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Synthesis of benzocyclobutadiene trimers and *all-Z*-tribenzo[12]annulene. A new family of concave π-systems

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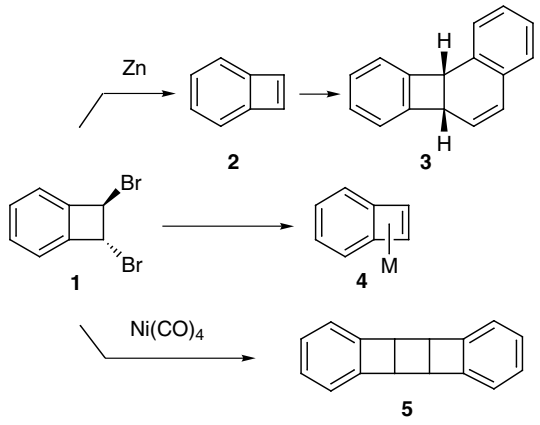
Abstract—Nickel-catalyzed oligomerization of *trans*-1,2-dibromobenzocyclobutene formed cyclic dimers and trimers. Upon heating, the major *anti*-cyclic trimer afforded a cage compound, whereas the minor *syn*-trimer produced *all-Z*-tribenzo[12]annulene. Dehydrogenation of the *anti*-trimer with DDQ resulted in the formation of an indenoazulene derivative, and a similar reaction of the *syn*-trimer yielded a bowl-shaped system. *All-Z*-tribenzo[12]annulene was also synthesized using a stepwise route starting from *o*-diiodobenzene and *o*-ethynylbenzyl alcohol, the overall yield being 22%. *All-Z*-tribenzo[12]annulene behaved like π-prismand and formed chromium(0) tricarbonyl and silver(I) complexes.

1. Introduction

Benzocyclobutadiene (**2**), which can be generated by the reduction of *trans*-1,2-dibromobenzocyclobutene (**1**), is a very unstable molecule,[1] and easily dimerizes to produce the so-called 'angular dimer' (**3**) (Scheme 1).[2,3] In contrast, the reaction of **2** with transition metals forms stable benzocyclobutadiene–metal complexes (**4**).[4] In the case of the reaction of **1** with $Ni(CO)_4$, the formation of the 'linear dimer' (**5**) via **4** [M=$Ni(CO)_2$] was reported.[5]



Scheme 1. Reactions of **1** via **2**.

Recently, we developed a simple and efficient method for the nickel-catalyzed cyclooligomerization of olefins and acetylenes.[6,7] Since our method produced cyclic trimers predominantly in some cases, we expected that the reaction of **1** with a nickel(0) catalyst could lead to the formation of the cyclic trimers (**6a** and **6b**) (Scheme 2). The cyclic trimers (**6a** and **6b**) can be regarded as a precursor of threefold-symmetric [4]phenylene **7**.[8] In addition, *all-Z*-tribenzo[12]annulene (**8**) with C_{3v} π-cavity was presumed to be obtained by the thermal ring-cleavage of *all-syn*-trimer **6b**.[9] A combination of the benzene rings and ethylenic bonds in **6** and **8** forms a concavity, and hence these molecules like 'π-prismand' might play an important role as a host molecule for metal ions (**9** and **10** in Scheme 2).[10] In order to examine the novel host properties of **8**, we also developed a new synthetic route to **8** starting from *o*-diiodobenzene (**11**) and *o*-ethynylbenzyl alcohol (**12**).

In a preliminary form, we reported the nickel-catalyzed cyclooligomerization of benzocyclobutadiene (**2**) and the synthesis and properties of *all-Z*-tribenzo[12]annulene (**8**).[11] In this paper, we describe the syntheses and properties of **6a**, **6b**, and **8** in detail, together with an attempted synthesis of **7** by aromatization of **6a** and **6b**.

2. Results and discussion

2.1. Cyclooligomerization of 1 with Ni(0) complexes

Although a number of cyclooligomerization methods of olefins and acetylenes have been reported up to now,[12] only limited reactions can be employed for selective

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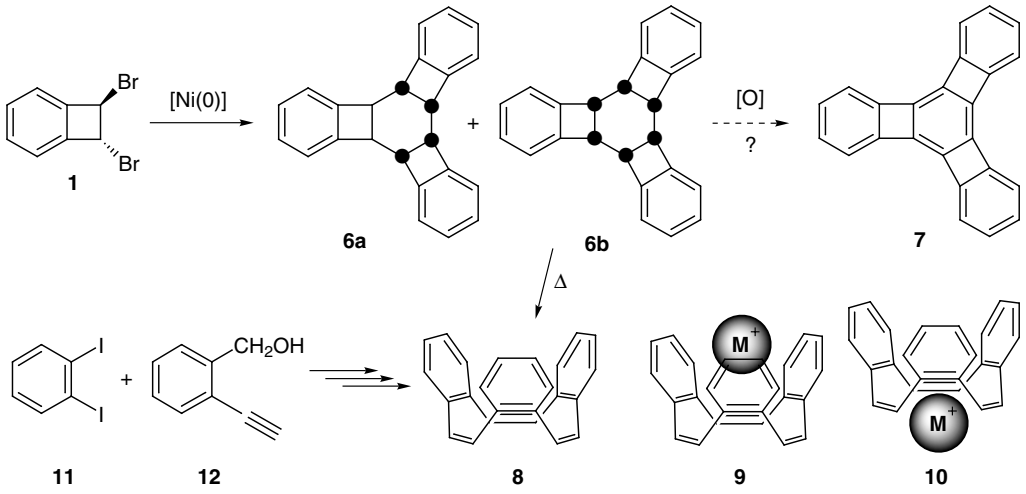
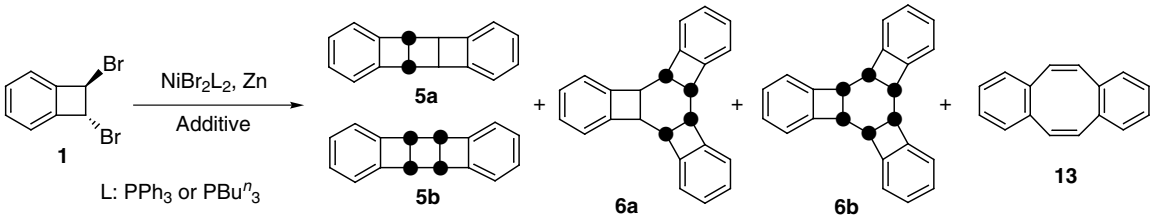


Scheme 2. Cyclic trimerization of **1** with Ni(0) and synthesis of **8**.



