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Synthesis of 1,4-Annulated Cyclooctatetraenophanes Based on a Novel Cubane Building Block Approach

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Received March 3, 2004

Abstract: A general synthetic approach to strained 1,4-annulated cyclooctatetraene-based cyclophanes is described. A key feature in this approach is exploitation of the cubane core as a masked cyclooctatetraene synthon. Thus, 1,4-disubstituted cubanes **3** and **4** used as precursors to cyclooctatetraenophanes have been prepared in four steps from the readily available 1,4-cubanedicarboxaldehyde (**5**). The synthesis of **3** was effected by palladium/copper-mediated coupling of 1,4-bis[(*Z*,*Z*)-2-iodovinyl]cubane (**6**) and 1,4-bis-[(*Z*,*Z*)-but-1-en-3-ynyl]cubane (**8**). For the synthesis of **4**, on the other hand, modified Eglington−Glaser coupling was applied for the macrocyclization step. The general characteristic of Rh(I) to induce [2 + 2] cycloreversion of the cubane core to *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene followed by thermal rearrangement to cyclooctatetraene was applied as a key structural transformation toward targeted cyclooctatetraenophanes **1** and **2**.

The view has long been held that strained [*m*.*n*]-cyclophanes constructed of decks possessing 4nπ-electrons or a combination of decks with 4n and (4n + 2) π-electrons will differ intrinsically in chemical properties from structural counterparts where both decks have (4n + 2) π-electrons.[1] The ability to alter cavity size reversibly by means of redox reactions holds particular fascination.[2] Unusual opportunities for metal complexation are also offered.[3] As well as addressing basic questions on aromaticity[4] and cyclic conjugation, a number of these macrocycles have been shown to function as high energy materials and as precursors to carbon nanotubes.[5] For these and many other reasons[6] strained [*m*.*n*](1,4)-cyclooctatetraenophanes with short unsaturated bridges constitute attractive synthetic targets. Since they are unknown, we have sought to develop new and versatile synthetic technology for their preparation. The substantial amount of strain incorporated in [*m*.*n*] *p*- and *m*-cyclophanes[7] and its lower homologues precluded ordinary synthetic methods for cyclophane synthesis. A viable alternative should therefore be based on transformation from high energy species such as strained polycyclic molecules. Three methods have been developed so far for the synthesis of strained cyclooctatetraenophanes, and all fulfill this criterion. The synthetic pathways that were developed to gain access more broadly to (1,2)- and (1,3)-annulated cyclooctatetraenophanes invariably capitalized on the disrotatory electrocyclization[8] of suitably functionalized bicyclo[4.2.0]octatrienes.[9] A notable landmark, the second route to strained (1,5)-cyclooctatetraenophanes, was achieved by Paquette and co-workers.[10] They reported that the thermal valence isomerization of semibullvalene proceeded smoothly giving (1,5)-cyclooctatetraenophanes in yields ranging from 30 to 80%. This reaction provided an entirely new general synthetic method for (1,5)-cyclooctatetraenophanes. A third method to cyclooctatetraenophanes[11] was based on the facile disrotatory opening of the central carbon−carbon bond in [5.4.2]propellatriene to afford the less strained bicyclic (1,4)-annulated [5]cyclooctatetraenophane.

We are interested in developing general synthetic methodology to bridged 4nπ cyclophanes, through which a wide variety of bridging groups can be incorporated and are particularly interested in the preparation of enyne-bridged cyclooctatetraenophanes. Herein, we detail the successful preparation of the first members of this series, [6.6](1,4)-cyclooctatetraenophane (**1**) and [8.8](1,4)-cyclooctatetraenophane (**2**) (Figure 1), and present an early glimpse at the properties inherent to these fascinating molecules. The only previous examples of enyne-bridged (4n + 2)-π-cyclophanes were prepared by Fallis et al. through the palladium-catalyzed reaction of terminal acetylenes with iodovinylbenzenes.[12] In this paper, we discuss the preparation of enyne-bridged dicubanes (**3**) and (**4**) by the palladium/copper-catalyzed coupling of cubyldienyne (**8**) with diiodovinylcubane (**6**) and by a route that involves Eglington−Glaser modified homocoupling of cubyldienyne (**8**). Additionally, we also discuss the preparation of the corresponding cyclooctatetraenophanes (**1**) and (**2**) through Rh(I)-catalyzed rearrangement of dicubane precursors **3** and **4**, respectively.

