Intermediate B would then rearrange to C in which the two bulky groups are kept apart by the CpCo moiety which is finally extruded to give the benzene **8d.** Electronic factors may also play a role in this remarkably selective transformation and this possibility is currently being tested. Another feasible route to C would involve intramolecular cobole formation followed by selective trimethylsilylacetylene insertion. Interestingly, the

Scheme III



degree of selectivity is somewhat decreased in the synthesis of **8f** which gives some of the (presumed) other isomer, 3,5-bis-(trimethylsilyl)-4-methoxymethylbenzocyclobutene.

The catalytic activity of the CpCo-cyclobutadiene complexes was tested to check on the occurrence of possible (if unlikely) cyclobutadienecobalt ⇆ metallocycle equilibria which might provide a reversible entry into the catalytic cycle. Indeed, in rigorously degassed solutions no catalytic activity was observed for complex **21b.** However, traces of air generated (seemingly by partial decomposition of complex) fine suspensions of a material that slowly and inefficiently catalyzed the trimerization of 1,5-hexadiyne to trimer **1.** To rule out direct catalytic involvement of **21b,** the 1,6-dideuterated diyne was exposed to the same reaction conditions leading to undetectable incorporation of deuterium in recovered "catalyst". It therefore seems unlikely that any cyclopentadienylcobalt based species is responsible for the observed catalytic activity of **21b** in the presence of traces of air.

Conclusion

We have demonstrated that cooligomerizations of α,ω-diynes with monoacetylenes to give benzocyclobutenes, indans, and tetralins should be viable alternatives to the synthesis of these molecules and in fact provide synthetic access to a variety of new derivatives. The yields of benzocycloalkenes are generally moderate but the use of bis(trimethylsilyl)acetylene provides a high-yield synthetic entry into this class of compounds. While lower yields might be tolerable in the synthesis of benzocyclobutene derivatives en route to strained molecules of theoretical interest, the BTMSA variation should be the method of choice in synthetic projects. In principle, complete control of benzene ring substitution is attainable, and in this respect the acetylene cyclization method offers considerable advantages over classical approaches. For steric considerations the efficient formation of penta- and hexasubstituted silylarenes cannot be accomplished at the present time but one would hope that an acetylene somewhat less bulky than BTMSA (e.g., the corresponding germanium or tin derivative) might effect such transformations more successfully. This reasoning also applies in the synthesis of higher benzocycloalkenes where the presently limiting factor lies in the rapid deactivation of cobalt catalyst to give inert cyclobutadiene complexes. The potential for further exploration seems promising in the area of anthraquinone synthesis (for example, in approaches to anthracyclinones[53]), applications of benzocyclobutene intermediates in the construction of natural products,[27] and the synthesis of strained ring benzenes.[26]

Experimental Section

Melting and boiling points are uncorrected. Melting points were performed on a Thomas-Hoover Unimelt apparatus. NMR spectra were recorded on a Varian T-60 NMR spectrometer and are reported in τ from Me_4Si. Unless otherwise stated CCl_4 was used as solvent. IR spectra were obtained with a Perkin-Elmer Model 137 spectrometer. Mass spectra and elemental analyses were provided by the Mass Spectral Service and the Microanalytical Laboratory, respectively, of the University of California, Berkeley, Calif. Analyses are within 0.3% of theoretical values unless mentioned otherwise. Electronic spectra were recorded on a Cary 118 UV spectrometer in 95% ethanol. Gas chromatography was performed on two instruments: a Hewlett-Packard 5710A gas chromatograph with a 20 ft × 0.125 in. 10% UCW 98 on 80–100 WAW-DMCB column, and a Varian Aerograph Model 920 with a 10 ft × 0.375 in. 20% UCW 98 on Chromosorb DMCS/AW 60/80 conditioned at 200 °C column. All chromatography was carried out on E. M. Reagents silica gel (70–230 mesh ASTM), and all preparative TLC on commerical silica gel plates (Merck) or on plates prepared with E. M. Reagents silica gel-PF 254 containing $CaSO_4$ and fluorescent indicator. Solvents were dried by distillation over an appropriate drying agent under nitrogen atmosphere and stored under nitrogen and over Linde molecular sieves (4Å).

Vacuum line operations were carried out on a high vacuum (mercury diffusion) multiple line apparatus. Solvents and reagents to be used in the presence of $CpCo(CO)_2$ were degassed on the vacuum line and purged with dried, air-free (MnO tower) nitrogen.

The reported IR figures are ν_{max} values (cm^{-1}), the UV figures λ_{max} values (nm), log ϵ in parentheses. The abbreviation UV conveniently stands for electronic spectrum. Only the strongest and/or structurally most important fragmentation peaks are reported in the mass spectra of new compounds. Peaks due to higher silicon isotopes are omitted.

Cyclization Method A. 4,5-Bis(trimethylsilyl)benzocyclobutene (8a). Although in smaller batches (2–5 mmol) yields over 60% can be obtained, in larger batches (more practical for synthetic purposes) the prolonged reaction times lead to more cycloaddition to **9.** Shorter reaction times give more diyne trimer **1** (n = 2) and oligomers. The following procedure is not optimized with respect to reaction temperature, catalyst concentration, speed of addition, and concentration of acetylene.

1,5-Hexadiyne (1 g, 12.8 mmol) in BTMSA (5 mL) containing $CpCo(CO)_2$ (20 μL) was added (syringe pump) to refluxing (oil bath 140 °C) BTMSA (35 mL) containing $CpCo(CO)_2$ (30 μL) (72 mg, 0.40 mmol total) under N_2, with magnetic stirring over a period of 72 h. The reaction flask was cooled and connected to a vacuum line and all the volatiles vacuum transferred off to give recovered solvent BTMSA usable as such in further cyclizations. The dark, oily residue was chromatographed on silica with pentane (100 g, 200-mL fractions). Fractions 2 and 3 gave product **8a** as a light yellow oil which was crystallized from methanol-ether at −20 °C (1.1 g, 44%, mp 43–44 °C): mass spectrum *m/e* (rel intensity) 248 (M^+, 27), 233 (90), 217 (100), 159 (30), 73 (94); IR (neat) 2950, 1245, 1090, 923, 837, 760 cm^{-1}; for NMR and UV spectra, see text. Anal. ($C_{14}H_{24}Si_2$) C, H.

Fraction 4 gave colorless crystals of cycloadduct **9**, recrystallized from methanol-ether at −20 °C (190 mg, 3.6%, mp 174–175 °C): mass spectrum *m/e* (rel intensity) 418 (M^+, 2), 416 (2), 344 (15), 330 (26), 257 (31), 241 (26), 73 (100); NMR τ 2.70 (s, 2 H), 6.77 (s, 4 H), 9.62 (s, 18 H), 9.72 (s, 18 H); UV (ether) large end absorption, 269, 273 sh, 278 nm sh; IR spectrum (KBr) 2950, 1260, 1240, 1110, 835, 745 cm^{-1}. Anal. ($C_{22}H_{42}Si_4$) C, H.

Eluting with pentane–ether (98:2) gave a yellow oil of cyclobutadiene complex **21b.** Crystallization from pentane–ether–methanol at −10 °C gave yellow crystals (55 mg, 31% based on $CpCo(CO)_2$, mp 115–118 °C): UV (cyclohexane) large end absorption, 272 (4.36), 276 (4.31), 303 sh (3.21), 392 nm (2.76); IR (KBr) 2930, 1240, 840 cm^{-1}; for mass and NMR spectra, see Table II. Anal. ($C_{25}H_{35}CoSi_2$) C, H, Co.