Scheme 3. Reaction of **1** with Ni(0) complexes.

cyclodimerization and cyclotrimerization of unsaturated molecules.[6,13] A well known example is the reaction of strained 3,3-dimethylcyclopropene with nickel(0) and palladium(0) complexes,[13] which yields the cyclic dimer and trimer, respectively, in good yields. Another example is the reaction of butatrienes with nickel(0) complexes, which produces the corresponding cyclic dimer ([4]radialenes) in THF and the cyclic trimer ([6]radialenes) in DMF, respectively.[6] Bearing these results in mind, we tried the reactions of **1** with nickel(0) complexes (Scheme 3) and we expected the cyclodimerization in THF and the cyclotrimerization in DMF. A typical procedure involved treatment of **1** (1 equiv.) at room temperature with a nickel(0) complex which was generated *in situ* by reduction of $NiBr_2L_2$ (L=PPh_3 or PBu_3) (0.2 equiv.) with activated zinc dust (4 equiv.) in the presence of a ligand (PPh_3 or $PBu^n{}_3$, 0.4 equiv.) or an iodide (Et_4NI or NaI, 2 equiv.) as an additive (see Table 1). The products obtained were the *anti*- and *syn*-dimers (**5a** and **5b**), the *anti*- and *syn*-trimers (**6a** and **6b**), and dibenzo[*a,e*]cyclooctene (**13**), which were isolated by column chromatography on silica gel. The obtained dimer by the reaction of **1** with $Ni(CO)_4$ was found to be identical with the *anti*-isomer (**5a**) by the melting point determination.[5]

As shown in Table 1, the nickel-catalyzed cyclooligomerization of **1** in benzene gave no detectable products and 83% of the starting material was recovered (entry 1). However, similar reactions of **1** in THF produced mainly the dimers **5** with smaller amounts of the trimers **6** (entry 2). The presence of an iodide ion in the reaction media (entry 3) accelerated the cyclooligomerization to increase the yields of the dimers **5** (44%) and the trimers **6** (21%). In contrast to the results in THF, the reaction of **1** with $Ni(PPh_3)_4$ in DMF formed predominantly the trimers **6** in 42% total yield with a small amount of dimers **5** (entry 5). The same treatment of **1** with $Ni(PBu^n{}_3)_4$ in DMF afforded a similar result (entry 8), although the reaction of **1** with $Ni(PBu^n{}_3)_4$ in THF gave a rather poor result (entry 4). The formation of dibenzo[*a,e*]-cyclooctene (**13**) in entries 2 and 4–8 may be due to the nickel-catalyzed ring-opening of the dimers **5**. The reactions of Ni(0) complexes in the presence of an iodide ion in DMF also resulted in the predominant formation of the trimers **6**

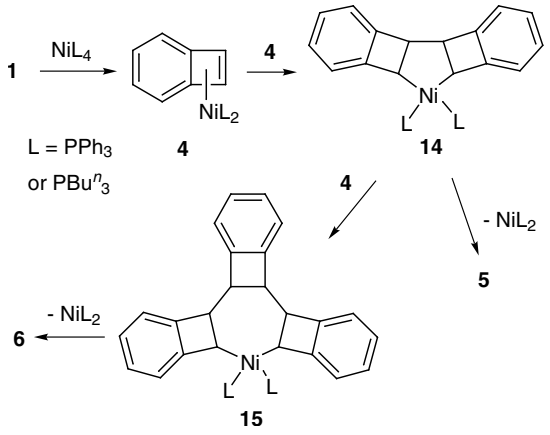
Table 1. Reaction of *trans*-1,2-dibromobenzocyclobutene (**1**) with nickel(0) complexes[a]

Entry	L	Additive	Solvent	Yields (%)[b]				
				5a	**5b**	**6a**	**6b**	**13**
1[c]	PPh_3	PPh_3	Benzene	0	0	0	0	0
2	PPh_3	PPh_3	THF	18	Trace	7	1	4
3	PPh_3	Et_4NI	THF	31	13	21	0	0
4	PBu_3	PBu_3	THF	7	2	5	0	8
5	PPh_3	PPh_3	DMF	6	Trace	38	4	1
6	PPh_3	Et_4NI	DMF	6	Trace	38	Trace	2
7	PPh_3	NaI	DMF	5	Trace	40	1	2
8	PBu_3	PBu_3	DMF	2	1	38	1	2

[a] A solution of *trans*-1,2-dibromobenzocyclobutene (**1**) (4 mmol) was added over 2 h at room temperature to a suspension of the nickel(0) complex generated from $NiBr_2L_2$ (0.8 mmol), zinc (16 mmol), and the additive [PPh_3 or $PBu^n{}_3$ (1.6 mmol), or Et_4NI or NaI (8 mmol)] in benzene, THF, or DMF as solvent, and the resulting mixture was stirred at room temperature for 15 h.

[b] Isolated yield.

[c] Starting material **1** was recovered (83%).



Scheme 4. Plausible mechanism of the nickel-catalyzed cyclooligomerization of **1**.

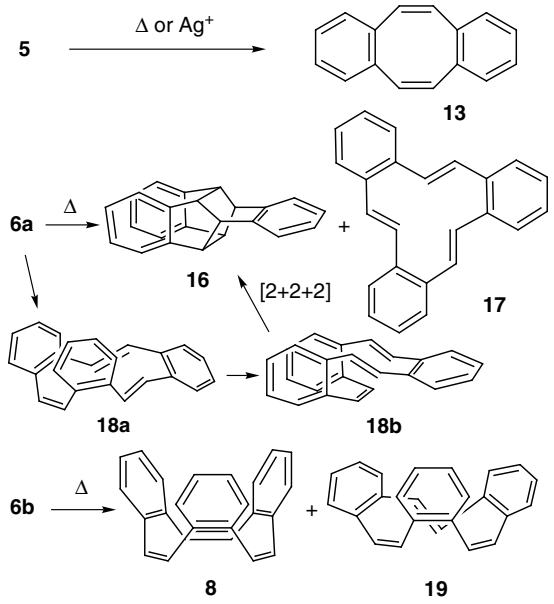
(entries 6 and 7). Palladium complexes are often employed for the dimerization and oligomerization of unsaturated compounds.[14] However, treatment of **1** with $PdCl_2(PPh_3)_2$ (0.2 equiv.), Zn (4 equiv.), and PPh_3 (0.4 equiv.) in DMF at room temperature afforded the dimers in very low yields (**5a**: 1.3% and **13**: 1.6%). In addition, the reaction of **1** with $CoCl(PPh_3)_3$[15] (2.4 equiv.) in benzene produced **5a** and **5b** in 11% and 1% yields, respectively.

The mechanism for the cyclooligomerization of **1** can be represented as shown in Scheme 4. The nickel-catalyzed coupling of benzyl halides usually proceeds smoothly to give the corresponding bibenzyls in good to high yields.[16] However, the reaction of **1** with the Ni(0) complex may first generate the benzocyclobutadiene complex **4** (M=NiL_2). This assumption follows from the observation that the reaction of **1** with $Ni(PPh_3)_4$ with benzene yielded neither the dimers nor the trimers, although the nickel-catalyzed coupling of benzyl halides proceeds smoothly in benzene as the solvent. The predominant formation of the trimers **6** in DMF may be attributable to the stability of the nickelacyclopentane intermediate **14** which is more stabilized in DMF and allowed to react with another molecule of **4**.

2.2. Thermal ring-opening of 5 and 6

It is known that the benzocyclobutadiene dimers **5** undergo thermal and silver-catalyzed isomerization to yield **13**.[5,17] In a similar manner, treatment of *anti*-trimer **6a** under reflux in *o*-dichlorobenzene for 15 h produced **16** in 71% yield, together with *all-E*-tribenzo[12]annulene (**17**) (2%) (Scheme 5). The formation of **16** can be explained by the initial formation of *E,E,Z*-tribenzo[12]annulene (**18**), followed by the intramolecular [2+2+2] cycloaddition. The thermal reaction of *syn*-trimer **6b** in refluxing *o*-dichlorobenzene for 16 h produced the *all-Z*-tribenzo[12]annulene (**8**) in 90% yield, together with *E,Z,Z*-tribenzo[12]annulene (**19**) (3%).