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10.1021/jo049643d CCC: $27.50
Published on Web 07/13/2004

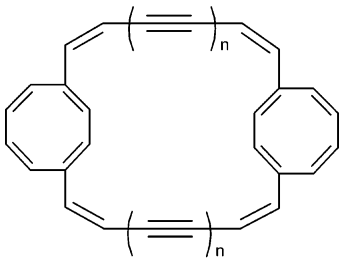

FIGURE 1. Structures of [6.6](1,4)-cyclooctatetraenophane (**1**) and [8.8](1,4) cyclooctatetraenophane (**2**).

We anticipated that a palladium/copper-catalyzed coupling route as well as Eglington−Glaser homocoupling would work with **3** and **4** because of the recent work of Fallis and co-workers,[12] who found that the synthesis of closely related phane molecules could be achieved very efficiently using virtually the same synthetic strategy. Our synthetic approach to these systems was based on the preparation of the key intermediates **6** and **8**. These were assembled from 1,4-cubanedicarboxaldehyde[13] **5** by a double-Wittig reaction, as illustrated in Scheme 1, to afford the *Z*-diiododiene **6** in 42% isolated yield. The stringent requirement that the homologation of **5** to **6** proceed with *Z* stereoselectivity in order to guarantee the orientation of this side chain capable of cyclization in the next step was ideally met by Wittig condensation with (iodomethylene)triphenylphosphorane.[14] In agreement with this assignment, the coupling constant observed for the vinylic protons located in the iodoethylene moiety of **6** is 8.9 Hz. Palladium(0)-based coupling of **6** with trimethylsilylacetylene generated the TMS-protected diacetylene **7**. The trimethylsilyl protecting groups of **7** were best removed with an aqueous THF solution of $(n\text{-Bu})_4NF$ to give 1,4-bis[(*Z*,*Z*)-but-1-en-3-ynyl]cubane (**8**) in 90% isolated yield as an air-stable white solid. The alternative procedure using 1−5 equiv of aqueous NaOH per TMS group of **7** required extended reaction times and resulted in the formation of a crude product of inferior purity.

The Sonogashira coupling reaction of diiodovinylcubane **6** with cubyldienyne **8** in the presence of $Pd(PPh_3)_4$ and CuI in *n*-butylamine at room temperature produced **3** in 25% yield, as shown in Scheme 2. The reaction was carried out at high-dilution conditions by adding a THF solution of **6** and **8** simultaneously with a syringe pump over a 12-h period. The structural assignment to **3** is in complete agreement with its spectroscopic features. The ^1H NMR spectrum ($CDCl_3$ solution) consists inter alia of a doublet (J = 10.5 Hz) at δ 5.81 due to the olefinic protons (4H), another doublet at δ 5.45 (J = 10.5 Hz) arising from the olefinic protons (4H), and a singlet at δ 4.10 attributable to the 12 cubane protons. The ^1H and ^{13}C NMR spectra of **3** showed no temperature dependence. Thus, the C_{2h}-symmetric spectra observed at room temperature remained almost unchanged upon cooling, even at −60 °C except for a slight broadening of the signals. This result suggests that the cubane moieties continued to rotate freely even at −60 °C on the NMR time-scale.

Copper-mediated Eglington−Glaser oxidative coupling of **8** with $Cu(OAc)_2$ in pyridine under pseudo-high-dilution conditions produced cyclic dimer **4** in 50% yield (Scheme 3).