Eluting with pentane–ether (97:3) gave trimer **1** (n = 2) as colorless crystals[7] (280 mg, 28%) followed by a mixture of higher unidentified oligomers (260 mg).

Cycloaddition of Dimethyl Maleate to 8a. Synthesis of Diester 10. Benzocyclobutene **8a** (19 mg, 0.077 mmol) and dimethyl maleate (14 mg, 0.1 mmol) were heated neat in an evacuated, sealed, thick-walled tube at 200 °C for 24 h. The light brown oil was dissolved in ether and exposed to preparative TLC (silica, pentane–ether, 70:30) to give three bands. The first two bands consisted of traces of unidentified products. The third band gave a colorless oil which was microdistilled to give

cycloadduct **10** (24 mg, 80%, 100 °C oil bath/0.05%): mass spectrum *m/e* (rel intensity) 392 (M^+, 2), 260 (42), 129 (23), 113 (59), 89 (44), 73 (100), 59 (51); NMR τ 2.75 (s, 2 H), 6.35 (s, 6 H), 6.91 (m, 6 H), 9.70 (s, 18 H); IR spectrum (neat) 2950, 1745, 1440, 1250, 1205, 1170, 838, 760 cm^{-1}. Anal. ($C_{20}H_{32}Si_2O_4$) C, H.

Cycloaddition of Maleic Anhydride to 8a. Synthesis of Anhydride 11. Benzocyclobutene **8a** (20 mg, 0.081 mmol) and maleic anhydride (8 mg, 0.08 mmol) were heated for 18 h at 200 °C in a sealed, evacuated tube. A light brown oil was obtained which crystallized on cooling. Recrystallization from ethyl acetate–pentane–ether gave colorless crystals of **11** (24 mg, 86%, mp 183–184 °C): mass spectrum *m/e* (rel intensity) 346 (M^+, 6), 331 (40), 315 (38), 73 (71), 44 (100); NMR ($CDCl_3$) τ 2.53 (s, 2 H), 6.43 (m, 2 H), 6.93 (m, 4 H), 9.63 (s, 18 H); IR spectrum ($CHCl_3$) 2955, 1785, 1255, 1075, 945, 845 cm^{-1}. Anal. ($C_{18}H_{26}Si_2O_3$) C, H.

Trimethylsilylpropargyl Methyl Ether (7, R_3 = $SiMe_3$; R_4 = CH_2OMe). Propargyl methyl ether[19] (3.47 g, 49.7 mmol) in dry ice cooled ether under nitrogen was treated with 2.4 M butyllithium in hexane (23 mL, 55 mmol). A thick white precipitate formed. Subsequently trimethylsilyl chloride (5.95 g, 55 mmol) was added in one portion. The resulting mixture was stirred at room temperature for 1 h, then at reflux for 5 h. Aqueous workup, drying ($MgSO_4$), and distillation gave a colorless liquid of **7** (R_3 = $SiMe_3$; R_4 = CH_2OMe) (6.40 g, 90%, bp 144–145 °C): NMR spectrum τ 6.00 (s, 2 H), 6.70 (s, 3 H), 9.83 (s, 9 H). Anal. ($C_7H_{14}SiO$) C, H.

Cyclization Method B. 4-Trimethylsilyl-5-methoxymethylbenzocyclobutene (8b). 1,5-Hexadiyne (780 mg, 10 mmol) and trimethylsilylpropargyl methyl ether (**7**, R_3 = $SiMe_3$; R_4 = CH_2OMe) (1.42 g, 10 mmol) in *n*-octane (12 mL) containing $CpCo(CO)_2$ (30 μL) were added slowly (syringe pump) to refluxing *n*-octane (60 mL) containing $CpCo(CO)_2$ (20 μL) over a period of 48 h. All volatiles were vacuum transferred off to leave a brown oil. Chromatography on silica (150 g, 200-mL fractions) gave on elution with pentane–ether (92:8) a pale yellow oil. Microdistillation yielded benzocyclobutene **8b** (1.20 g, 55%, 60 °C oil bath/0.01 Torr): mass spectrum *m/e* (rel intensity) 220 (M^+, 3), 205 (60), 175 (100), 131 (33), 73 (19), 59 (39); NMR τ 2.88 (bs, 1 H), 3.02 (bs, 1 H), 5.58 (bs, 2 H), 6.72 (s, 3 H), 6.83 (s, 4 H), 9.72 (s, 9 H). Anal. ($C_{13}H_{20}SiO$) C, H.

Further elution by increasing the ether content in pentane gave several fractions (total of 190 mg) containing higher oligomers of diyne with some trimethylsilyl group incorporation (NMR). Pentane–ether (1:1) eluted a yellow fraction (90 mg) in which the presence of a cyclobutadienecyclopentadienylcobalt complex of the type **21** was detected: mass spectrum *m/e* (rel intensity) 422 (M^+, 13), 408 (79), 294 (63), 155 (47), 73 (100), 59 (35), 45 (35); NMR spectrum τ 3.10 (m), 5.27 (s), 5.62 (bs), 6.77 (s), 6.7–7.4 (m), 9.87 (s). Further purification of this fraction was unsuccessful.

1,8-Dimethoxy-2,6-octadiyne (6, R_1 = R_2 = CH_2OMe). To a stirred solution of methyllithium (1.8 M in ether, 34 mL, 62 mmol) in dry THF (30 mL) at −70 °C under N_2 were added three portions (1 mL each) of neat 1,5-hexadiyne (2.40 g, 31 mmol). The exothermic reaction resulted in a thick, white precipitate of the dilithiodiyne within 3 min. Chloromethyl methyl ether (5.5 mL, 5.4 g, 67 mmol) (*Caution! carcinogenic*) was then added in one portion and the cooling bath removed. Reaction went to completion within 5 min to give a colorless solution containing precipitated lithium chloride. The mixture was worked up with ether–water and dried ($MgSO_4$). Evaporation of solvent gave a slightly yellow liquid which was distilled to give the dimethyl ether **6** (R_1 = R_2 = CH_2OMe) (4.78 g, 93%, bp 73–78 °C (9 Torr)): mass spectrum *m/e* (rel intensity) 166 (M^+, 0.4), 151 (7), 13 (40), 121 (28), 104 (100), 91 (100), 82 (85), 78 (81); NMR spectrum τ 6.03 (bs, 4 H), 6.70 (s, 6 H), 7.58 (bs, 4 H). Anal. ($C_{10}H_{14}O_2$) C, H.

3,6-Dimethoxymethyl-4-trimethylsilylbenzocyclobutene (8c). This compound was first obtained (5–7%) from a reaction of **6** (R_1 = R_2 = CH_2OMe) with BTMSA, one of the highly hindered trimethylsilyl groups being hydrolyzed off during the reaction (or on chromatography). Better yields were obtained with BTMSA as solvent and excess trimethylsilylacetylene as reactant.

A solution of trimethylsilylacetylene[46] (540 mg, 5.5 mmol) and diether **6** (R_1 = R_2 = CH_2OMe) (120 mg, 0.72 mmol) in BTMSA (5 mL) containing $CpCo(CO)_2$ was added to a refluxing solution of $CpCo(CO)_2$ (30 μL) and **6** (0.1 g, 0.6 mmol) in BTMSA (4 mL) over a period of 40 h (syringe pump). The volatiles were removed on the vacuum line and the residue chromatographed on silica gel. Elution with pentane–ether (90:10) gave benzocyclobutene **8c** as a light yellow oil (90 mg, 26%): mass spectrum *m/e* (rel intensity) 264 (M^+, 10), 249 (73), 219 (100), 145 (75), 89 (63), 73 (43); NMR τ 2.87 (s, 1 H), 5.63 (s, 2 H), 5.70 (s, 2 H), 6.70 (s, 6 H), 6.87 (s, 4 H), 9.67 (s, 9 H); IR spectrum (neat) 2940, 1450, 1400, 1370, 1250, 840, 760 cm^{-1}. Anal. ($C_{15}H_{24}SiO_2$) C, H.