As shown in Scheme 5, the thermal ring-opening of **6a** and **6b** is considered to proceed almost keeping the configuration of the starting materials, presumably due to the rigidity of their molecular framework. The X-ray analysis of **6a** shown in Fig. 1 reveals an almost planar cyclohexane ring, and the maximum atomic deviation from the least-



Scheme 5. Thermal ring-opening of **5** and **6**.

squares plane of the central six-membered ring is 0.05 Å. It is worth noting that the C_{sp^3}—C_{sp^3} bond lengths of the central cyclohexane ring have a bond alternation. Thus, the C_{sp^3}—C_{sp^3} bond lengths fused by the benzocyclobutene ring are 1.59–1.60 Å, which are slightly longer than that of benzocyclobutene (0.02 Å, averaged value),[18] whereas the C_{sp^3}—C_{sp^3} bond lengths between the four-membered rings are 1.52–1.54 Å. The existence of this bond-alternation in **6a** might be favorable for the thermal ring-cleavage.

As shown in Table 2, the parameters of the thermal ring-cleavages indicate that the activation enthalpy ($\Delta H^{\ddagger}$) for **5a** or **5b→13** is much smaller than those for **6a** or **6b→16** or **8**. Interestingly, $\Delta H^{\ddagger}$ for **6a→16** is almost the same as that for

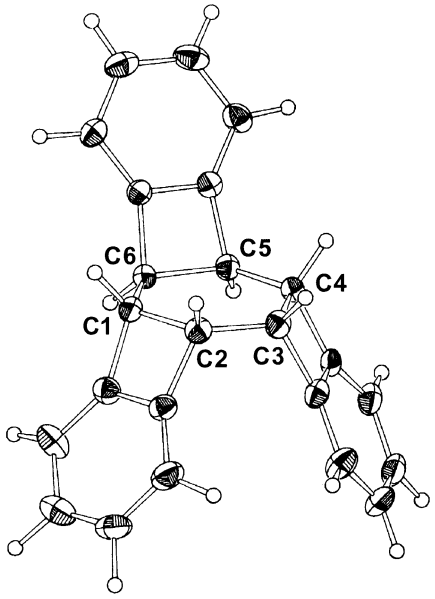
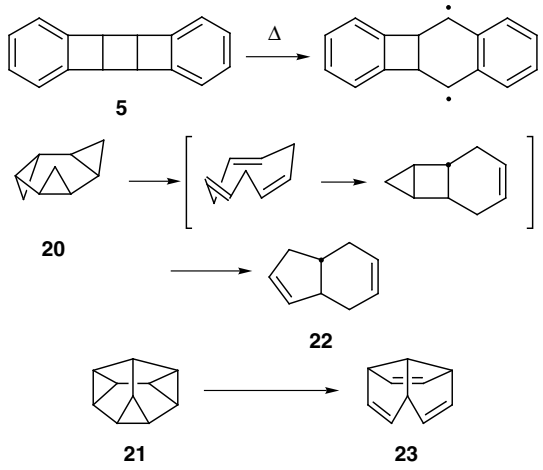


Figure 1. Molecular structure of **6a**. Selected bond lengths (Å) and angles (°): C1—C2, 1.590(3); C2—C3, 1.538(3); C3—C4, 1.593(3); C4—C5, 1.526(3); C5—C6, 1.597(3); C6—C1, 1.517(3); C1—C2—C3, 118.8(2); C2—C3—C4, 120.3(2); C3—C4—C5, 120.5(2); C4—C5—C6, 118.8(2); C5—C6—C1, 120.5(1).

Table 2. Parameters of the thermal reaction of **5a**,[a] **5b**,[b] **6a**,[c] **6b**,[d] **20**,[e] and **21**[f]

Compound	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1}·K)
5a	27.54±0.06	2.8±0.2
5b	28.31±0.21	3.3±0.6
6a	42.0±1.2	13.3±2.5
6b	32.7±0.9	1.8±2.0
20	41.3±0.9	0.75
21	31.0±0.7	6.5±0.8

[a] Parameters from **5a** to **13**.
[b] Parameters from **5b** to **13**.
[c] Parameters from **6a** to **16**.
[d] Parameters from **6b** to **8**.
[e] Parameters from **20** to **22**.
[f] Parameters from **21** to **23**.

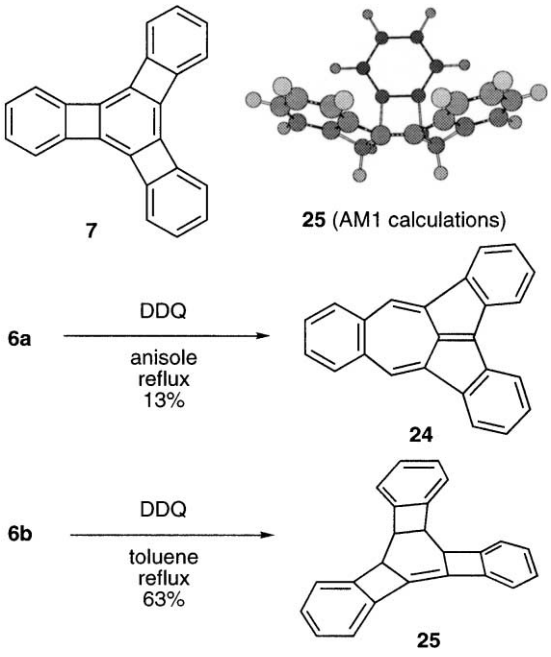


Scheme 6. Thermal reactions of **5**, **20**, and **21**.

20→22,[9c] whereas $\Delta H^{\ddagger}$ for **6b→8** is similar to that for **21→23**[19] (Scheme 6). Since $\Delta S^{\ddagger}$ in the latter is comparable, the transition state in the two reactions is similar. In the former, however, $\Delta S^{\ddagger}$ for **6a→16** is much larger than that for **20→22**, and hence the transition states between these two cases are different. The rate-controlling step for **6a→16** may be the isomerization **18a→18b**, reflecting a large $\Delta S^{\ddagger}$ value. The thermal reaction of **5a** may proceed with inversion of stereochemistry via the *o*-xylylene derivative (Scheme 6).[17b] Surprisingly, $\Delta H^{\ddagger}$ for **5a→13** with inversion is smaller than that for **5b→13** without inversion.[17b–e]