The FAB mass spectrum of the coupling product recorded in CF_3COOH solution displayed only a single cluster of isotopic peaks, the most intense of which occurred at m/z = 405. The intensity and distribution pattern of the latter isotope cluster corresponded exactly to that calculated for the M + 1 isotopic envelope of the structure depicted for **4**. The high-resolution FAB mass spectrum of the latter M + 1 isotopic cluster also confirmed the exact elemental composition of the product to be $C_{32}H_{21}$, i.e., that expected for the macrocyclic structural assignment for **4** plus a hydrogen atom. The infrared spectrum of the coupling product of **8** also reinforced the above structural assignment to that of **4**. The IR was surprisingly simple, displaying only five strong bands, and indicative of a highly symmetric structure such as **4**. In addition, the normally very intense peak originating from the ν(C−H) stretch of a terminal ethyne was completely absent in the IR spectrum of the coupling product of **8**. This observation rules out the possibility of the product being a linear oligomer with terminal unreacted ethyne groups and establishes that it is a macrocyclic entity. The ^{13}C NMR spectrum of the product from the coupling of **8** was also consistent with that of a macrocyclic structural identity and displayed the expected six peaks, two of which corresponded to the carbons of two chemically and magnetically inequivalent difunctionalized ethynes at 82.3 and 77.4 ppm. The proton NMR spectrum of the coupling product of **8** was additionally supportive of the cyclic structure illustrated for **4** in Scheme 3, displaying the expected three peaks, and with a complete absence of any bands originating from the protons of terminal ethynes.

Halpern, Cassar, and Eaton showed years ago that the cubane skeleton is readily rearranged in the presence of Rh(I).[15] The unique ability of Rh(I) to promote unparalled rearrangement of the cubyl system has been amply exploited herein in the synthesis of 4nπ cyclophanes **1** and **2**. This general characteristic of Rh(I) is demonstrated as witnessed by the reaction of **3** and **4** with catalytic amounts of $[Rh(norbornadiene)Cl]_2$ (2.5 mol %) in dry toluene at 50 °C, as illustrated in Scheme 4.

In a typical experiment, $[Rh(norbornadiene)Cl]_2$ was added to a solution of enyne-bridged cubane in toluene at 50 °C, and the reaction was followed by ^1H NMR spectroscopy. Over a period of a few hours, the cubyl protons at δ 4.0 completely disappeared and at the same time were replaced by broad resonances around 6 ppm, characteristic of cyclooctatetraenes. Silica gel column chromatography afforded **1** (61%) and **2** (70%) as slightly unstable yellow oils.

(13) The cubane-1,4-dicarboxaldehyde **5** was readily prepared from commercially available dimethyl-1,4-cubanedicarboxylate via a conventional two-step sequence according to the published procedure; see: Eaton, P. E.; Gallopini, E.; Gilardi, R. *J. Am. Chem. Soc.* **1994**, *116*, 7588.

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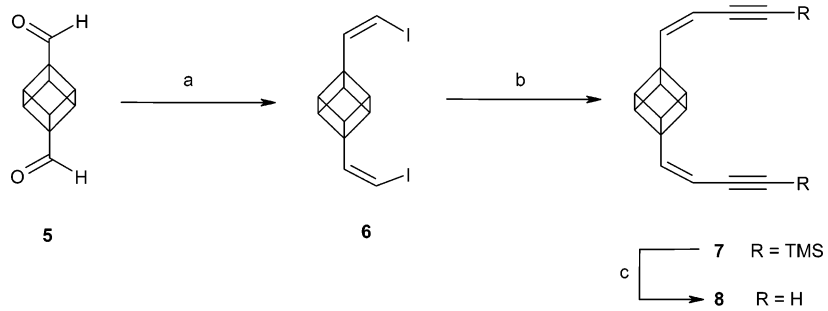
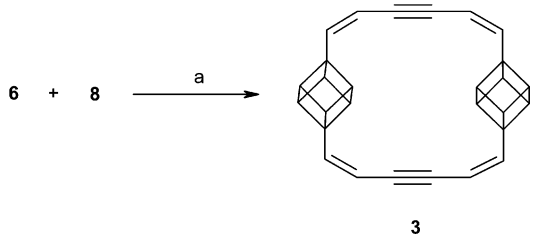
SCHEME 1. Synthesis of Key Intermediates 6 and 8[a]



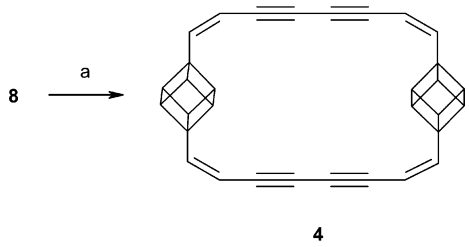
[a] Reagents and conditions: (a) $Ph_3P^+CH_2I\ I^-$, $NaN(TMS)_2$, THF, −78 °C, 0.5 h; (b) TMSacetylene, $Pd(PPh_3)_4$, CuI, DIPEA, rt, 5 h; (c) $(n\text{-Bu})_4NF$, aq THF, rt, 3 h.