Further elution (increasing the ether content in pentane) gave some starting diyne and higher oligomers.

1-Trimethylsilyl-1,5-hexadiyne (6, R_1 = $SiMe_3$; R_2 = H). A 2.5 M solution of butyllithium in hexane (2.68 mL, 6.70 mmol) was added to a stirred solution of TMEDA (0.78 g, 6.70 mmol) in dry THF (50 mL) at −60 °C. Subsequently, 1-trimethylsilylpropyne[19] (0.75 g, 6.70 mmol) in dry THF (10 mL) was syringed in over a period of 1 h and stirring was continued for an additional 1 h at −60 °C. Propargyl bromide (0.84 g, 7.0 mmol) in dry THF (10 mL) was then added over approximately 2 min. The color of the reaction mixture changed from yellow to colorless after half the propargyl bromide had been added. Removing the cold bath and stirring for another 3 h gave a brown solution containing precipitated lithium bromide. Extraction with water to remove LiBr, THF, and TMEDA and isolation of the organic material in ether gave, after evaporation of solvent, crude material (600 mg). Column chromatography on silica gel (eluting with pentane–ether, 97:3) followed by distillation gave pure diyne **6** (R_1 = $SiMe_3$; R_2 = H) as a colorless liquid (400 mg, 40%, bp 35–40 °C (0.5 Torr)): mass spectrum *m/e* (rel intensity) 150 (M^+, 4), 135 (100), 83 (80), 73 (39); NMR τ 7.93 (bs, 4 H), 8.13 (m, 1 H), 9.83 (s, 9 H); IR spectrum (neat) 3300, 2990, 2200, 1950, 1250 cm^{-1}. Anal. ($C_9H_{14}Si$) C, H.

An alternative and more convenient procedure involves the trimethylsilylation of 1,5-hexadiyne monomagnesium bromide.[52] A solution of EtMgBr in dry THF (75 mL) was prepared in the usual fashion (2.50 g of Mg (103 mmol), 11.2 g of EtBr (103 mmol)) at room temperature. It was subsequently transferred by syringe into a stirred solution of 1,5-hexadiyne (8.1 g, 103 mmol) in dry THF (75 mL), the total addition time being approximately 25 min. This solution was left to stir at room temperature for 2 h. Trimethylsilyl chloride (11.2 g, 103 mmol) was then added to the reaction mixture and the solution was left to stir for 24 h. The resulting suspension was poured into saturated NH_4Cl–ether, extracted with water, and dried ($MgSO_4$). Evaporation of solvent gave a yellow liquid which was fractionated to give diyne **6** (R_1 = $SiMe_3$; R_2 = H) (4.53 g, 29%, bp 38–42 °C (0.5 Torr)). The remaining yellow oil contained NMR-pure 1,6-bis(trimethylsilyl)-1,5-hexadiyne (5.3 g, 46% based on Me_3SiCl).

3,4-Bis(trimethylsilyl)benzocyclobutene (8d). 1-Trimethylsilyl-1,5-hexadiyne (**6**, R_1 = $SiMe_3$; R_2 = H) (776 mg, 5.17 mmol), trimethylsilylacetylene[46] (1.49 g, 15.2 mmol), and $CpCo(CO)_2$ (30 μL) in *n*-octane (10 mL) were reacted according to method B. Chromatography on silica gel gave on elution with pentane benzocyclobutene **8d** as a colorless oil (280 mg, 22%, mp 18–19 °C): mass spectrum *m/e* (rel intensity) 248 (M^+, 21), 233 (79), 145 (14), 73 (100); IR (neat) 2900, 1400, 1240, 840 cm^{-1}; for NMR and UV spectra, see text. Anal. ($C_{14}H_{24}Si_2$) C, H.

1,6-Bis(trimethylsilyl)-1,5-hexadiyne (6, R_1 = R_2 = $SiMe_3$). To a solution of 2.4 M butyllithium–hexane (20 mL, 48 mmol) in dry ether (30 mL) under N_2 was added 1,5-hexadiyne (1.87 g, 24 mmol), dropwise with stirring and ice cooling. Subsequently trimethylsilyl chloride (5.2 g, 48 mmol) was added in one portion to the brown suspension, and the mixture stirred overnight at room temperature and refluxed for 3 h. The white precipitate of lithium chloride was filtered off and washed with ether, and the solvent was evaporated to give a light yellow oil. Distillation gave a colorless liquid of **6** (R_1 = R_2 = $SiMe_3$) (4.5 g, 84%, bp 132–134 °C (29 Torr), mp 20–25 °C): NMR spectrum τ 7.63 (s, 4 H), 9.85 (s, 18 H). Anal. ($C_{12}H_{22}Si_2$) C, H.

3,4,6-Tris(trimethylsilyl)benzocyclobutene (8e). To a stirred solution of $CpCo(CO)_2$ (20 μL) in 1,6-bis(trimethylsilyl)-1,5-hexadiyne (4 mL) at 140 °C was added a solution of trimethylsilylacetylene[46] (0.75 g, 7.65 mmol) containing $CpCo(CO)_2$ (20 μL). No additional solvent was used. Addition time (syringe pump) was 24 h. The crude material was chromatographed directly on silica gel (150 g, 100-mL fractions, pentane). Fractions 3 and 4 gave a pale yellow oil of benzocyclobutene **8e** (50 mg, 2%): mass spectrum *m/e* (rel intensity) 320 (M^+, 23), 305 (58), 290 (9), 217 (32), 73 (100); NMR τ 2.60 (s, 1 H), 6.95 (m, 4 H), 9.72 (s, 18 H), 9.83 (s, 9 H); IR spectrum (neat) 2950, 1405, 1300, 1250, 1100, 1020, 915, 835, 753 cm^{-1}. Anal. ($C_{17}H_{32}Si_3$) C, H.

Elution with ether gave recovered solvent diyne.

3,4-Bis(trimethylsilyl)-5-methoxymethylbenzocyclobutene (8f).

1-Trimethylsilyl-1,5-hexadiyne (**6**, R_1 = $SiMe_3$; R_2 = H) (844 mg, 5.62 mmol) and trimethylsilylpropargyl methyl ether (**7**, R_3 = $SiMe_3$; R_4 = CH_2OMe) (797 mg, 5.61 mmol) were reacted by method B. Column chromatography (100 g of silica gel, 150-mL fractions) gave, eluting with pentane–ether (99:1), a light yellow oil of benzocyclobutene **8f** (1.02 g, 63%): mass spectrum *m/e* (rel intensity) 292 (M^+, 2), 173 (56), 117 (85), 73 (100); NMR τ 3.1 (bs, 1 H), 5.58 (bs, 2 H), 6.79 (s, 3 H), 6.84 (m, 4 H), 9.65 (s, 9 H); IR spectrum (neat) 2900, 1245, 1115, 926, 882, 848, 760 cm^{-1}. Anal. ($C_{16}H_{28}Si_2O$) C, H.

Analysis of the vacuum transferred volatiles revealed the presence of traces of propargyl ether and diyne. Product **8f** was contaminated by a small inseparable amount (<15%) of what presumably is the 3,5-bis(trimethylsilyl)-4-methoxymethyl isomer as evidenced by NMR τ 2.90 (bs), 9.72 (s), 9.77 (s).

