Alkynylcubanes as Precursors of Rigid-Rod Molecules and Alkynylcyclooctatetraenes

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Abstract: We have developed new methodology for the synthesis of alkynylcubanes and have used these compounds to make rigid-rod molecules constructed of cubane and acetylene subunits. Terminal and substituted alkynylcubanes **7a**, **7b**, **8a**, **8b**, **12a**, and **12b** were synthesized by *n*-BuLi-promoted elimination of halogen from 1,1-dibromovinylcubanes **6a**, **6b**, and **11**, followed by quenching with electrophiles. Systems with one or two acetylenic units between two cubanes were also prepared: dicubylacetylene (**15**) was obtained via reaction of the lithium ylide of (trimethylsilyl)diazomethane with dicubyl ketone (**14**); 1,4-dicubyl-1,3-butadiyne (**16**) was made by oxidative dimerization of ethynylcubane (**7a**). Dimerizations and cross-coupling reactions of various 1,4-diethynylcubanes afforded longer rods, e.g., 1,4-bis-((trimethylsilyl)ethynyl)cubyl-1,3-butadiyne (**18**) and 1-(4-((trimethylsilyl)ethynyl)cubyl)-4-cubyl-1,3-butadiyne (**21**). Rh(I)-promoted ring opening of the cubane subunit(s) of these compounds into the corresponding tricyclooctadiene followed by thermal rearrangement to the cyclooctatetraene was used to convert **7a**, **8a**, and **12a** into the mono- and disubstituted alkynylcyclooctatetraenes **22a**, **22b**, and **23** and to take **15** and **16** into the alkynyl-bridged cyclooctatetraenes **24a** and **24b**, respectively. X-ray crystallographic analysis of **12a**, **15**, **16**, and **18** revealed interesting details about their structures.

Introduction

Because of their well-defined dimensionality and rigid-rod geometry, alkynylcubanes (cubylacetylenes) will prove to be important building blocks for new oligomeric compounds in the developing world of nanoarchitecture.[1-5] Our ultimate goals are long (100–200 Å) rods of exactly defined structure and, further in the future, extended three-dimensional networks of dimensionally-fixed, electron-rich cavities repeating through a diamond lattice constructed of 1,3,5,7-tetraethynylcubane units (T_d symmetry).[6] Figure 1 shows a segment of such a network; the central 10 cubanes form an adamantane-shaped cage. The density is calculated to be only about 0.5 g/cc; the diameter of the internal cavity (H to H) is about 9.3 Å, much larger than that in C_{60} fullerene or common zeolites. The very open nature of this structure and its homologues would provide generous room for guests and permit movement from enclosure to enclosure.

We present in this paper good synthetic procedures for the preparation of alkynylcubanes. We show how to effect their dimerization and cross-coupling to substantially-sized, high-energy rigid rods composed of alternate cubane and diacetylenic units. Incidentally, we demonstrate that alkynylcubanes can be readily transformed into alkynylcyclooctatetraenes, systems that might be converted into highly unsaturated materials of unique redox and photochemical properties.[7]

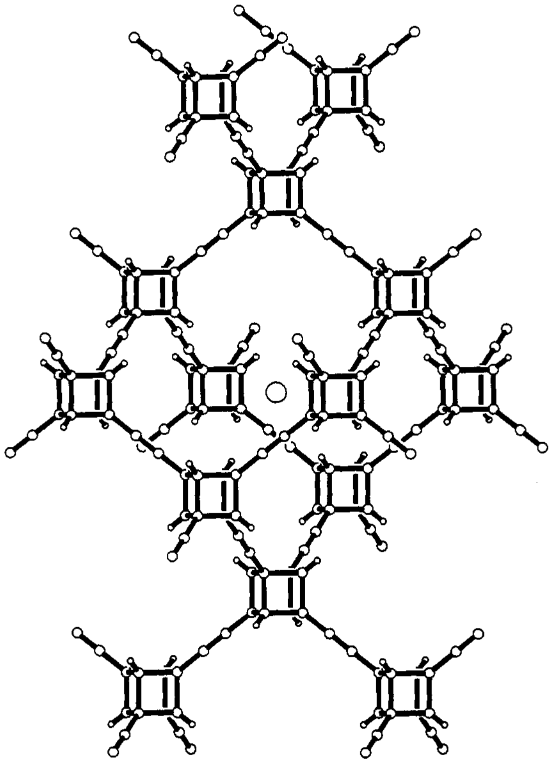

Figure 1. Fourteen-cubane segment of a hypothetical three-dimensional polymer comprised of tetrahedrally substituted cubane moieties linked by ethyne bridges. A dummy atom is shown at the center of the adamantane-like cage formed by 10 of the cubanes. This dummy atom is calculated to be 4.66 Å from the nearest hydrogen atoms and 5.48 Å from the nearest carbons. The gateways between such cages are at least as large.