SCHEME 2. Synthesis of [6.6](1,4)-Cubanophane (3)[a]



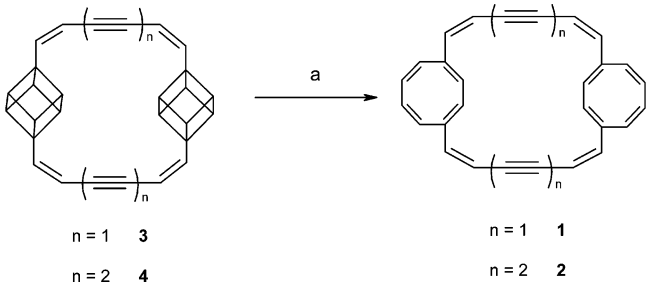
[a] Reagents and conditions: (a) $Pd(PPh_3)_4$, CuI, n-$BuNH_2$, rt, 12 h.

SCHEME 3. Synthesis of [8.8](1,4)-Cubanophane (4)[a]



[a] Reagents and conditions: (a) $Cu(OAc)_2$, pyridine, rt.

SCHEME 4. [6.6](1,4)-Cyclooctatetraenophane (1) and [8.8](1,4)-Cyclooctatetraenophane (2)[a]



[a] Reagents and conditions: (a) $[Rh(nor)Cl]_2$, toluene, 50 °C, 3 h.

Such conversions of cubanes to cyclooctatetraene analogues complement the work of Eaton and Stössel[16] and most importantly give access to 1,4-annulated cyclooctatetraenyl enynes for which there is, to our knowledge, no precedent in the literature. In our view, the synthetic methodology outlined herein should be amenable to modifications that allow for control of the length, chemical constitution, and location of the interconnective bridges. We hope to report on such developments and on the further chemical modification of structurally related cyclooctatetraene compounds at a later date.

(16) Eaton, P. E.; Stössel, D. *J. Org. Chem.* **1991**, *56*, 5138.

Experimental Section[17]

Caution. *Cubanes are high-energy materials. Therefore, it is recommended to run reactions behind safety shields. Crude reaction mixtures should not be evaporated at elevated temperature, especially in the presence of acidic or metallic contaminants.*

1,4-Bis[(*Z*)-2-iodovinyl]cubane (6). To a suspension of (iodomethyl)triphenylphosphonium iodide (2.37 g, 4.47 mmoL) in dry THF (10 mL) was added sodium hexamethyldisilazane (4.32 mL of 1.0 M solution in THF) at 0 °C. The resultant solution was cooled to −78 °C, aldehyde **5** (320.8 mg, 2.0 mmoL) was introduced, and stirring was maintained at this temperature for 1 h prior to quenching with saturated NH_4Cl solution (5 mL). The reaction mixture was allowed to warm to room temperature before pentane (50 mL) was added. The reaction mixture was washed twice with brine, dried, and evaporated to give 343.2 mg (42%) of **6** as a colorless oil which was used without further purification in the next step: FAB-MS (*m*/*z*, relative intensity) 409 ($M^+ + 1$, 84); IR (KBr) 2988, 2922, 1612, 951; ^1H NMR (400 MHz, $CDCl_3$) 6.89 (d, 2H, J = 8.9 Hz, C═C), 6.27 (d, 2H, J = 8.9 Hz, C═C), 4.10−4.03 (s, 6H, cubyl H-2, 6, 8 and H-3, 5, 7). ^{13}C NMR (100 MHz, $CDCl_3$) 141.34 (s, 2C, C═C), 109.11 (d, 2C, C═C), 60.53 (s, 2C, cubyl C-1 and C-4), 47.93 (d, 6C, cubyl C-2, 6, 8 and C-3, 5, 7). Anal. Calcd for $C_{12}H_{10}I_2$: C, 35.32; H, 2.47. Found: C, 35.18; H, 2.59.