2.3. Dehydrogenation of 6

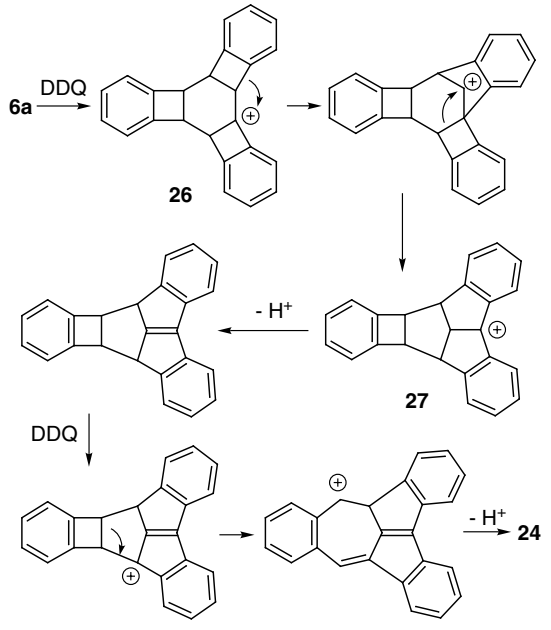
Tris(benzocyclobutadieno)benzene (**7**) is of considerable interest because of its unique π-electron system.[8,21] If the central cyclohexane ring in **6** is dehydrogenated to the benzene ring, it may be a simple method for preparing **7**. However, dehydrogenation of **6a** with DDQ (3 equiv.) in refluxing anisole for 3 h resulted in the formation of dibenzo[*a*,*e*]indeno[1,3-*c*,*d*]azulene (**24**) in 13% yield (Scheme 7). The formation of **24** can be detected easily, because **24** shows an intense red color in solution, reflecting its azulene chromophore.[22] On the other hand, treatment of **6b** with DDQ (3 equiv.) in refluxing toluene for 3 h produced the didehydrogenated derivative **25** in 63% yield. The compound **25** is stable to prolonged heating with DDQ or



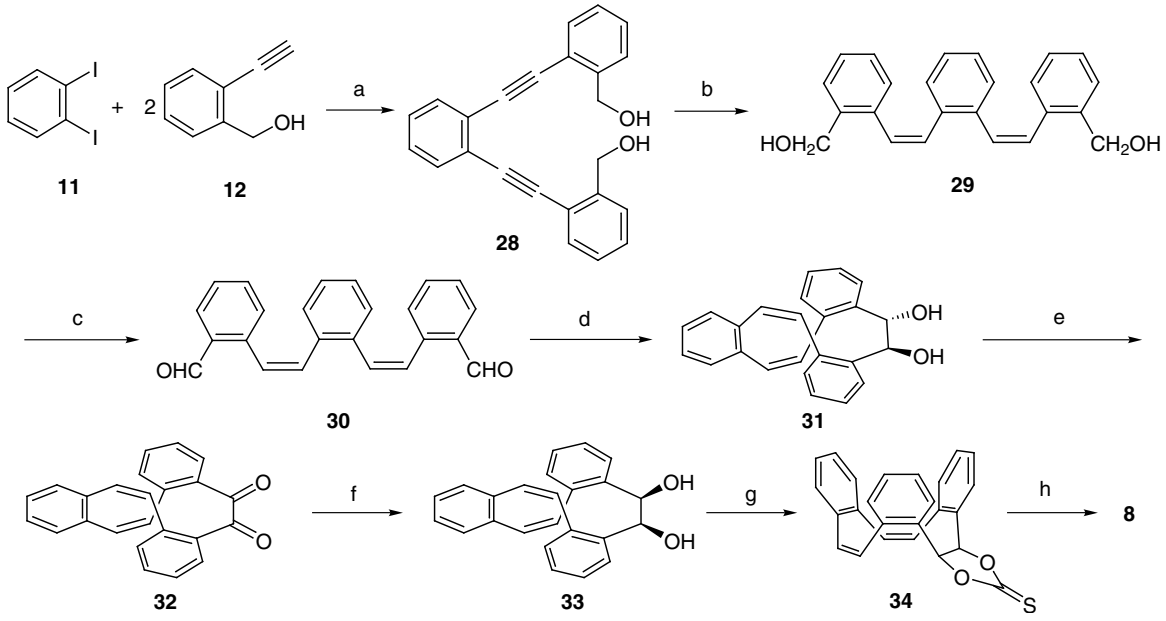
Scheme 7. Dehydrogenation of **6**.

to dehydrogenation with Pd–C in refluxing *p*-cymene. It is worth noting that the ^{1}H NMR spectrum of **25** shows fairly high field shifts of AA′BB′ signals [δ 6.45–6.48 (AA′, 2H), 6.79–6.82 (BB′, 2H)]. As shown in Scheme 7, the molecular structure of **25** estimated by MOPAC AM1 calculations adopts a concave π-system, and one benzene ring locates in the shielding region of the other two benzene rings.

The formation of **24** can be explained by the skeletal rearrangement from the cationic intermediate **26**, which can be generated by a direct hydride abstraction or a stepwise oxidation via a radical intermediate.[20] As shown in Scheme 8, oxidation of **6a** with DDQ affords the cation **26**, which undergoes 1,2-alkyl-shifts on two occasions to



Scheme 8. Plausible mechanism for the formation of **24**.



Scheme 9. Synthesis of **8**. Conditions: (a) $Pd(PPh_3)_4$, CuI, Et_3N; (b) H_2, Lindlar catalyst, THF; (c) PCC, CH_2Cl_2; (d) $VCl_3(THF)_3$, Zn, THF; (e) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (f) $NaBH_4$, EtOH, CH_2Cl_2, 0°C; (g) TCDI (thiocarbonyldiimidazole), toluene, reflux; (h) DMPD (1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine), benzene, reflux.

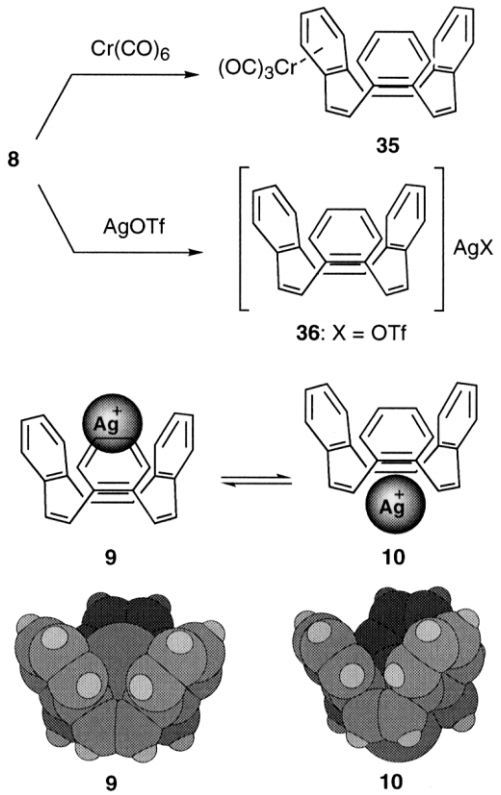
form the isomeric cation **27**. Deprotonation of **27**, followed by dehydrogenation with DDQ and ring-opening, produces the indenoazulene derivative **24**.