Alkynylcubanes had not been reported prior to Eaton and Stössel's attempts to prepare them by palladium-catalyzed

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(1) (a) Drexler, K. E. *Nanosystems, Molecular Machinery, Manufacturing, and Computation*; Wiley & Sons Inc.: 1992. (b) For a discussion about building blocks for nanoarchitecture, see: Michl, J.; Kaszynsky, P.; Friedli, A. C. *Strain and Its Implications in Organic Synthesis*; NATO ASI Series 273; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; pp 463–482. The saturated rigid-rod systems known to date are derived from [2.2.2]bicyclooctanes,[2] [1.1.1]bicyclopentanes,[3] cubanes,[4] or *p*-carboranes.[5]

(2) Zimmerman, H. E.; King, R. K.; Meinhardt, M. B. *J. Org. Chem.* **1992**, *57*, 5484 and earlier papers in the series.

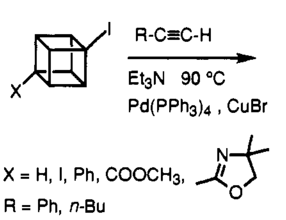
(3) (a) Kaszynsky, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601. (b) Schlüter, A. D.; Bothe, H.; Gosau, J. M. *Makromol. Chem.* **1991**, *192*, 2497. (c) Bunz, U.; Szeimies, G. *Tetrahedron Lett.* **1989**, *30*, 2087.

(4) (a) Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232. (b) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421 and references therein.

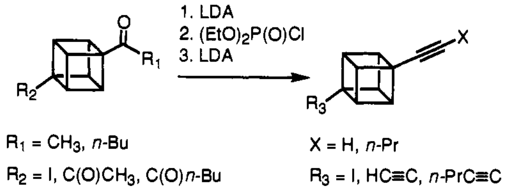
(5) (a) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719. (b) Müller, J.; Base, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721.

(6) Related polymeric systems are mentioned in a review by: Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101.

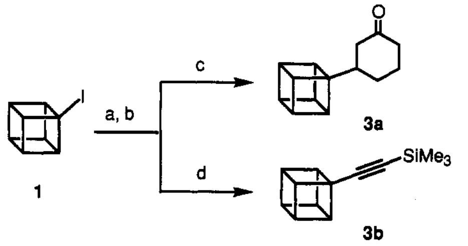
Scheme 1



Scheme 2



Scheme 3[a]



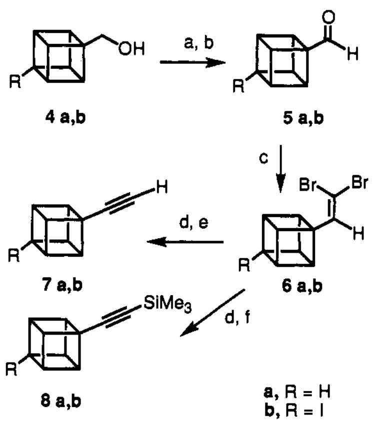
[a] (a) *t*-BuLi, THF, −78 °C; (b) (2-thienyl)CuCNLi; (c) 2-cyclohexen-1-one; (d) $Me_3SiC{\equiv}CPhI(OTf)$ (**2**).

reaction of iodocubanes with terminal acetylenes under Heck reaction conditions. Such reactions led instead (and inexplicably) to alkynylcyclooctatetraenes, and a variety of 1,4-disubstituted alkynylcyclooctatetraenes were so obtained (Scheme 1).[8] Staley and Siesel more recently provided a higher yield approach to such cyclooctatetraenes using palladium-catalyzed coupling reactions of bromocyclooctatetraene with alkynylstannanes or terminal alkynes.[9]

The first alkynylcubanes themselves were obtained by Eaton and Stössel from the diethyl phosphate enolates of cubyl ketones using an extension of the Negishi methodology (Scheme 2).[8] The yields were only modest at very best (5–32%). Clearly, better procedures are needed if cubylacetylenes are ever to play a significant role as building blocks for nanoarchitecture projects. These are developed here.