5,6-Bis(trimethylsilyl)indan (14a). 1,6-Heptadiyne (151 mg, 1.64 mmol) and BTMSA were brought to reaction by method A. Column chromatography on silica (80 g) eluting with pentane (200-mL fractions) gave fractions 2 and 3 containing a light yellow oil that crystallized on standing. Recrystallization from ether–methanol at −60 °C gave indan **14a** (344 mg, 80%, mp 68–69 °C): mass spectrum *m/e* (rel intensity) 262 (M^+, 18), 247 (85), 231 (100); IR (CCl_4) 2900, 1250, 1110, 935, 858, 837 cm^{-1}. For NMR and UV spectra, see text. Anal. ($C_{15}H_{26}Si_2$) C, H.

When the above reaction was carried out using only a fivefold excess of BTMSA in refluxing *n*-octane[1b] column chromatography as above gave **14a** (215 mg, 50%), followed by a yellow fraction which on evaporation of solvent resulted in a yellow oil of cyclobutadiene complex **21c** (43 mg, 22% based on catalyst): IR (neat) 2930, 1240, 837 cm^{-1}; for mass and NMR spectra, see Table II. Anal. ($C_{27}H_{39}CoSi_2$) C, H.

5,6-Dicarbomethoxyindan (14b). 1,6-Heptadiyne (460 mg, 5 mmol) and dimethyl acetylenedicarboxylate (710 mg, 5 mmol) in toluene–*n*-octane (50:50 by volume, 25 mL) were cooligomerized as in method B (1 h addition time). Column chromatography (100 g of Alcoa F-20 alumina) gave trimer **1** (*n* = 3, 70 mg, 15%)[7] on elution with pentane. Changing the solvent to ether gave a colorless oil which was sublimed (108 °C oil bath, 0.05 Torr) to give colorless crystals of indan **14b** (230 mg, 20%, mp 67–68 °C (lit.[47] mp 68 °C)): mass spectrum *m/e* (rel intensity) 234 (M^+, 19), 203 (100), 175 (13); NMR τ 2.61 (s, 2 H), 6.26 (s, 6 H), 7.10 (bt, *J* = 7 Hz, 4 H), 7.90 (quintet, *J* = 7 Hz, 2 H); IR spectrum (CCl_4) 2930, 1735, 1430, 1325, 1275, 1205, 1120, 1030, 970, 892 cm^{-1}. Anal. ($C_{13}H_{14}O_4$) C, H.

5-Phenylindan (14c). 1,6-Heptadiyne (460 mg, 5 mmol) and phenylacetylene (510 mg, 5 mmol) in *n*-octane (25 mL) were reacted as in method B (3 h addition time). Column chromatography on silica gel (100 g) eluting with pentane gave colorless crystals of product in the first fractions, which were recrystallized from ether–methanol (1:5) to give pure 5-phenylindan (**14c**), 250 mg (26%), mp 74–75 °C (lit.[48] bp 108–110 °C (0.09 Torr)): mass spectrum *m/e* (rel intensity) 194 (M^+, 100), 117 (20); NMR τ 2.75 (m, 8 H), 7.13 (bt, *J* = 7 Hz, 4 H), 7.95 (quintet, *J* = 7 Hz, 2 H); IR spectrum (CCl_4) 3020, 2950, 2850, 1550, 1480, 1440, 1260, 1050, 1020, 888, 870 cm^{-1}. Anal. ($C_{15}H_{14}$) C, H.

5,6-Diphenylindan (14d). Diphenylacetylene (1.78 g, 10 mmol) was dissolved in *n*-octane (30 mL) and $CpCo(CO)_2$ (50 μL) added. This solution was brought to reflux (under dry N_2) and 1,6-heptadiyne (460 mg, 5 mmol) in *n*-octane (20 mL) was added over a 20-h period using a syringe pump. Column chromatography on silica gel (100 g) gave eluting with pentane unreacted diphenylacetylene (170 mg, 10%), Further elution gave *trans*-stilbene (115 mg, 6%) identified by comparison with authentic material (NMR, TLC). Continued elution with pentane resulted in colorless crystals which were recrystallized to give diphenylindan **14d** (345 mg, 24%, mp 119–120 °C): mass spectrum *m/e* (rel intensity) 270 (M^+, 100), 241 (24); NMR τ 2.80 (s, 2 H), 2.90 (s, 10 H), 7.05 (bt, *J* = 7 Hz, 4 H), 7.85 (quintet, *J* = 7 Hz, 2 H); IR spectrum (CCl_4) 3020, 3000, 2910, 2820, 1590, 1470, 1425, 1070, 1020, 912, 883 cm^{-1}. Anal. ($C_{21}H_{18}$) C, H.

5-*n*-Hexylindan (14e). 1,6-Heptadiyne (460 mg, 5 mmol) and 1-octyne (470 mg, 4.3 mmol) were reacted according to method B. Column chromatography of all nonvolatiles on silica gel (100 g) eluting with pentane gave indan **14e** in the first few fractions as a colorless oil, purified by microdistillation (120 mg, 14%, bp 43 °C oil bath (0.2 Torr), lit.[49] 161.5–161.9 °C (17 Torr)): mass spectrum *m/e* (rel intensity) 202 (M^+, 17), 131 (100), 117 (22); NMR τ 3.07 (m, 3 H), 7.15 (bt, *J* = 7 Hz, 4 H), 7.47 (bt, *J* = 7 Hz, 2 H), 7.98 (quintet, *J* = 7 Hz, 2 H), 8.63 (m, 8 H), 9.10 (m, 3 H); IR spectrum (neat) 2990, 2850, 1495, 1490, 1485, 1370, 1310, 870, 818, 788 cm^{-1}. Anal. ($C_{15}H_{22}$) C, H.

6,7-Bis(trimethylsilyl)tetralin (15a). 1,7-Octadiyne (174 mg, 1.64 mmol) and BTMSA were brought to reaction as described in method A. Column chromatography on silica (100 g, 200-mL fractions) eluting with pentane gave fractions 2 and 3 containing a pale yellow oil which was crystallized from pentane–ether at −70 °C to give colorless crystals of tetralin **15a** (366 mg, 83%, mp 45–46 °C): mass spectrum *m/e* (rel intensity) 276 (M^+, 20), 261 (100), 73 (85); IR spectrum (KBr) 2900, 1550, 1440, 1430, 1400, 1290, 1240, 1170, 1125, 1010, 945, 922, 833, 753 cm^{-1}. For NMR and UV spectra, see text. Anal. ($C_{16}H_{28}Si_2$) C, H.

Fraction 4 gave a yellow oil which was crystallized from ether–methanol at −10 °C to give orange crystals of the biscyclobutadiene complex **20b** (15 mg, 10% based on catalyst, mp 143–144 °C): IR (KBr) 2950, 1243, 840 cm^{-1}; for mass and NMR spectra, see Table II. Anal. ($C_{34}H_{56}Co_2Si_4$) C, H.

Fractions 5 and 6 gave a yellow oil of cyclobutadiene complex **21d** (31 mg, 16% based on catalyst): IR (neat) 2920, 1237, 837 cm^{-1}; for mass and NMR spectra, see Table II.