2.4. Stepwise synthesis of *all-Z*-tribenzo[12]annulene (8)

Since *all-Z*-tribenzo[12]annulene (**8**) bears a rigid, crown-like structure with C_{3v} symmetry, **8** can be expected to behave like a π-prismand.[10] In addition, **8** contains three ethylene groups arranged with C_3 symmetry, and hence these ethylene groups can take part in the metal complexation as a π-host molecule. The synthetic route for **8** starting from **1** is quite short, but the total yield of **8** is not sufficiently high to allow investigation of the properties of **8**. Therefore, we developed a new route to synthesize **8** (Scheme 9). The palladium-catalyzed cross-coupling reaction of 2-hydroxymethylphenylacetylene (**12**) (2 equiv.) with 1,2-diiodobenzene **11** (1 equiv.) in refluxing triethylamine in the presence of CuI for 15 min produced **28** in 94% yield. Partial reduction of **28** using the Lindlar catalyst [Pd–$Pb(OAc)_2$ on $CaCO_3$] in THF at room temperature (70–77%), followed by oxidation of **29** with PCC (82%), afforded the corresponding diene-dialdehyde **30**. Pinacol-coupling of the dialdehyde **30** with a low-valent vanadium complex[23] in THF at room temperature for 5 h yielded the *threo*-diol **31** (82%). Swern oxidation of the diol **31** produced the annulenedione **32** in 86% yield. Reduction of **32** with $NaBH_4$ in ethanol–CH_2Cl_2 afforded the *erythro*-isomer **33** (80%) with a small amount of the *threo*-isomer **31**. The reaction of **33** with TCDI (thiocarbonyldiimidazole) in refluxing toluene led to the thionocarbonate **34** (78%) which was converted into **8** (84%) by the reaction with DMPD (1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine) [modified Corey–Winter procedure].[24] *Z,Z,Z*-Tribenzo[12]annulene (**8**) was synthesized in 22% overall yield based on **12**.

2.5. Synthesis, structure, and properties of metal complexes derived from 8

On the basis of the calculated molecular structure of **8** by MOPAC AM1, π-electrons of the benzene rings and the ethylene linkages are orthogonal and cannot conjugate with each other. Thus, (**8**) shows no delocalization in the



Scheme 10. Metal complexes of **8**.

macrocyclic ring, but a face-to-face geometry of the three benzene rings and three ethylene units in **8** makes it possible for **8** to behave like π-prismand. In order to evaluate the possibility of π-electron delocalization among its three benzene rings, the (η^6-arene)chromium tricarbonyl complex **35** was prepared by treatment of **8** with $Cr(CO)_6$ in diglyme–THF (4:1) under reflux for 10 h. However, the electronic spectra of **35** and **8** showed no through-space and through-bond interaction of the benzene rings, in contrast to the case of deltaphane.[10b]

Secondly, we attempted to synthesize the complexes **9** and **10** (Scheme 10) with AgOTf, since B3LYP density functional calculations for **9** and **10** suggest that **9** is less stable than **10**, but the energy difference in the heat of formation between **9** and **10** is small (E_{Ag}=2.4 kcal mol^{-1}).[11d] The reaction of **8** with AgOTf (1.5 equiv.) in THF afforded the corresponding silver complex **36** in 82% yield. The ^{1}H NMR spectrum of **36** clearly indicates formation of the silver complex in solution. Since the olefinic protons at δ 6.76 in **8** shift to downfield δ 7.48, the structure of the complex can be assigned to the olefinic complex **10**. However, the aromatic protons at δ 6.95 and 7.07 in **8** also shift to downfield δ 7.09 in **36**, and the benzenoid complex **9** might coexist at equilibrium in solution. The ^{1}H NMR signal of the olefinic protons in **36** was observed as a broad singlet at room temperature, also due to an equilibrium in solution.

Single crystals of **36** were obtained by recrystallization from hexane–dichloromethane, and its crystal structure was determined by X-ray analysis. As shown in Fig. 2a, the silver atom in **36** locates in the center of the cavity of the [12]annulene. The Ag—C(olefin) distances of the complex **36** vary only in the range from 2.530(9) to 2.687(9) Å (average 2.61 Å), indicating almost equal coordination with the three ethylene units. The average Ag—C distance (2.61 Å) is longer than those (2.36–2.53 Å) of most of the reported silver complexes with alkenes,[25,26] and is comparable to that (2.65 Å) of the $AgNO_3$ 1:1 adduct with cyclooctatetraene.[27] The annulene ring shows no large distortion, and the distances [average C═C(alkene) 1.33 Å estimated by B3LYP calculation] and angles of the alkene parts are similar values to those of **8**. Interestingly, the plane Ag1–C1–C2 is not perpendicular to the C1–C2–C3–C12 plane but rather forms an angle of 76° with it. Thus, the silver ion is distorted by an average 14° in the direction of the *cis* hydrogens; i.e., Ag^+ locates slightly outside the coordination site of the three alkene ligands. A similar observation was made for the $AgNO_3$ 3:1 complex with *Z,Z,Z*-1,4,7-cyclononatriene.[27] As shown in Fig. 2b, the silver ion is bonded to two oxygen atoms of the different

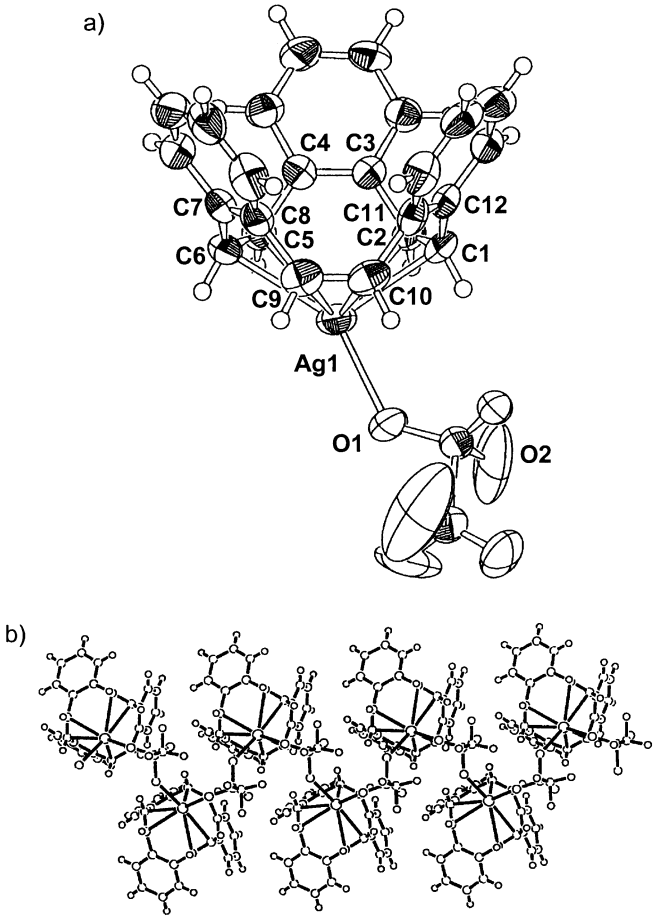


Figure 2. ORTEP diagram of **36**: (a) side view; (b) packing diagram. Selected bond lengths (Å) and angles (°): Ag1—O1, 2.404(6); Ag1—O2, 2.506(9); Ag1—C1, 2.530(9); Ag1—C2, 2.532(8); Ag1—C5, 2.573(8); Ag1—C6, 2.611(9); Ag1—C9, 2.687(9); Ag1—C10, 2.624(9); C1—C2, 1.31(1); C2—C3, 1.490(10); C3—C4, 1.39(1); C4—C5, 1.47(1); C1—C12, 1.51(1); C1—C2—C3, 124.5(7); C2—C3—C4, 122.4(7); C2—C1—C12, 126.6(7).

counter anions at Ag—O distances of 2.404(6) and 2.506(9) Å to form a one-dimensional polymer. There is no interaction observed between the silver ion and the benzene rings.

In summary, we have shown two routes for the synthesis of **8**, a cage molecule with a concave π-system. Since **8** can behave as a biconcave host like **9** and **10**, an interesting host–guest chemistry might be expected using **8** and its derivatives.