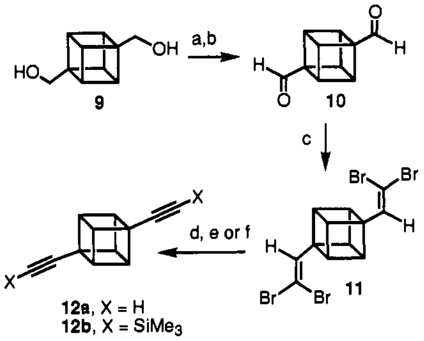
Synthesis of Terminal Cubylacetylenes. Stang and Kitamura have reported coupling of alkenylcopper reagents with alkynyliodonium tosylates to produce 1,3-enynes.[10] As the hybridization of cubyl C–H (31% s) is much like that of vinyl C–H (33% s),[11] we applied their approach to the synthesis of "cubylynes". Addition of cubyllithium to lithium 2-thienylcyanocuprate[12] in THF at −78 °C gave a cubyl cuprate, proven by isolation in excellent yield (91%) of 3-cubylcyclohexan-1-one (**3a**) from its reaction with 2-cyclohexen-1-one (Scheme 3).[13] Unfortunately, we were not able to obtain better than 30% yield of ((trimethylsilyl)ethynyl)cubane (**3b**) from the cross-coupling reaction of the cuprate with phenyl((trimethylsilyl)ethynyl)iodonium triflate[14] (**2**, Scheme 3).

Scheme 4[a]



[a] (a) $(COCl)_2$, DMSO; (b) Et_3N; (c) CBr_4, PPh_3; (d) *n*-BuLi or MeLi; (e) H_2O; (f) Me_3SiCl.

Scheme 5



We turned next to the procedure of Corey and Fuchs for the conversion of aldehydes to acetylenes.[15] This proved very successful (Scheme 4). Reaction of PPh_3/CBr_4 with cubanecarboxaldehydes **5a** and **5b** afforded the crystalline dibromovinyl compounds **6a** and **6b** in 82 and 67% yield, respectively. On treatment with *n*-butyllithium in THF at −78 °C each gave the corresponding lithium acetylide (methyllithium was used with **6b** to avoid metal–halogen exchange). Protonation afforded ethynylcubane (**7a**) from **6a** in 85% yield and (4-iodocubyl)acetylene (**7b**) from **6b** in 90% yield. Quenching of the acetylide salts with Me_3SiCl gave the corresponding trimethylsilyl derivatives **8a** (=**3b**) and **8b** in 91 and 82% yield, respectively. Clearly, the synthesis of a wide variety of other cubylacetylenes would be possible by treatment of the intermediate lithium cubylacetylide with other electrophiles (e.g., CO_2, halogens).

This methodology proved to be successful also for the synthesis of 1,4-diethynylcubanes. Treatment of 1,4-bis(2,2-dibromovinyl)cubane (**11**, obtained in 84% yield from the dialdehyde **10**) with *n*-butyllithium afforded 1,4-diethynylcubane (**12a**) in 95% yield and, separately, the corresponding trimethylsilyl derivative **12b** in 92% yield (Scheme 5).

All the alkynylcubanes we have examined are crystalline solids, stable in the dark away from air. Still, as both the cubyl and the acetylene unit are high-energy moieties, it is prudent to be very cautious. The reaction scale should be kept small (<1 mM), and safety shields should always be employed. In one instance an old, crude sample of 4-iodoethynylcubane exploded with great force on being touched with a spatula. The simplest alkynylcubane, cubylacetylene itself (**7a**), is colorless and low-melting

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(7) The synthesis and properties of oligo(1,5-cyclooctatetraenylene)-vinylenes have been described: Auchter-Krummel, P.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1003. Our approach would afford oligo-(1,4-cyclooctatetraenylene)ethynylenes.

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

(9) (a) Siesel, D. A.; Staley, S. W. *Tetrahedron Lett.* **1993**, *34*, 3679. (b) Siesel, D. A.; Staley, S. W. *J. Org. Chem.* **1993**, *58*, 7870.

(10) Stang, P. J.; Kitamura, T. *J. Am. Chem. Soc.* **1987**, *109*, 7561.

(11) (a) Ermer, O.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *25*, 447. (b) Della, E. W.; Hine, T. W.; Patney, H. K. *J. Org. Chem.* **1977**, *42*, 2940.

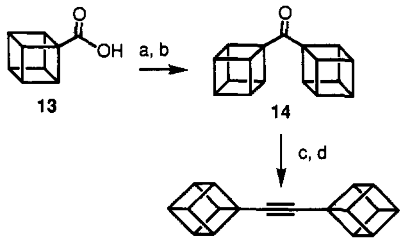
(12) Lipshutz, B. H.; Koerner, M.; Parker, D. A. *Tetrahedron Lett.* **1987**, *28*, 945. 2-Thienylcyanocuprate is now commercially available from Aldrich.