1,4-Bis[4-trimethylsilyl-(*Z*,*Z*)-but-1-en-3-ynyl]cubane (7). Diisopropylethylamine (22 mL) was added via syringe to a mixture of TMS-acetylene (1.58 g, 16.0 mmoL), vinyl iodide **6** (2.49 g, 6.1 mmoL), and $Pd(PPh_3)_4$ (142.6 mg, 0.123 mmoL) under an atmosphere of argon and the suspension stirred for 0.2 h. A solution of copper(I) iodide (83.8 mg, 0.44 mmoL) in 2 mL of DIPEA was then added via syringe, and stirring was continued for 48 h at ambient temperature. During this time, the initially formed khaki precipitate became dark brown in color. After 48 h, all solvent was removed under reduced pressure and the residue extracted with boiling hexane (4 × 20 mL). The combined hexane extracts were filtered, the solvent distilled off under reduced pressure, and the residue flash chromatographed on silica eluting with 9:1 hexane/Et_2O. The product thus obtained was finally boiled in 50 mL of MeOH with Norit A decolorizing charcoal (100 mg), the mixture filtered, and the solvent removed under reduced pressure. Further drying under vacuum (0.01

(17) For details on the general experimental methods, see: Mutak, S.; Maršić, N.; Dominis Kramarić, M.; Pavlović, D. *J. Med. Chem.* **2004**, *47*, 411.

mmHg) yielded 1.46 g (70%) of **7** as a pale yellow oil that slowly crystallized to a cream solid upon standing for several days: FAB-MS (*m*/*z*, relative intensity) 349 ($M^+ + 1$, 78); IR (KBr) 2985, 2920, 2851, 2088 (νC≡C), 1635, 949, 839, 760;. ^{1}H NMR (400 MHz, $CDCl_3$) 6.13 (d, 2H, J = 11.1 Hz, C═C−H), 5.40 (d, 2H, J = 11.1 Hz, C═C−H), 4.08 (s, 6H, cubyl H-2, 6, 8 and H-3, 5, 7), 0.18 (s, 18H, Me_3Si); ^{13}C NMR (100 MHz, $CDCl_3$) 143.85 (d, 2C, C═C−H), 107.49 (d, 2C, C═C−H), 103.89 (s, 2C, acetylenic C), 94.86 (s, 2C, acetylenic C), 59.87 (s, 2C, cubyl C-1, 4), 46.56 (d, 6C, cubyl C-2, 6, 8 and C-3, 5, 7), −0.15 (q, 6C, Me_3Si). Anal. Calcd for $C_{22}H_{28}Si_2$: C, 75.79; H, 8.10. Found: C, 75.65; H, 8.28.

1,4-Bis[(*Z*,*Z*)-but-1-en-3-ynyl]cubane (8). A solution of (*Z*,*Z*)-enyne **7** (144.0 mg, 0.4 mmoL) in 10 mL of 20% aqueous THF was treated with (*n*-Bu)$_4$NF (1.4 mL of 1.0 M THF solution) and stirred at room temperature for 3 h. By this time, all the starting **7** had disappeared as judged by TLC (9:1 hexane/Et_2O, silica). The reaction solution was poured onto brine and extracted with Et_2O (40 mL). The organic layer was washed with distilled water (2 × 20 mL), dried ($MgSO_4$), and filtered and the solvent evaporated off at room temperature under reduced pressure. The remaining oil crystallized upon drying under vacuum to give 75.9 mg (90%) of **8** of sufficient purity for the subsequent preparation of **3** and **4**. Further purification could, however, be achieved upon flash column chromatography on silica with 9:1 hexane/Et_2O as eluant, followed by washing the product with a small portion of hexane and drying under vacuum at 0.01 mmHg. Compound **8** underwent partial decomposition upon attempted purification by sublimation: mp 123−125 °C; FAB-MS (*m*/*z*, relative intensity) 205 ($M^+ + 1$, 64), 204 (M^+, 23), 189 (47), 165 (52), 153 (9), 128 (33), 115 (3); IR (KBr) 3275 (ν≡CH), 2983, 2920, 2853, 2097 (νC≡C), 1632, 951, 829, 626, 572; ^{1}H NMR (400 MHz, $CDCl_3$) 6.17 (d, 2H, $J_{1,2}$= 11.2 Hz, C═C−H), 5.42 (dd, 2H, $J_{1,2}$= 11.2 Hz, $J_{1,3}$= 2.2 Hz, C═C−H), 4.12 (s, 6H, cubyl H-2, 6, 8 and H-3, 5, 7), 3.14 (d, 2H, J = 2.2 Hz, acetylenic C−H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.91 (d, 2C, C═C−H), 109.71 (d, 2C, C═C−H), 83.01 (s, 2C, acetylenic C), 77.40 (d, 2C, acetylenic C), 59.71 (s, 2C, cubyl C-1,4), 46.51 (d, 6C, cubyl C-2, 6, 8 and C-3, 5, 7). Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.19; H, 6.12.