3. Experimental

3.1. General

Melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with Hitachi EPI-G3 or Perkin–Elmer 1600 spectrometers and only significant maxima are described. Electronic spectra were measured with Shimadzu U-3400 or UV-3101PC spectrometers. Mass spectra were recorded with JEOL JMS01SG-2, JMS-SX102 or JMS-AX500 spectrometers using a direct-inlet system. ^{1}H-NMR spectra were recorded on a Varian XL-100A (100 MHz) or JEOL JNM-LA500 (500 MHz) spectrometer with TMS as the reference. ^{13}C-NMR spectra were recorded on a JEOL FX90Q (22.5 MHz) or JNM-LA500 (125 MHz) spectrometers with TMS or $CDCl_3$ (77.02 ppm) as the reference.

The reaction solvents were distilled after an appropriate drying procedure. Progress of reactions was followed by TLC on Merck pre-coated silica gel (Kieselgel $60F_{254}$). Alumina (Merck, activity II–III) or silica gel (Daiso gel 1001W or Merck Art. 1097) was used for column chromatography.

3.2. General procedure for cyclooligomerization of 1 (Table 1)

A suspension of $NiBr_2L_2$ (L=PPh_3 or PBu^n_3, 0.8 mmol), activated zinc powder (1.05 g, 16 mmol), and an additive [1.6 mmol of PR_3 (R=Ph or Bu^n) or 8.0 mmol of iodide: Et_4NI or NaI] in dry solvent (benzene, THF or DMF; 10 ml) was degassed and the flask was filled with gaseous argon. Then the suspension was irradiated with ultrasonic waves for 5 min and was stirred for 45 min under argon atmosphere. To the suspension was added dropwise with a syringe over 2 h a degassed solution of compound **1** (1.05 g, 4.0 mmol) in each solvent (10 ml) and the reaction mixture was stirred for 15 h at room temperature. The mixture was filtered off and washed with benzene. The filtrate and washings were combined and concentrated, and the residue was passed through a short plug of alumina eluted by a mixture of benzene and hexane. After concentration of the elution, the residue was chromatographed on silica gel. The fractions eluted with hexane–benzene afforded the products.

3.2.1. *anti*-Dimer 5a. Colorless crystals (hexane), mp 132.5–133.5°C (decomp.); MS (EI) *m/z* 204 (M^+); IR (KBr) 2968, 1453, 1148, 997, 754, 746 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 257sh (3.28), 265sh (3.53), 271 (3.82), 278 (3.93) nm; ^{1}H-NMR (100 MHz, $CDCl_3$) δ 7.20 (8H, brs), 3.76 (4H, s); ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ 147.6, 127.5, 122.8, 49.8. Anal. Found: C, 93.74; H, 5.91%. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92%.

3.2.2. *syn*-Dimer 5b. Colorless crystals (hexane), mp 122.5–123.5°C (decomp.); MS (EI) *m/z* 204 (M^+); IR (KBr) 2990, 1457, 1172, 740, 462 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 257sh (3.15), 263 (3.58), 269 (3.54), 276 (3.51) nm; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 6.98–6.72 (8H, m), 4.09 (4H, s); ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ 145.7, 126.8, 122.6, 41.4. Anal. Found: C, 93.94; H, 5.93%. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92%.

3.2.3. *anti*-Trimer 6a. Colorless prisms (CH_2Cl_2–hexane), mp 161.5–163.5°C (decomp.); MS (EI) *m/z* 306 (M^+); IR (KBr) 3056, 2898, 1600, 1457, 1181, 1154, 996, 935, 745, 553 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 213sh (3.75), 262 (2.95), 268 (3.11), 274 (3.08) nm; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30–7.26 (2H, m), 7.23–7.20 (2H, m), 7.09–7.00 (8H, m), 4.16–4.11 (2H, m), 4.09 (2H, s), 4.04–3.99 (2H, m); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 148.4, 148.3, 146.8, 127.6, 126.8, 126.7, 124.0, 121.6, 121.1, 42.9, 42.5, 40.5. Anal. Found: C, 94.13; H, 5.92%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

3.2.4. *syn*-Trimer 6b. Colorless needles (CH_2Cl_2–hexane), mp 191.5–192.5°C (decomp.); MS (EI) *m/z* 306 (M^+); IR (KBr) 3057, 2920, 1455, 1360, 1203, 1106, 998, 747, 655, 582, 495 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 218sh (4.23), 262 (3.53), 268 (3.63), 275 (3.54) nm; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.02–6.99 (6H, m), 6.98–6.95 (6H, m), 4.19 (6H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 147.2, 126.4, 123.7, 40.6. Anal. Found: C, 93.96; H, 5.90%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

3.3. X-ray crystallography of 6a

X-ray diffraction data were collected on a Rigaku AFC5R diffractometer with $Mo_{K\alpha}$ radiation. The structures were solved by direct method and refined using full-matrix least-squares analysis. Anisotropic thermal parameters were used for non-hydrogen atoms. Crystal data: $C_{24}H_{18}$, M_w=306.41, monoclinic, space group $P2_1/n$ (No. 14), a=9.199(1) Å, b=14.770(2) Å, c=12.348(1) Å, β=106.887(9)°, V=1605.4(3) Å^3, Z=4, D_c=1.27 g cm^{-3}, R=0.043, R_w=0.053, GOF=1.40 for 2300 reflections with $I>3.0\sigma(I)$.

3.4. Thermal isomerization of the trimers (6a, 6b)

A solution of *anti*-trimer (30.8 mg, 0.10 mmol) in *o*-dichlorobenzene (50 ml) was heated under reflux for 15 h in an argon atmosphere. After cooling to room temperature, the reaction mixture was concentrated to dryness under reduced pressure and the residue was separated by chromatography on silica gel with hexane as eluent. The products (**16**: 21.9 mg, 71%; **17**: 0.65 mg, 2%) isolated here showed spectroscopic data identical with those in the literature.[21]

In a similar manner, **8** (82.5 mg, 90%) and **19** (2.9 mg, 3%) were obtained from thermal reaction of **6b** (92 mg, 0.30 mmol) in diclorobenzene (50 ml) for 16 h.

3.4.1. *All-Z*-tribenzo[12]annulene (8). Colorless plates (EtOH), mp 185.5–186.0°C; MS (EI) *m/z* 306 (M^+); IR (KBr) 2990, 1690, 1635, 1467, 1449, 1392, 1087, 948, 863, 802, 773, 746, 704, 662, 570, 490 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 219sh (4.50), 267sh (3.23) nm; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.09–7.05 (6H, m), 6.96–6.93 (6H, m), 6.76 (6H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.2, 132.2, 129.9, 125.8. Anal. Found: C, 94.03; H, 5.96%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%.