(13) Cf.: Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *56*, 5138.

(14) Bachi, M. D.; Bar-Ner, N.; Crittel, C. M.; Stang, P. J.; Williamson, B. L. *J. Org. Chem.* **1991**, *56*, 3912.

(15) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.

Scheme 6[a]



[a] (a) EtMgBr, THF, −10 °C; (b) cubyllithium; (c) *n*-BuLi, Me_3SiCHN_2, THF, −78 °C; (d) H_2O.

(43–45 °C) and volatile and easily lost on the rotary evaporator. When exposed to air the terminal alkynylcubanes turn yellow over a few days and are partly transformed into resinous, insoluble materials. Nonetheless, there is no problem working with these compounds as such. Their trimethylsilyl derivatives are yet more stable in air and light, less volatile, and more easily crystallized. Desilylation occurs smoothly on treatment with aqueous NaOH in MeOH.[16]

The cubyl proton resonances in the ^{1}H NMR spectra of the terminal alkynes **7a**, **7b**, and **12a** are in the 3.9–4.3 ppm region (quite typical of many other cubanes); the acetylenic proton signal appears at 2.7 ppm. In the IR spectra, the alkynyl C—H stretch is at 3300 cm^{-1} and the $C\equiv C$ bond stretch at 2100 cm^{-1}, all quite normal values.

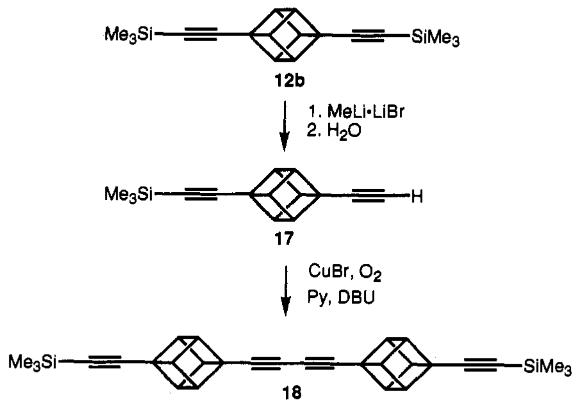
Synthesis of Dicubylacetylene. A quite different approach was required to place an alkynyl group spacer between two cubane units effectively. We employed the exceptionally clever methodology of Colvin and Hamill[17] in which a ketone is homologated (in a variant of the Peterson reaction) to a vinyl diazo compound using the lithium ylide of (trimethylsilyl)diazomethane. Elimination of dinitrogen and rearrangement of the intermediate vinylcarbene affords the internal alkyne. In this way dicubylketone (**14**, easily available from the reaction of the bromomagnesium salt of cubanecarboxylic acid (**13**) with cubyllithium) was converted in 52% yield to dicubylacetylene (**15**, Scheme 6).[18]

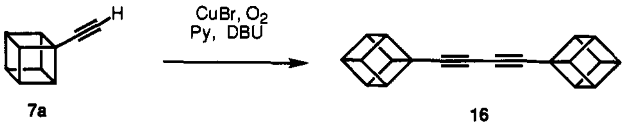
As anticipated from symmetry considerations, no $C\equiv C$ stretch is observed in the IR spectrum of **15**. In the ^{1}H NMR the pattern of the cubyl protons is identical to that of cubylacetylene. In the ^{13}C NMR spectrum the chemical shift of the acetylenic carbon is 89.4 ppm. The corresponding resonance in diphenylacetylene is positioned similarly at 89.6 ppm, but in di-*tert*-butylacetylene it is somewhat upfield (86.9 ppm). Aromatic and cubyl carbons have similar s character in their exocyclic bonding orbitals.[5a,11]

Dicubylacetylene forms flat, light, colorless crystals. We are encouraged to pursue our stated goal by the fact that dicubylacetylene is very stable to air and light; its thermal decomposition does not start until about 185 °C.

Homocoupling of Cubylacetylenes. Synthesis of 1,3-Diynes. In 1,4-dicubyl-1,3-butadiynes the linearly arranged four carbons of the diyne unit separate two cubanes. We found that classical,[19] copper-catalyzed oxidative dimerizations of terminal cubyl acetylenes were quite successful for the synthesis of these rod-like molecules. 1,4-Dicubyl-1,3-butadiyne (**16**) was obtained as a crystalline solid in 75% yield by bubbling oxygen through a solution of cubylacetylene in pyridine containing cuprous bromide and a small amount of DBU (eq 1).[20] Although it is somewhat less stable than the monoyne **15**, its decomposition in air is still quite slow.