Fractions 7 and 8 gave trimer **1** (*n* = 4) (10 mg, 6%).[7]

6,7-Dicarbomethoxytetralin (15b). 1,7-Octadiyne (530 mg, 5 mmol) and dicarbomethoxyacetylene (710 mg, 5 mmol) were reacted as in method B (1 h addition time). Loss of the monoyne was followed by GLC and was complete within 6 h. Column chromatography on 100 g of Alcoa alumina F-20 gave on elution with pentane trimer **1** (*n* = 4) (70 mg, 13%).[7] Changing the solvent to ether resulted in the isolation of a slightly yellow oil which was microdistilled to give a colorless liquid of tetralin **15b** (320 mg, 26%, bp 115 °C oil bath (0.05 Torr), lit.[47] bp 157–158 °C (3 Torr)): mass spectrum *m/e* (rel intensity) 248 (M^+, 15), 217 (100), 189)15); NMR τ 2.70 (s, 2 H), 6.24 (s, 6 H), 7.20 (m, 4 H), 8.20 (m, 4 H); IR spectrum (neat) 2930, 1730, 1620, 1570, 1430, 1280, 1215, 1165, 1130, 1050, 975, 933, 910, 877, 830, 793, 772 cm^{-1}. Anal. ($C_{14}H_{16}O_4$) C, H.

6-Phenyltetralin (15c). 1,7-Octadiyne (530 mg, 5 mmol) and phenylacetylene (510 mg, 5 mmol) were reacted as described in method B (3 h addition time). Column chromatography on silica gel (100 g) eluting with pentane gave a colorless oil in the first fractions. Microdistillation gave tetralin **15c** (185 mg, 18%, bp 97 °C oil bath (0.5 Torr)): mass spectrum *m/e* (rel intensity) 208 (M^+, 100), 180 (83); NMR τ 2.4–3.2 (m, 8 H), 7.25 (m, 4 H), 8.22 (m, 4 H); IR spectrum (neat) 2970, 2900, 2820, 1470, 1435, 1420, 905, 829, 760, 696 cm^{-1}. Anal. ($C_{16}H_{16}$) C, H.

6,7-Diphenyltetralin (15d). 1,7-Octadiyne (530 mg, 5 mmol) and diphenylacetylene (890 mg, 5 mmol) in toluene (20 mL) were cyclized according to method B. Column chromatography with pentane on silica gel (100 g) gave *trans*-stilbene (75 mg, 8%, mp 120–122 °C), identical with authentic material (TLC, NMR, mass spectrum). Further elution with pentane gave a fraction containing colorless crystals. Recrystallization from ether–methanol gave diphenyltetralin **15d** (295 mg, 21%, mp 110.5–112 °C): mass spectrum *m/e* (rel intensity) 284 (M^+, 72), 194 (100); NMR τ 3.03 (bs, 10 H), 3.07 (s, 2 H), 7.25 (m, 4 H), 8.20 (m, 4 H); IR spectrum (CCl_4) 3030, 3000, 2900, 2835, 1600, 1550, 1470, 1440, 1390, 1345, 1240, 1070, 1020, 990, 925, 912, 875, 702 cm^{-1}. Anal. ($C_{22}H_{20}$) C, H.

6-*n*-Hexyltetralin (15e). 1,7-Octadiyne (530 mg, 5 mmol) and 1-octyne (550 mg, 5 mmol) were reacted as in method B. Column chromatography on silica gel (100 g) gave a colorless oil which was microdistilled to give tetralin **15e** (155 mg, 14%, bp 83 °C oil bath (0.02 Torr), lit.[51] bp 120.5–122 °C (0.8 Torr)): mass spectrum *m/e* (rel intensity) 216 (M^+, 26), 145 (100); NMR τ 3.25 (bs, 3 H), 7.32 (m, 4 H), 7.53 (t, *J* = 7.5 Hz, 2 H), 8.23 (m, 4 H), 8.65 (m, 8 H), 9.12 (bt, *J* = 5.5 Hz, 3 H); IR spectrum (neat) 2920, 2850, 1500, 1450, 1430, 912, 827, 811 cm^{-1}. Anal. ($C_{16}H_{24}$) C, H.

6-Trimethylsilyl-7-methyltetralin (15f).[50] 1,7-Octadiyne (1.06 g, 10 mmol) and 1-trimethylsilyl-1-propyne[19] (2.24 g, 20 mmol) were cyclized as described in method B. The residue was chromatographed on silica (120 g, eluted with hexane, 50-mL fractions). Fractions 2–5 contained an oil that was distilled through a Kugelrohr to give a colorless liquid of tetralin **15f** (750 mg, 34%, bp 90 °C bath (0.15 Torr)): mass spectrum *m/e* (rel intensity) 218 (M^+, 33), 204 (37), 203 (100), 73 (31), 59 (48), 45 (20); NMR τ 3.00 (bs, 1 H), 3.27 (bs, 1 H), 7.34 (m, 4 H), 7.67 (s, 3 H), 8.27 (m, 4 H), 9.74 (s, 9 H); UV 268 nm sh (3.11), 273 (3.14), 283 (3.00); IR spectrum (neat) 2900, 1600, 1440, 1430, 1380, 1300, 1260, 1240, 1220, 1165, 1030, 945, 935, 922, 870, 840, 760, 742, 709, 697 cm^{-1}. High-resolution *m/e:* calcd for

$C_{14}H_{22}Si$, 218.1491; found, 218.1493. Protodesilylation gave 6-methyltetralin,[54a] identified by its spectral data.

7,8-Bis(trimethylsilyl)benzocycloheptene (16a). 1,8-Nonadiyne (246 mg, 2 mmol) was brought to reaction according to method A. Column chromatography of the residue (70 g of silica, 200-mL fractions) gave, eluting with pentane, in fraction 1 a colorless oil which was microdistilled to give benzocycloheptene **16a** (17 mg, 3%, bp oil bath 130 °C (0.01 Torr)): mass spectrum *m/e* (rel intensity) 290 (M^+, 29), 275 (100), 259 (55), 244 (23), 203 (39), 73 (79), 59 (25), 45 (24), 43 (13); NMR τ 2.78 (s, 2 H), 7.25 (m, 4 H), 8.28 (m, 6 H), 9.83 (s, 18 H); IR spectrum (neat) 2920, 2850, 1450, 1250, 1135, 850, 830, 750 cm^{-1}.

Protodesilylation gave benzocycloheptene,[54b] identified by its spectral data. Further elution gave in fractions 3 and 4 a yellow oil of biscyclobutadiene complex **20c** (48 mg, 34% based on catalyst): IR (neat) 2940, 1250, 835 cm^{-1}; for mass and NMR spectra, see Table II. Anal. ($C_{35}H_{58}Co_2Si_4$) C, H.

Fractions 5 and 6 gave a yellow oil of cyclobutadiene complex **19b** (65 mg, 39% based on catalyst): IR (neat) 3280, 2920, 2120, 1430, 1335, 1240, 870, 805 cm^{-1}; for mass and NMR spectra, see Table II.

2,3-Bis(trimethylsilyl)anthraquinone (18a). 1,2-Bis(propiolyl)benzene[21] (350 mg, 2.3 mmol) was dissolved in diglyme (8 mL) and added over 36 h (with a syringe pump) to a refluxing solution of BTMSA (5 mL) and $CpCo(CO)_2$ (60 μL) in *n*-octane (70 mL), under a dry N_2 atmosphere. Removal of solvent and unreacted BTMSA by vacuum transfer followed by column chromatography on silica gel (100 g) eluted with pentane–ether (80:20) a yellow oil which solidified on standing. Recrystallization from methanol gave orange crystals of anthraquinone **18a** (120 mg, 15%, mp 69–71.5 °C): mass spectrum *m/e* (rel intensity) 352 (M^+, 14), 337 (17), 73 (67), 57 (79), 55 (77), 43 (100), 41 (67); NMR τ 1.50 (s, 2 H), 1.70 (m, 2 H), 2.23 (m, 2 H), 9.51 (s, 18 H); IR spectrum (CCl_4) 2900, 1670, 1540, 1320, 1290, 1250, 1005, 980, 952, 932 cm^{-1}. Anal. ($C_{20}H_{24}O_2Si_2$) C, H.