3.5. Dehydrogenation of the trimers (6a, 6b)

A solution of the trimer **6a** (152 mg, 0.50 mmol) and DDQ (380 mg, 1.6 mmol) in anisole (30 ml) was heated under reflux for 3 h in an argon atmosphere. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and the residue was separated by chromatography on silica gel with CH_2Cl_2–hexane as eluent. The red elution was collected and evaporated to afford **24** (20 mg, 13%), the spectral data of which were identical with those of the literature.[22]

In a similar manner, *syn*-trimer **6b** (8.0 mg, 26 μmol) was dehydrogenated with DDQ (20 mg, 78 μmol) in refluxing toluene (8 ml) for 3 h to afford **25** (5.0 mg, 63%); colorless plates (hexane), mp 178.5–179.5°C; MS (EI) *m/z* 304 (M^+); IR (KBr) 3052, 2911, 1461, 1435, 1362, 1196, 1157, 990, 910, 757, 743, 722, 662, 582, 471 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 226 (4.02), 236 (3.93), 246 (3.82), 267sh (3.96), 273 (4.08), 283 (4.20), 293sh (4.18), 296 (4.22), 306sh (4.25), 311 (4.56), 322sh (4.34), 328 (4.65) nm; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39–7.36 (2H, m), 7.21–7.17 (4H, m), 7.04–7.01 (2H, m), 6.82–6.79 (2H, m), 6.48–6.45 (2H, m), 4.34–4.33 (2H, m), 4.26–4.23 (2H, m); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 149.8, 144.2, 143.8, 127.95, 127.93, 127.8, 126.8, 122.69, 122.68, 119.9, 48.33, 48.26. Anal. Found: C, 94.41; H, 5.34%. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30%.

3.6. 1,2-Phenylenebis(2-ethynylbenzyl alcohol) (28)

To a solution of ethynylbenzyl alcohol (8.22 g, 62 mmol) and *o*-diiodobenzene (9.90 g, 30 mmol) in triethylamine (150 ml) were added copper(I) iodide (116 mg, 0.6 mmol) and $Pd(PPh_3)_4$ (356 mg, 0.3 mmol). The resultant mixture was heated to reflux and stirred for 15 min under Ar atmosphere. After cooling to room temperature, the reaction mixture was diluted with 2 M HCl (250 ml) and saturated aqueous NH_4Cl (250 ml) and extracted with dichloromethane. The combined organic extracts were washed with saturated aqueous NH_4Cl and dried over $MgSO_4$. After evaporation of the solvent, the residual solid was purified with chromatography on silica gel with a mixture of benzene and ethyl acetate as eluent. The solid product obtained by concentration of the elution was recrystallized from acetone–benzene to afford 9.57 g (94%) of colorless needles, mp 124.0–125.6°C; IR (KBr) 3337, 3246, 1490, 1032, 756 cm^{-1}; UV (THF) λ_{max} (log ε), 314 (4.49), 261 (4.77), 255 (4.78), 249 (4.79), 243 (4.77) nm; MS (EI) 338 (M^+); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.60–7.57 (4H, m), 7.45 (2H, d, J=7.5), 7.38–7.35 (2H, m), 7.29 (2H, t, J=7.5), 4.84 (4H, d, J=6.0), 2.64 (1H, t, J=6.0); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 142.8, 132.4, 132.2, 129.1, 128.4, 127.8, 127.6, 125.2, 121.2, 92.6, 90.9, 63.8. Anal. Found: C, 85.03; H, 5.27%. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%.

3.7. 1,2-Phenylenebis(2-*Z*-ethenylbenzyl alcohol) (29)

In a 300 ml round-bottomed flask, 500 mg of Lindlar catalyst (Pd–$Pb(OAc)_2$ on $CaCO_3$) was added to a solution of the diyne **28** (1.69 g, 5.00 mmol) in THF (150 ml) and the mixture was vigorously stirred for 14 h under H_2 atmosphere. The reaction mixture was filtered and evaporated to dryness under reduced pressure. The residual solid was purified by recrystallization from acetone–isopropyl ether to afford 1.31 g (77%) of the diene-diol **29** as colorless needles, mp 111.4–113.5°C; IR (KBr) 3211, 2869, 1458, 1046, 1020, 777, 749 cm^{-1}; UV (THF) λ_{max} (log ε), 261 (4.54), 255 (4.60), 249 (4.59) nm; MS (EI) 342 (M^+); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.37 (2H, d, J=7.5), 7.19 (2H, t, J=7.5), 7.05 (2H, t, J=7.5), 6.96–6.93 (2H, m), 6.91–6.89 (4H, m), 6.81 (4H, s), 4.65 (4H, s), 1.75 (2H, brs); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.4, 135.9, 135.7, 130.2, 129.7, 129.4, 128.9, 127.9, 127.50, 127.46, 126.8, 63.4. Anal. Found: C, 84.22; H, 6.55%. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48%.

3.8. 1,2-Phenylenebis(2-*Z*-ethenylbenzaldehyde) (30)

To a solution of the diene-diol **29** (524 mg, 1.5 mmol) in CH_2Cl_2 (80 ml) was added pyridinium chlorochromate (1.29 g, 6 mmol) and the resulting suspension was stirred at room temperature for 2 h. The reaction mixture was diluted with ether and filtered through a Celite pad, which was washed with ether. The combined filtrate and washings were concentrated under reduced pressure and the residual oil was purified by column chromatography on silica gel eluted by benzene–ethyl acetate. After evaporation of the solvent, 418 mg (82%) of the dialdehyde **30** was obtained as colorless solid. Pure sample was obtained by recrystallization from isopropyl ether, mp 98.8–101.1°C; IR (KBr) 3060, 2841, 2720, 1693, 1594, 782, 764 cm^{-1}; UV (THF) λ_{max} (log ε), 260 (4.59), 254 (4.67), 249 (4.68) nm; MS (EI) 338 (M^+); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 10.21 (2H, s), 7.81 (2H, dd, J=7.0, 2.0), 7.37–7.32 (4H, m), 7.10 (2H, d, J=12.0), 6.96 (2H, dd, J=7.0, 2.0), 6.92 (2H, d, J=12.0), 6.91–6.87 (4H, m); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 192.0, 140.1, 135.4, 133.5, 131.6, 130.8, 130.2, 129.9, 128.4, 127.6, 127.1. Anal. Found: C, 85.04; H, 5.33%; Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36%.

3.9. *threo*-Pinacol 31

In a three-necked 100 ml flask attached with a dropping funnel, a three-way stop cock connected to an N_2 supply and a stopper, was placed $VCl_3(THF)_3$ (1.21 g, 3.2 mmol) under nitrogen atmosphere, which was dissolved in 20 ml of THF. Zn powder (212 mg, 3.2 mmol) was added and the resultant mixture was stirred for 30 min. A solution of the dialdehyde **30** (678 mg, 2.0 mmol) in 20 ml of THF was added dropwise for 2.5 h to the stirred mixture. After additional stirring for 2.5 h, the reaction mixture was diluted with ethyl acetate (40 ml) and saturated aqueous $NaHCO_3$ (50 ml) was added. The resultant mixture was stirred for 1 h

and filtered by suction. The organic phase of the filtrate was separated and the aqueous phase was extracted with ethyl acetate (2×50 ml). The combined organic phase was washed with saturated aqueous NH_4Cl and dried over $MgSO_4$. After removal of the solvent, the residual solid mass was separated by chromatography on silica gel with benzene–ethyl acetate as eluent. The solid product obtained by concentration of the corresponding fraction was purified by recrystallization from dichloromethane and isopropyl ether to afford 556 mg of colorless prisms, mp 216.3–217.7°C; IR (KBr) 3354, 3056, 2915, 1400, 1026, 799, 766 cm^{-1}; UV (THF) λ_{max} (log ε), 260 (4.46), 255 (4.51), 249 (4.54) nm; MS (EI) 340 (M^+); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.85 (2H, d, J=7.5), 7.24–7.21 (4H, m), 7.05–7.03 (2H, m), 6.93 (2H, t, J=7.5), 6.63 (2H, d, J=7.5), 5.89 (2H, d, J=12.0), 5.70 (2H, d, J=12.0), 4.91 (2H, s), 3.37 (2H, brs); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 137.4, 137.2, 133.6, 132.0, 129.2, 127.6, 127.45, 127.37, 127.27, 126.8, 124.5, 73.4. Anal. Found: C, 84.50; H, 5.79%; Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92%.