4-[6-Cuban-4-ylhexa-(*Z*,*Z*)-1,5-dien-3-ynyl]-1-hepta-1,5-dien-3-ynylcubane (3). To a mixture of Pd(PPh$_3$)$_4$ (66.1 mg, 0.057 mmoL) and CuI (36.0 mg, 0.189 mmoL) in *n*-BuNH_2 (180 mL) were added a THF solution of **6** (163.2 mg, 0.4 mmoL, 10 mL of 0.04 M solution) and **8** (81.7 mg, 0.4 mmoL, 10 mL of 0.04 M solution) with a dual syringe pump over a 12 h period. The reaction was stirred at room temperature for an additional 5 h. After removal of solvent, the residue was boiled in 25 mL of hexane. The hexane extracts was flash chromatographed on a column of silica, eluting with 9.5:0.5 pentane/Et_2O, to yield an oil which solidified upon cooling after removal of solvent by distillation on a water bath. The solid was subsequently dried under vacuum (20 °C/0.1 mmHg) to yield 37.2 mg (26%) of **3** (mp 56−57 °C) as volatile colorless crystals. The product could also be readily sublimed under vacuum (50 °C/0.1 mmHg): FAB-MS (*m*/*z*, relative intensity) 357 ($M^+ + 1$, 82), 356 (M^+, 40); IR (KBr) 2980, 2918, 2850, 2140 (νC≡C), 1631, 1220, 840; ^{1}H NMR (400 MHz, $CDCl_3$) 5.81 (d, 4H, J = 10.5 Hz, C═C−H), 5.45 (d, 4H, J = 10.5 Hz, C═C−H), 4.10 (s, 12H, cubyl H-2, 6, 8 and H-3, 5, 7); ^{13}C NMR (100 MHz, $CDCl_3$) 142.70 (d, 4C, C═C−H), 109.53 (d, 4C, C═C−H), 80.58 (s, 4C, acetylenic C), 59.12 (s, 4C, cubyl C-1 and C-4), 45.92 (d, 12C, cubyl C-2, 6, 8 and C-3, 5, 7); HRMS (FAB) calcd for $C_{28}H_{21}$ $[MH]^+$ 357.1643, found 357.1639. Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.47; H, 5.63.

4-[8-Cuban-4-yl-octa-(*Z*,*Z*)-1,7-dien-3,5-diynyl]-1-nona-(*Z*,*Z*)-1,7-dien-3,5-diynylcubane (4). To a suspension of anhydrous Cu(OAc)$_2$ (440.0 mg, 2.42 mmoL) in dry pyridine (125 mL) was added **8** (81.7 mg, 0.40 mmoL) dissolved in dry pyridine (8 mL) over a 12 h period by syringe pump (rate of addition = 0.57 mL/h). The reaction mixture was stirred for 16 h at room temperature and partitioned between hexane (160 mL) and 30% aqueous $CuSO_4$ (60 mL). The aqueous phase was extracted with hexane (2 × 50 mL), and the combined organic extracts were washed with 30% aqueous $CuSO_4$ (120 mL), water (60 mL), and brine (60 mL). The organic extracts were dried (Na_2SO_4) and filtered, and the solvent was removed in vacuo on a rotary evaporator. The crude product was finally purified by column chromatography on silica (9:1, pentane/Et_2O) to afford **4**, sufficiently pure that it crystallized when the solvent was removed (80.9 mg, 50%): mp 133−135 °C; FAB-MS (*m*/*z*, relative intensity) 405 ($M^+ + 1$, 68), 404 (M^+, 36); IR (KBr) 2985, 2955, 2145 (νC≡C), 1628, 1238, 838; ^{1}H NMR (400 MHz, $CDCl_3$) 6.50 (d, 4H, J = 11.1 Hz, C═C−H), 5.45 (d, 4H, J = 11.1 Hz, C═C−H), 3.89 (s, 12H, cubyl H-2, 6, 8 and H-3, 5, 7); ^{13}C NMR (100 MHz, $CDCl_3$) 146.05 (d, 4C, C═C−H), 108.56 (d, 4C, C═C−H), 82.33 (s, 4C, acetylenic C), 77.40 (s, 4C, acetylenic C), 58.94 (s, 4C, cubyl C-1 and C-4), 46.70 (d, 12C, cubyl C-2, 6, 8 and C-3, 5, 7); HRMS (FAB) calcd for $C_{32}H_{21}$ $[MH]^+$ 405.1643, found 405.1648. Anal. Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98. Found: C, 94.88; H, 4.99.