1,2-Bis(trimethylsilylpropiolyl)benzene (17b). Ethylmagnesium bromide prepared from magnesium (750 mg, 31 mmol) and ethyl bromide (3.30 g, 30 mmol) in dry THF (70 mL) was treated with trimethylsilylacetylene (2.94 g, 30 mmol), addition time ca. 2–3 min. After gas evolution ceased, the solution was warmed to gentle reflux.

o-Phthalaldehyde (2.07 g, 15 mmol) in dry THF (25 mL) was then added over 3–5 min with mild frothing, and the solution was refluxed for 2 h. After cooling, the reaction was quenched with saturated NH_4Cl (300 mL), the aqueous layer was extracted with ether (3 × 70 mL), and all organic phases were combined and dried over $MgSO_4$. Evaporation of solvent gave a light brown oil (5.32 g) which showed no aldehydic protons in the NMR spectrum.

Jones oxidation with a stock solution (prepared from 34 g of CrO_3, 28 mL of concentrated H_2SO_4, and 200 mL of H_2O) was carried out by adding the oxidizing solution (20 mL) to all of the brown oil from above in acetone (200 mL). The temperature was kept at 5–10 °C, and the solution allowed to warm gradually to room temperature and stirred for 2 h. The resulting solution was added to water (400 mL) and extracted with ether (3 × 150 mL). The organic phase was washed with saturated $NaHCO_3$ (50 mL) and then several portions (50 mL) of water until the aqueous washes were clear. Washing once with brine and drying over $MgSO_4$ gave a light yellow oil after removal of ether. Crystallization from methanol gave colorless crystals of diketodiyne **17b** (3.54 g, 72%, mp 48–50 °C): mass spectrum *m/e* (rel intensity) 326 (M^+, 37), 311 (37), 237 (24), 73 (100); NMR τ 2.37 (AA′BB′, 4 H), 9.73 (s, 18 H); IR spectrum (neat) 2930, 2150, 1650, 1245, 1060, 1015, 850, 763, 727 cm^{-1}. Anal. ($C_{18}H_{22}Si_2O_2$) C, H.

1,4-Bis(trimethylsilyl)-2-*n*-hexylanthraquinone (18b). 1-Octyne (132 mg, 1.2 mmol) in *n*-octane (7 mL) was added to a solution of diketodiyne **17b** (390 mg, 1.2 mmol) and $CpCo(CO)_2$ (50 μL) in *n*-octane (20 mL) over a period of 18 h under N_2 with reflux. Evaporation of solvent and column chromatography on silica gel (100 g) eluting with pentane–ether (90:10) gave a yellow-brown oil. Crystallization from pentane–methanol gave orange crystals of anthraquinone **18b** (110 g, 21%, mp 118–120 °C): mass spectrum *m/e* (rel intensity) 436 (M^+, 2), 421 (20), 97 (29), 95 (32), 83 (32), 81 (34), 73 (23), 43 (100); NMR τ 1.83 (m, 2 H), 3.10 (m, 3 H), 7.10 (t, J = 7 Hz, 2 H), 8.63 (m, 8 H), 9.10 (m, 3 H), 9.80 (s, 9 H), 9.82 (s, 9 H); IR spectrum (CCl_4) 2900, 1655, 1540, 1240, 1005 cm^{-1}. Anal. ($C_{26}H_{36}O_3Si_2$) C, H.

Further elution with pentane–ether (90:10) gave a brown oil which crystallized on standing. Recrystallization from ether–methanol at −20 °C gave orange crystals of cyclobutadiene complex **22** (15 mg, 8%, mp 155–157 °C dec): mass spectrum *m/e* (rel intensity) 450 (100), 435 (9), 360 (39), 312 (29), 73 (69); NMR τ 1.98 (m, 2 H), 2.43 (m, 2 H), 5.20 (s, 5 H), 9.67 (s, 9 H); IR spectrum (CCl_4) 2940, 1665, 1600, 1550, 1250, 1220, 1010, 959 cm^{-1}. Anal. ($C_{23}H_{27}CoO_2Si_2$) C, H.

Reaction of 1,5-Hexadiyne with Di-*tert*-butylacetylene in the Presence of $CpCo(CO)_2$. 1,5-Hexadiyne (400 mg, 5.1 mmol) in *n*-octane (5 mL) was added (syringe pump) to a solution of di-*tert*-butylacetylene (2.5 g, 18 mmol) and $CpCo(CO)_2$ (50 μL) in refluxing *n*-octane (40 mL) under N_2 over a period of 20 h. The volatiles were removed on the vacuum line and the residual oil chromatographed on silica (100 g). Eluting with pentane–ether (98:2) gave a yellow oil consisting of a mixture of cyclobutadiene complex **21a** and trimer **1** (n = 2). The trimer was crystallized in ether–methanol at −20 °C to give mother liquors containing spectrally pure complex **21a** (15 mg, 9% based on $CpCo(CO)_2$): IR (neat) 2940, 1475, 1350, 805 cm^{-1}; for mass and NMR spectra, see Table II.

Further elution gave trimer **1** (n = 2) (230 mg, 57%)[7] followed by a yellow fraction containing a mixture of **1, 20aα,** and **20aβ** (80 mg). This mixture was rechromatographed on alumina (50 g, Woelm II) eluting with pentane which resulted in clean separation of **1** from the two crystalline isomers of **20.** Isomer **20aα** was obtained pure by repeated fractional crystallization to give yellow plates (16 mg, 7% based on $CpCo(CO)_2$, mp 189–191 °C): IR (KBr) 2920, 1360, 1005, 807 cm^{-1}; for mass and NMR spectra, see Table II. Anal. ($C_{36}H_{52}Co_2$) C, H, Co.

Isomer **20bβ** could not be purified completely owing to the scarcity of material and was contaminated (ca. 20%) with **20aα** (13 mg, 5%, mp 164–174 °C): IR (neat) 2910, 1350, 1110, 1000, 805 cm^{-1}; for mass and NMR spectra, see Table II.

Further elution of the original silica gel column with pentane–ether (98:2) gave a yellow oil. This oil was rechromatographed on silica gel (50 g) eluting with pentane (200-mL fractions) to give in fraction 7 a yellow oil of complex **19a** (20 mg, 15% based on $CpCo(CO)_2$): IR (neat) 3250, 2930, 2110, 1345, 806 cm^{-1}; for mass and NMR spectra, see Table II. Anal. Calcd for $C_{21}H_{29}Co$: C, 74.10; H, 8.59. Found: C, 74.93; H, 9.02.

Tests of the Catalytic Activity of Complex 21b. 1,5-Hexadiyne (80 mg, 1 mmol) in *n*-octane (40 mL) that had not been thoroughly degassed (10 min N_2 purge) was brought to reflux under N_2 in the presence of **21b** (50 mg) and the decrease in diyne concentration monitored by GC. After 3 days 40% of the acetylene had disappeared and the solution had the appearance of a cloudy suspension. At this stage an additional amount of complex **21b** (50 mg) was added and the heating continued for a further 3 days at which time 90% of diyne had disappeared. The solvent was evaporated and the residue chromatographed by preparative TLC (silica, pentane eluent) to give a yellow band of complex **21b** (20 mg, 20% recovered) and a second colorless band of trimer **1** (n = 2) (9 mg, 11%).[7]

When this reaction was repeated with 1,6-dideuterio-1,5-hexadiyne (75% deuterated) the corresponding deuterated trimer **1** (n = 2)[7] was obtained: mass spectrum *m/e* (rel intensity) 240 (M^+, 0.1), 239 (0.7), 238 (1.4), 237 (1.3), 236 (0.7), 235 (0.4), 234 (0.7), 117 (100); NMR shows an appropriately decreased absorption (35%) for the aromatic protons when compared with the methylene absorptions; IR spectrum (neat) ν_{C-D} 2250 cm^{-1}.