Scheme 7





Dicubylacetylene (**15**), with one ethyne spacer, and 1,4-dicubyl-1,3-butadiyne (**16**), with two, are rigid rods with tip-to-tip lengths (H to H) along the body diagonal of 11.5 and 14.0 Å, respectively (*vide infra*). While **15** is poorly soluble, compound **16**, though longer, is very soluble in most organic solvents.

Oxidative dimerization can be used to produce yet longer rods. The "monomer" 1-((trimethylsilyl)ethynyl)-4-ethynylcubane (**17**) was prepared in 33% yield by monodesilylation of 1,4-bis((trimethylsilyl)ethynyl)cubane (**12b**) using 1 equiv of $CH_3Li\cdot LiBr$ complex[21] followed by hydrolysis. Some (44%) starting material was recovered and a little (7%) of 1,4-diethynylcubane was also isolated. Although this conversion to **17** was not very satisfactory, it did provide enough material to proceed. Homocoupling afforded 1,4-bis((trimethylsilyl)ethynyl)cubyl-1,3-butadiyne (**18**) in 87% yield (Scheme 7).

Compound **18** crystallizes as thin, colorless needles, soluble in benzene and chlorinated solvents but barely so in ethers. Within this molecule is a rigid carbon rod 17.36-Å long. The carbon–carbon tip-to-tip length of **18** is comparable to that of the longest rods yet synthesized and characterized: [4]carborods (17.21 Å);[5b] [4]rodanes (15.40 Å);[2] and [5]staffanes (15.10 Å).[3] It is "set-up" for lengthening via further couplings.

Interestingly, the solubility of alkynylcubane-based rods is higher than that of the somewhat shorter rod (15.0 Å) made up of 4-para-linked cubanes.[5c] The Et_3Si-capped analogue of **18** is yet more soluble, dissolving freely even in ethers. These observations are encouraging, as one of the major problems encountered in the preparation of rod-like molecules is their low solubility.

Cross-Coupled Alkynylcubanes. As dimerization reactions can lead only to symmetrical rods, we have started to investigate cross-coupling reactions. While numerous methods for the dimerization of acetylenes are available, there are fewer procedures for the controlled synthesis of asymmetric diacetylenes.[19] The procedure reported by Zweifel and Miller by which bromoacetylenes are cross-coupled with cuprous acetylides has proven to be useful in our initial explorations.[21] In one example, the bromoacetylene 1-(bromoethynyl)-4-((trimethylsilyl)ethynyl)cubane (**19**) was prepared, in 44% yield overall by partially monodesilylating 1,4-bis((trimethylsilyl)ethynyl)cubane (**12b**)

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[16] Roser, J.; Eberbach, W. *Synth. Commun.* **1989**, *16*, 983.

[17] Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 869. See also: Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1979**, *44*, 4997. Ohira, S.; Okai, K.; Moritani, T. *J. Chem. Soc., Chem. Commun.* **1992**, 721.

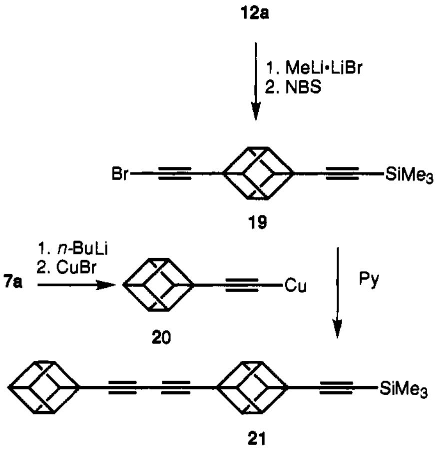
[18] Compound **15** could also be obtained in two steps from dicubyl ketone (**14**) in 13% yield overall, by Fritsch–Buttemberg–Wiechell rearrangement of 1-chloro-2,2-dicubylethylene following the literature procedure for dicyclopropylacetylene: (a) Köbrich, G.; Trapp, H.; Flory, K.; Drischel, W. *Chem. Ber.* **1966**, *99*, 689. (b) Köbrich, G.; Merkel, D.; Thiem, K.-W. *Chem. Ber.* **1972**, *105*, 1683.

[19] For a review on methods for sp–sp coupling: Sonogashira, K. *Comprehensive Organic Synthesis*; Pergamon Press: New York, 1991; Vol. 3, p 551.

[20] Brandsma, L.; Verkruijsse, H. D.; Walda, B. *Synth. Commun.* **1991**, *21*, 137.