3.10. *erythro*-Pinacol 33

A solution of oxalyl chloride (0.8 ml, 9.2 mmol) in 30 ml of CH_2Cl_2 was cooled to −78°C (bath temp.) and a solution of dimethylsulfoxide (1.0 ml, 14.1 mmol) in 10 ml of CH_2Cl_2 was added dropwise. After stirring for 15 min, a solution of **31** (683 mg, 2.0 mmol) in THF (30 ml) was added dropwise and the resulting mixture was warmed to ca. −60°C and stirred for 15 min. A solution of Et_3N (2.0 ml, 14.3 mmol) in THF (10 ml) was added dropwise, and the resultant mixture was stirred with gradual warming to −30°C for 1 h. After additional stirring for 1 h with removal of the cold bath, the reaction mixture was poured into saturated aqueous NH_4Cl and extracted with ether (3×50 ml). The combined extract was washed with water and saturated aqueous NH_4Cl successively and dried over $MgSO_4$. After evaporation of the solvent, the residual oil was purified by chromatography on silica gel with benzene as eluent. Recrystallization of the solid mass obtained by evaporation of the corresponding elution afforded the dione **32** (578 mg, 86%) as yellow needles, mp 198.1–199.8°C; MS (EI) 336 (M^+); Anal. Found: C, 85.49; H, 4.60%; Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%.

The dione **32** (336 mg, 1.0 mmol) was dissolved in a mixture of ethanol and CH_2Cl_2 (10 ml each) and $NaBH_4$ (38 mg, 1.0 mmol) was added. After stirring for 1.5 h at room temperature, the reaction mixture was poured into saturated aqueous NH_4Cl (100 ml) and extracted with ether (3×30 ml). After drying over $MgSO_4$, the combined extract was concentrated to dryness under reduced pressure and the residual solid was purified by chromatography on silica gel to afford *erythro*-diol **33** (271 mg, 80%) together with *threo*-diol **31** (15 mg, 5%) after evaporation of the corresponding fraction followed by recrystallization from ether–hexane. The *erythro*-diol **33** was obtained as colorless plates, mp 203.4–204.4°C; IR (KBr) 3421, 3060, 2890, 1486, 1070, 1021, 798, 767 cm^{-1}; MS (EI) 340 (M^+); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.90 (1H, d, J=7.5), 7.32 (1H, d, J=7.5), 7.24–7.17 (3H, m), 7.11–7.06 (3H, m), 6.92 (1H, t, J=7.5), 6.84 (1H, t, J=7.5), 6.67 (1H, d, J=12.5), 6.59 (1H, d, J=7.5), 6.57 (1H, d, J=7.5), 6.01 (1H, d, J=12.5), 5.73 (1H, d, J=12.5), 5.60 (1H, d, J=12.5), 5.26 (1H, dd, J=3.5, 2.0), 5.21 (1H, dd, J=4.0, 2.0), 4.51 (1H, d, J=4.0), 4.47 (1H, d, J=3.5); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.6, 138.2, 135.6, 135.2, 134.1, 133.4, 132.1, 131.8, 130.7, 129.7, 129.1, 128.6, 127.9, 127.8, 127.62, 127.59, 127.5, 127.2, 127.01, 126.95, 126.7, 125.1, 82.63, 73.41.

3.11. Thionocarbonate 34

A solution of *erythro*-diol **33** (204 mg, 0.6 mmol) and thiocarbonyl-diimidazole (TCDI, 125 mg, 0.7 mmol) in toluene (15 ml) was heated under reflux for 18 h in an argon atmosphere. After cooling to room temperature, the reaction mixture was concentrated to dryness and the residual solid was purified by column chromatography on silica gel with benzene–hexane as eluent. The solid product obtained by concentration of the corresponding fraction was recrystallized from CH_2Cl_2–isopropyl ether to afford 179 mg (78%) of colorless plates, mp 231.1–232.3°C; IR (KBr) 3004, 1470, 1366, 1325, 1308, 1273, 1160, 970, 935, 743 cm^{-1}; MS (EI) 382 (M^+); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.28–7.24 (4H, m), 7.16–7.13 (2H, m), 7.02 (2H, d, J=7.5), 6.99 (2H, td, J=7.5, 1.5), 6.94 (2H, td, J=7.5, 1.5), 6.83 (2H, d, J=12.2), 6.77 (2H, d, J=12.2), 6.43 (2H, s); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 191.1, 135.4, 134.9, 134.2, 130.7, 130.5, 129.9, 129.5, 128.4, 127.0, 126.6, 126.3, 83.4. Anal. Found: C, 78.29; H, 5.02%; Calcd for $C_{25}H_{18}O_2S$: C, 78.51; H, 4.74%.

3.12. *All-Z*-tribenzo[12]annulene (8)

A solution of thionocarbonate (37.8 mg, 0.1 mmol) and 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DMPD, 42.5 mg, 0.2 mmol) in benzene (4 ml) was heated under reflux for 15 h in an argon atmosphere. After cooling to room temperature, the reaction mixture was concentrated and the residual oil was separated by chromatography on silica gel with benzene–hexane as eluent. The product (**8**, 25.3 mg, 84%) was obtained after concentration of the corresponding fraction.

3.13. Tribenzo[12]annulene chromium tricarbonyl complex (35)

A solution of **8** (30 mg, 0.10 mmol) and $Cr(CO)_6$ (66 mg, 0.30 mmol) in a mixture of diglyme (20 ml) and THF (5 ml) was heated under reflux for 10 h in an argon atmosphere. After cooling to room temperature, the reaction mixture was concentrated and the residual solid was separated by chromatography on silica gel with CH_2Cl_2–hexane as eluent. The crude product obtained by concentration of the corresponding fraction was recrystallized to afford yellow needles (**35**, 16 mg, 36%), mp ca. 160°C (decomp.); IR (KBr) 1960, 1887 cm^{-1} (C═O); UV (cyclohexane) λ_{max} (log ε), 326 (3.88), 254sh (3.87) nm; MS (EI) 442 (M^+); ^{1}H-NMR (90 MHz, $CDCl_3$) δ 7.26–7.07 (8H, m), 6.87 (2H, d, J=12), 6.66 (2H, s), 6.62 (2H, d, J=12), 5.26–5.14 (2H, m), 5.02–4.92 (2H, m).

3.14. Tribenzo[12]annulene silver triflate complex (36)

Tribenzo[12]annulene **8** (10 mg, 33 mmol) was treated with AgOTf (12 mg, 49 mmol) in THF (5 ml) under argon

atmosphere. After stirring for 30 min, the reaction mixture was concentrated to dryness and the residual solid was recrystallized from CH_2Cl_2–hexane to afford 15 mg (82%) of colorless prisms, mp 180–181°C (decomp.); ^{1}H-NMR (500 MHz, $CDCl_3$, −30°C) δ 7.54 (6H, s), 7.13 (6H, s).

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