General Procedure for the Preparation of [6.6](1,4)-Cyclooctatetraenophane (1) and [8.8](1,4)-Cyclooctatetraenophane (2). Norbornadienerhodium(I) chloride dimer ([Rh(nor)Cl$_2$); 2.5 mol %] was added to a stirred solution of the cubanophane (0.1 mmoL) in dry toluene (1.0 mL) at room temperature. The solution was stirred at 50 °C in nitrogen atmosphere for 3 h, at which time the reaction was judged complete by NMR examination of an aliquot or TLC analysis (5% Et_2O/pentane). The solution was passed through a short column of silica gel containing polymer-supported Ph_3P using CH_2Cl_2. The solvent was removed in vacuo, and the oily residue was purified by column chromatography eluting with 5% Et_2O in pentane to afford the corresponding product as a yellow oil.

[6.6](1,4)-Cyclooctatetraenophane (1). A 22.6 mg (61%) amount was prepared by the above procedure from 37.0 mg of **3**: FAB-MS (*m*/*z*, relative intensity) 357 ($M^+ + 1$, 100); IR (KBr) 3003, 2960, 2924, 2845, 2175 (νC≡C), 1634, 1100, 1020, 810; ^{1}H NMR (400 MHz, acetone-d_6, −60 °C) 6.30−6.05 (m, 4H), 5.95−5.65 (m, 8H), 5.78 (d, 4H, J = 10.4 Hz, C═C−H), 5.43 (d, 4H, J = 10.4 Hz, C═C−H); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) 6.30−5.70 (m, 12H), 5.75 (d, 4H, J = 10.4 Hz, C═C−H), 5.48 (d, 4H, J = 10.4 Hz, C═C−H); ^{13}C NMR (100 MHz, acetone-d_6, −60 °C) 142.70 (d, 4C, C═C−H), 137.91, 137.82, 132.85, 132.52, 131.97, 131.65, 130.59, 124.50, 109.51 (d, 4C, C═C−H), 86.93 (s, 4C, acetylenic C); HRMS (FAB) calcd for $C_{28}H_{21}$ $[MH]^+$ 357.1643, found 357.1647. Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.23; H, 5.78.

[8.8](1,4)-Cyclooctatetraenophane (2). A 28.3 mg (70%) amount was prepared by the above procedure from 40.4 mg of **4**: FAB-MS (*m*/*z*, relative intensity) 405 ($M^+ + 1$, 100); IR (KBr) 3004, 2968, 2923, 2200 (νC≡C), 1630, 1128, 1021, 805; ^{1}H NMR (400 MHz, acetone-d_6, −60 °C) 6.43 (d, 4H, J = 10.8 Hz, C═C−H), 6.32−6.00 (m, 4H), 5.85−5.60 (m, 8H), 5.41 (d, 4H, J = 10.8 Hz, C═C−H); ^{13}C NMR (100 MHz, acetone-d_6, −60 °C) 146.53 (d, 4C, C═C−H), 139.85, 132.52, 132.19, 131.11, 131.02, 130.36, 130.00, 124.17, 107.96 (d, 4C, C═C−H), 81.80 (s, 4C, acetylenic C), 71.80 (s, 4C, acetylenic C); HRMS (FAB) calcd for $C_{32}H_{21}$ $[MH]^+$ 405.1643, found 405.1642. Anal. Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98. Found: C, 94.74; H, 5.29.

Acknowledgment. We acknowledge the University of Illinois at Chicago for generous support of this research.

JO049643D