[21] Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128.

Scheme 8



with $CH_3Li{\cdot}LiBr$ and then reacting the acetylide so formed with *N*-bromosuccinimide. Reaction of this bromoacetylene with cubylethynylcopper (**20**), prepared *in situ* from the lithium salt of **7a** and CuBr, gave the cross-coupled product 1-(4-((trimethylsilyl)ethynyl)cubyl)-4-cubyl-1,3-butadiyne (**21**) in 56% isolated yield (Scheme 8). The dimerization of **19** to **18** was eliminated almost completely by slow addition of a dilute solution of the bromoacetylene *to* the solution of **20**.

Compound **21** forms small crystals and is a stable material, soluble in most organic solvents. We are at present investigating the possibility of using a combination of cross-coupling and dimerization reactions for the controlled growth of larger rigid-rod systems.

Structure, Shape, and Size of Cubylacetylenes. The crystal structures of **12a**, **15**, **16**, and **18** were determined by single-crystal X-ray diffraction analyses.[22] Parameter tables are provided as supplementary material. The packing patterns are of particular interest.

There are two different kinds of molecules in the asymmetric unit of 1,4-diethynylcubane (**12a**).[24] The asymmetric unit is two half-molecules (Figure 2); the other half of each molecule is generated by a crystallographic inversion center, located at the midpoint of the cube. There are no significant intramolecular differences between these mathematically distinct molecules and only a slight difference in the way they pack in the crystal. The molecules pack in planar layers which stack parallel to the −1,0,1 crystal planes; within each layer, the molecules display a herringbone pattern, and each terminal ethynyl group approaches (at roughly a right angle) the side of an ethynyl group of a molecule in the next row.

In the crystal of dicubylacetylene (**15**) the cubyl groups at the two ends of the molecule are staggered so that the long axis of the molecule is essentially a sixfold rotation–reflection axis;[25] the end-on projection appears hexagonal. All molecules, throughout the crystal, are packed with their long axes coparallel (Figure 3). However, the dumbbell-shaped molecules slide past one another in a direction parallel to this axis, with the result that the acetylene linkage of each molecule is surrounded by cubyl portions from six near neighbors.

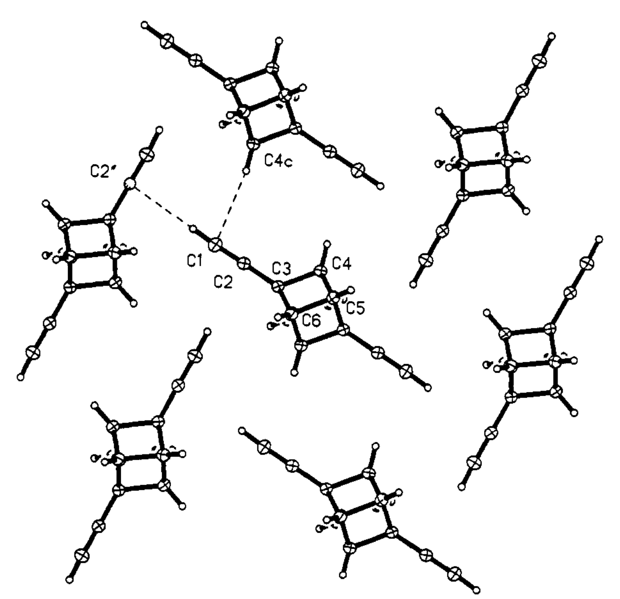


Figure 2. Planar sheet illustrating the primary packing approaches in crystals of **12a**. Close intermolecular distances indicated by dashed lines are 2.71 Å from the ethynyl hydrogen, H1, to an ethynyl carbon, C2″, 2.80 Å from a cubyl hydrogen, H4, to an ethynyl carbon, C2″, and 2.80 Å from a cubyl hydrogen, H4, to the ethynyl carbon, C1. A solid-state reaction, hastened by the X-rays used for structure analysis, led to a loss of crystallinity within a day and may be due to alkyne–alkyne reactions.

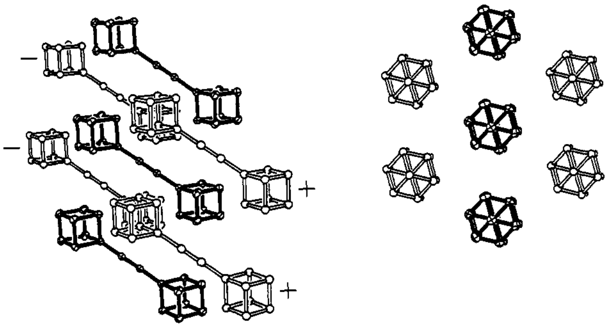


Figure 3. Arrangement of nearest neighbors about a central molecule of **15**. On the left, the molecules marked with a + and − are above and below the plane of the paper, respectively. At the right, the same assemblage is seen viewed end-on, illustrating the pseudohexagonal packing.