When this reaction was repeated with 1,7-octadiyne (160 mg, 1.51 mmol) and complex **21b** (50 mg) in *n*-octane (0.5 mL) in a vacuum sealed and degassed ampule at 170 °C for 17 h, evaporation of solvent and preparative TLC gave two yellow bands. The first consisted of starting complex **21b** (15 mg, 30% recovery). The second band gave a yellow oil of a presumed (impure) cycloadduct of diyne to **21b** (22 mg, 36%): mass spectrum *m/e* (rel intensity) 556 (M^+, 17), 554 (9), 450 (12), 333 (47), 294 (20), 225 (20), 163 (43), 155 (21), 141 (25), 124 (28), 73 (100), 43 (85); IR spectrum $\nu_{C\equiv C}$ 3280, 2130 cm^{-1}. This material was not investigated or purified further.

Benzocyclobutene and 4,5-Dideuteriobenzocyclobutene. 4,5-Bis(trimethylsilyl)benzocyclobutene (**8a,** 200 mg, 0.81 mmol) was dissolved in methylene chloride (5 mL) and trifluoroacetic acid (2 mL) added in one portion with stirring and ice cooling. The solution was warmed to room temperature, water added (50 mL), and the mixture extracted with ether (20 mL). The ether layer was washed with water (3 × 30 mL) and dried ($MgSO_4$). The ether was removed by distillation and the residue exposed to preparative GLC to give pure ben-

zocyclobutene (66 mg, 78%), identical (GC, NMR, IR) with a sample prepared by another route.[25a] If the protodesilylation of **8a** is carried out in an NMR tube (CCl_4) quantitative conversion is observed.

Similar reaction with deuteriotrifluoroacetic acid (with or without added D_2SO_4) gave 4,5-dideuteriobenzocyclobutene: mass spectrum *m/e* (rel intensity) 106 (M^+, 100), 80 (45), 52 (27); NMR spectrum τ 3.02 (bs, 2 H), 6.83 (s, 4 H).

Kinetic Measurements of Deuteriodesilylation of Benzocycloalkenes 8a, 8d, 14a, and 15a. Kinetic data were obtained by dissolving ca. 5–7 mg of the bissilyl compound in 0.50 g of CCl_4 containing 2% Me_4Si, this in a standard NMR sample tube. The spectrometer was tuned for optimum resolution on this sample. The tube was then removed from the probe and treated with 0.51 g of a stock solution of the deuterated acids (wt % 14.8% CF_3COOD, 12.7% CD_3COOD, and 71.9% CCl_4). This combined solution was then shaken vigorously as a stopwatch was started, and the tube was returned to the NMR probe. The spectrum was then scanned periodically over the region from 0.7 to 0.0 ppm downfield from Me_4Si. The frequency of the scans was generally every minute for the first 15 min of the reaction, followed by lengthening this to 10–15 min during the second desilylation step. The reactions were followed to completion. The disappearance of starting material and appearance of product was measured relative to internal standard Me_4Si (which is unaffected by the reaction conditions) and plotted in a standard Arrhenius plot. Observed pseudo-first-order rate constants (min^{-1}) follow: **8a:** $k_1 = 0.175$, $k_2 = 4.63 \times 10^{-3}$; **14a,** $k_1 = 0.19$, $k_2 = 5.3 \times 10^{-3}$; **15a**, $k_1 = 0.16$, $k_2 = 3.8 \times 10^{-3}$; **8d**, $k_1 = 0.19$, $k_2 = 3.8 \times 10^{-4}$.

3,5-Bis(trimethylsilyl)benzocyclobutene (25a). The ortho isomer **8a** (270 mg) was dissolved in CCl_4–methanol (1:1) and trifluoroacetic acid added (25 μL). The mixture was stirred for 7 h and the solvent evaporated. An NMR spectrum showed 65% rearrangement to **25a.** Purification was achieved by preparative GC (5 ft × 0.25 in. SS 1.5% OV 101 on 100/120 Chromosorb G, 155 °C column temperature) which gave **25a** (retention time 4 min) and **8a** (retention time 7 min). Compound **25a** crystallized on cooling (mp 20–25 °C): mass spectrum *m/e* (rel intensity) 248 (M^+, 15), 233 (100), 109 (14), 73 (32), 43 (18); IR (neat) 2950, 1470, 1250, 1155, 953, 895, 870, 840, 770, 755, 693 cm^{-1}. For NMR and UV spectra, see text. Anal. ($C_{14}H_{24}Si_2$) C, H.

4-Trimethylsilyl-5-bromobenzocyclobutene (23c). To 4,5-bis(trimethylsilyl)benzocyclobutene (**8a**, 936 mg, 3.77 mmol) and pyridine (304 μL, 3.77 mmol) in CCl_4 (10 mL) was added bromine (1.20 g, 7.50 mmol) with ice cooling and magnetic stirring. After 20 min the mixture was worked up with ether–aqueous $Na_2S_2O_3$, washed with water, and dried (Na_2SO_4). The NMR spectrum of the crude product showed clean monobromination. Crystallization from ether–methanol at −70 °C gave colorless crystals of bromide **23c** (884 mg, 92%, mp 55–56 °C): mass spectrum *m/e* (rel intensity) 256, 254 (M^+, 1:1, 1.4) 159 (100); NMR τ 2.88 (bs, 1 H), 3.00 (bs, 1 H), 6.90 (s, 4 H), 9.63 (s, 9 H); IR spectrum (neat) 2930, 1440, 1410, 1375, 1330, 1310, 1240, 1200, 1185, 1120, 1070, 1060, 950. 940, 905, 840, 754, 690 cm^{-1}. Anal. ($C_{11}H_{15}BrSi$) C, H, Br.

4,5-Dibromobenzocyclobutene (24c). Monobromide **23c** (100 mg, 0.39 mmol) in CCl_4 (3 mL) was reacted with bromine (70 mg, 0.44 mmol) for 6 h. The resulting solution was worked up with aqueous $Na_2S_2O_3$, washed with water, and dried ($MgSO_4$). Evaporation of solvent and crystallization from ether–methanol gave colorless crystals of dibromide **24c** (97 mg, 95%, mp 72–73 °C): mass spectrum *m/e* (rel intensity) 264, 262, 260 (M^+, 1:2:1, 49), 102 (100); NMR τ 2.73 (s, 2 H), 6.93 (s, 4 H); IR spectrum (neat) 2940, 1435, 1400, 1335, 1260, 1220, 1100, 1070, 1020, 875, 862, 800, 722 cm^{-1}. Anal. ($C_8H_6Br_2$) C, H, Br.

4,5-Bromoiodobenzocyclobutene (24d). Monobromide **23c** (884 mg, 3.47 mmol) in CCl_4 (20 mL) was reacted with iodine monochloride (620 mg, 3.77 mmol) at room temperature for 17 h. The mixture was washed with aqueous $Na_2S_2O_3$, then water, and dried ($MgSO_4$). Evaporation of solvent and recrystallization of the crystalline residue gave colorless crystals of bromoiodide **24d** (1.01 g, 95%, mp 49–51 °C): mass spectrum *m/e* (rel intensity) 310, 308 (1:1, M^+, 34), 102 (100); NMR τ 2.47 (bs, 1 H), 2.67 (bs, 1 H), 6.83 (s, 4 H); IR spectrum (neat) 2960, 2920, 2850, 1580, 1570, 1440, 1430, 1415, 1110, 880, 858, 819, 708 cm^{-1}. Anal. (C_8H_6BrI) C, H.