The estimated standard deviations for the individual atom structural parameters from the X-ray analysis of crystalline 1,4-dicubyl-1,3-butadiyne (**16**) are large (R = 0.109).[26] The imprecision is caused by a problem with overlapping data from stacked laminar twins. Several crystals were surveyed, and all appeared to twin, with both twin contributions about equal in weight. Once the twinning was recognized, it was possible to find reflections from each lattice and then to use data from just one lattice to obtain accurate lattice parameters. Intensity data

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[22] All diffraction experiments were performed at NRL on an automated Siemens diffractometer equipped with a Cu X-ray tube [λ(Cu Kα) = 1.541 84 Å] and an incident-beam graphite monochromator. Data for the analyses described below were collected at room temperature (T = 294 K). After every 97 reflection intensity measurements, three "standards" were recollected to monitor the stability of the crystal. All structures were solved and refined with the aid of the SHELXTL system of programs.[23]

[23] Sheldrick, G. M. *SHELXTL80. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Federal Republic of Germany, 1980.

[24] $C_{12}H_8$; FW = 152.2; monoclinic space group $P2_1/n$; a = 8.568(2), b = 7.247(2), c = 13.736(2) Å; β = 106.56(2)°; V = 817.5(2) Å^3; Z = 4; ρ_{calcd} = 1.236 mg mm^{-3}; μ = 0.530 mm^{-1}; $F(000)$ = 320. A translucent white 0.12 × 0.45 × 0.45 mm^3 crystal, in the shape of a parallelepiped was used. There were 1302 unique reflections, and 1175 were observed with $F_o > 3\sigma(F_o)$. R = 0.045 and R_w = 0.056.

[25] $C_{18}H_{14}$; FW = 230.3; triclinic space group $P1$; a = 5.390(2), b = 5.380(2), c = 10.211(3) Å; α = 84.12(2), β = 76.29(2), γ = 75.61(2)°; V = 278.4(1) Å^3; Z = 1; ρ_{calcd} = 1.374 mg mm^{-3}; μ = 0.585 mm^{-1}; $F(000)$ = 122. A clear colorless 0.03 × 0.15 × 0.50 mm^3 crystal, a thin plate, was used for data collection. There were 890 unique reflections, and 812 were observed with $F_o > 3\sigma(F_o)$. R = 0.042 and R_w = 0.052.

[26] $C_{20}H_{14}$; FW = 254.3; monoclinic space group $P2_1/c$; a = 5.396(3), b = 10.302(4), c = 11.606(3) Å; β = 90.89(3)°; V = 645.0(5) Å^3; Z = 2; ρ_{calcd} = 1.309 mg mm^{-3}; μ = 0.560 mm^{-1}; $F(000)$ = 268. A slightly cloudy, colorless, lath-shaped (0.05 × 0.20 × 0.50 mm^3) crystal was used. There were 923 unique reflections, and 710 were observed with $F_o > 3\sigma(F_o)$. R = 0.109 and R_w = 0.137.

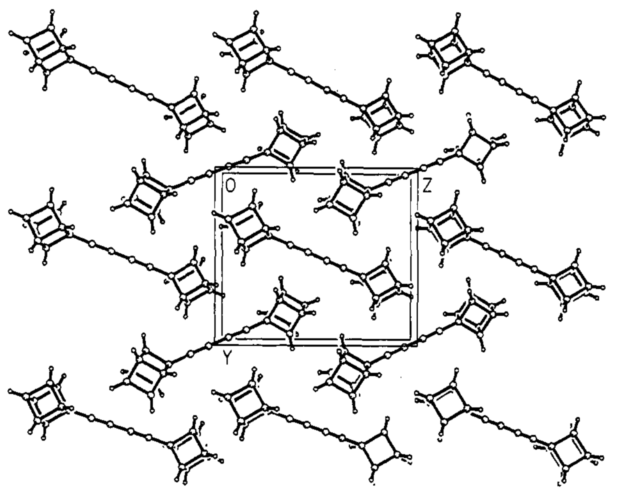


Figure 4. View down the axis of the full contents of the unit cell of **16**. The actual packing is not quite as simple. Molecules are tipped about 23° out of the *yz* plane to provide an alternation of height between all near-neighbor cubyl groups.