4,5-Bromoacetylbenzocyclobutene (24e). Monobromide **23c** (30 mg, 0.12 mmol) in CS_2 (5 mL) was stirred with acetyl chloride (11 mg, 0.13 mmol) and $AlCl_3$ (60 mg, 0.45 mmol) at room temperature for 5 h. The mixture was quenched with water, extracted with ether, and dried ($MgSO_4$). The solvent was evaporated and the residue subjected to preparative TLC (silica, pentane–ether, 90:10) to give two bands. The first band contained a colorless liquid that was microdistilled to give pure ketone **24e** (15 mg, 56%, bp 100 °C oil bath (0.05 Torr)): mass spectrum *m/e* (rel intensity) 226, 224 (1:1, M^+, 27), 209 (100); NMR τ 2.78 (bs, 1 H), 2.98 (bs, 1 H), 6.82 (s, 4 H), 7.44 (s, 3 H); IR spectrum (neat) 2970, 2940, 1700, 1265, 1095, 1070, 877, 807 cm^{-1}. Anal. ($C_{10}H_9BrO$) C, H. Br: calcd, 35.50; found, 35.92. The second band (5 mg) was not investigated.

4,5-Diiodobenzocyclobutene (24f). Bissilyl compound **8a** (482 mg, 1.94 mmol) was stirred in CCl_4 (10 mL) and iodine monochloride added (650 mg, 4 mmol). After 17 h the mixture was washed with aqueous $Na_2S_2O_3$, then water, and dried ($MgSO_4$). Evaporation of solvent gave a light yellow oil which crystallized on standing. Recrystallization from ether–methanol at −20 °C gave colorless crystals of the diiodide (**24f**) (652 mg, 94%, mp 89–90 °C): mass spectrum *m/e* (rel intensity) 356 (M^+, 100), 102 (58); NMR τ 2.42 (s, 2 H), 6.88 (s, 4 H); IR spectrum (KBr) 2900, 1425, 1320, 1260, 1215, 1080, 858, 702 cm^{-1}. Anal. ($C_8H_6I_2$) C, H, I.

5,6-Bromoiodoindan (26). Bis(trimethylsilyl)indan **14a** (205 mg, 0.785 mmol) was brominated as described in the synthesis of **23c** to give a light yellow oil of 5,6-bromotrimethylsilylindan (215 mg): NMR spectrum τ 2.67 (bs, 1 H), 2.77 (bs, 1 H), 7.17 (bt, J = 7 Hz, 4 H), 7.98 (quintet, J = 7 Hz, 2 H), 9.57 (s, 9 H). This material was redissolved in CCl_4 (10 mL), iodine monochloride added (130 mg, 0.8 mmol), and the solution stirred for 40 h. Workup as above gave a light yellow oil of bromoiodide **26** (255 mg, 100%) not purified any further: NMR spectrum τ 2.37 (bs, 1 H), 2.58 (bs, 1 H), 7.17 (bt, J = 7 Hz, 4 H), 7.97 (quintet, J = 7 Hz, 2 H). Treatment of this material with magnesium gave 2,3:6,7-dicyclopentenobiphenylene.[26d]

6,7-Bromoiodotetralin (27). Bis(trimethylsilyl)tetralin **15a** (205 mg, 0.745 mmol) was exposed to bromine as described in the synthesis of **23c** to give 6,7-bromotrimethylsilyltetralin (210 mg): NMR spectrum τ 2.87 (bs, 1 H), 3.00 (bs, 1 H), 7.35 (m, 4 H), 8.27 (m, 4 H), 9.63 (s, 9 H). This material was reacted with iodine monochloride (125 mg, 0.77 mmol) and worked up as above to give a light yellow oil of bromoiodide **27** (248 mg, 99%): NMR spectrum τ 2.53 (bs, 1 H), 2.75 (bs, 1 H), 7.37 (m, 4 H), 8.30 (m, 4 H). Treatment of this product with magnesium gave 2,3:6,7-dicyclohexenobiphenylene.[26d]

4-Bromo-5-methoxymethylbenzocyclobutene (28). To 4-trimethylsilyl-5-methoxymethylbenzocyclobutene (**8b,** 1.20 g, 5.45 mmol) in CCl_4 (20 mL) was added bromine (870 mg, 5.45 mmol) in CCl_4 (10 mL) with ice cooling. The mixture was stirred for 30 min, extracted with aqueous $Na_2S_2O_3$, then water, and dried. Evaporation of solvent followed by column chromatography of the residue on silica eluting with pentane–ether (97:3) gave a light yellow oil, distilled by microdistillation to yield the bromide **28** as a colorless oil (804 mg, 65%, bp 60 °C oil bath (0.01 Torr)): mass spectrum *m/e* (rel intensity) 228, 226 (1:1, M^+, 29), 147 (100); NMR spectrum τ 2.87 (bs, 2 H), 5.60 (bs, 2 H), 6.60 (s, 3 H), 6.85 (bs, 4 H). Anal. ($C_{10}H_{11}BrO$) C, H, Br.

This material gave, on treatment with butyllithium in THF followed by aqueous workup, 1,2-cyclopropa-4,5-cyclobutabenzene and mainly 4-methoxymethylbenzocyclobutene.[26f]

3,6-Bis(methoxymethyl)-4-iodobenzocyclobutene (29). To silylbenzocyclobutene **8c** (267 mg, 1 mmol) in CCl_4 (20 mL) at 0 °C was added a 0.146 M solution (6.86 mL, 1 mmol) of iodine monochloride in CCl_4. Usual workup gave the crude product (325 mg) which was chromatographed on silica, eluting with pentane–ether (98:2), to give the pure iodide **29** as a colorless oil (293 mg, 92%): mass spectrum *m/e* (rel intensity) 318 (M^+, 82), 303 (14), 286 (13), 273 (21), 258 (100), 115 (89); NMR τ 2.47 (s, 1 H), 5.67 (s, 2 H), 5.75 (s, 2 H), 6.62 (s, 3 H), 6.68 (s, 3 H), 6.88 (m, 4 H); IR spectrum (neat) 2900, 2820, 1440, 1385, 1360, 1185, 1140, 1090, 867, 787 cm^{-1}. Anal. ($C_{12}H_{15}O_2I$) C, H, I.

3-Trimethylsilyl-5-methoxymethylbenzocyclobutene (30). Bissilylated benzocyclobutene **8f** (800 mg, 2.74 mmol) was treated with a CCl_4 solution of CF_3COOH (312 mg, 2.74 mmol) and CH_3COOH (658 mg, 11 mmol). Stirring at room temperature for 20 min followed by workup with saturated aqueous $NaHCO_3$, washing with water, and drying ($MgSO_4$) gave a light yellow oil. Column chromatography on silica, eluting with pentane–ether (1:1), gave the product benzocyclobutene **30** as a colorless oil (470 mg, 78%): mass spectrum *m/e* (rel intensity) 220 (M^+, 42), 205 (100), 189 (14), 175 (25); NMR τ 2.87 (bs, 1 H), 3.03 (bs, 1 H), 5.70 (s, 2 H), 6.75 (s, 3 H), 6.87 (s, 4 H), 9.75

(s, 9 H); IR spectrum (neat) 2940, 1250, 1110, 877, 842 cm^{-1}. Anal. ($C_{13}H_{20}SiO$) C, H.

Structural proof was obtained by further desilylation to 4-methoxymethylbenzocyclobutene.[26f]

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