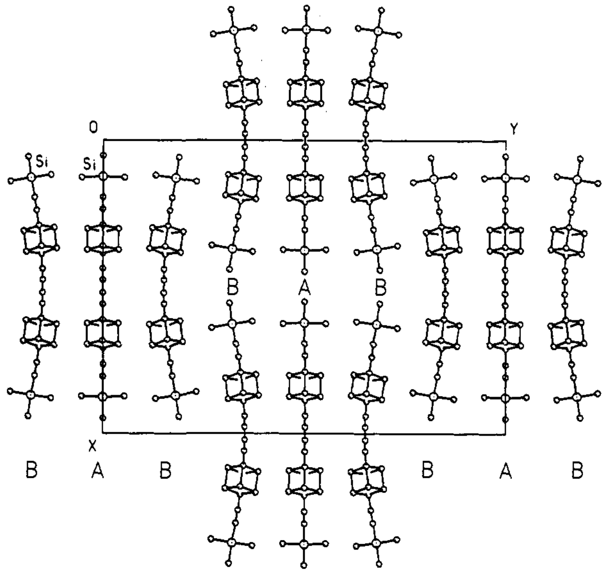


Figure 5. Crystal packing in **18**. Two chemically identical, but physically different types of molecules occur in this complex scheme. Molecules labeled A in the diagram (and in the supplementary tables) are strictly planar, lying on a 2/*m* symmetry site. Molecules labeled B are curved but still have a two-fold axis of symmetry in the plane of the paper, bisecting the central bond of the molecule. Each end of the B molecule is bent about 8° away from the direction of the central bond.

were collected from (as far as could be told) one of the two patterns. Such were sufficient to clearly indicate the molecular conformation and the packing in the crystal (Figure 4). However, there are large regions of space where the lattices of the two twins essentially overlap. The twinning is merohedral, with a twin rotation of 180° about the *a* axis of the unit cell.

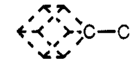
In the crystal of **18** there are two distinct molecules; one is straight (A) and one is bent (B, Figure 5).[27] In the asymmetric unit there are one quarter-molecule and one half-molecule (six total in the unit cell) distributed over two different types of sites. The quarter-molecule lies in a mirror plane at one of the 2/*m* sites (0.5, 0, 0.05); the half-molecule is bisected by a two-fold axis at (0.5, *y*, 0). Measurable X-ray data were sparse, due to tiny crystal size. To minimize the parameter-to-observation ratio, the cubane moieties were retrained to be rigid ideal cubes but allowed to vary in size. The cube edge refined to reasonable values of 1.552 Å in the A molecule and 1.546 Å in the B molecule. The overall lengths [Si to Si′] are 20.896 Å in the bent molecules and 21.010 Å in the straight molecules. In the bent ones the angle between a line drawn from the center to the Si atom and a line through the central bond is 8.2°. While both halves are equally curved, the curvature is not all in one plane. The atoms of one half-molecule curve within an (approximate) plane; those of the other half curve in a plane perpendicular to the first. Although each individual bond angle along the axis of B deviates less than 3° from a "straight-rod" value, the cumulative effect is substantial and is immediately apparent in the drawings.

Table 1. Tip-to-Tip (Carbon-to-Carbon) Distances in Å of Alkynylcubane Rods

	obsd	calcd[a]
12a	7.96[b]	7.93
15	9.50	9.42
16	12.08	11.80
18	17.36[c]	17.03

[a] Calculated using MM2 (PCmodel, Serena Software). [b] Average for two molecules in the crystal asymmetric unit. [c] For the straight molecule (see text).

Table 2. Modules[a] for Predicting Rigid-Rod Cubyl Assemblies

	2.72	Cubane body diagonal
	5.64	1,4-Disubstituted cubane
	1.46	Cubane-substituent bond
C≡C	1.19	Alkyne Triple Bond
≡C—C	1.41	Alkyne-substituent bond
C—≡—C	4.02	1,2-Disubstituted alkyne

[a] Distance (Å) between labeled atoms.

In each of the molecules analyzed the bond length between the cubyl carbon and the attached acetylenic carbon is significantly shorter (e.g., 1.439 Å in **12a**) than that of a typical sp^3–sp bond in tertiary aliphatic systems (e.g., 1.495 Å in *tert*-butylacetylene) but is essentially indistinguishable from that in the sp^2–sp bond of phenylacetylene systems. For a comparison, 86 examples of phenyl–ethynyl fragments in the crystal structure data base[28] were examined. Their average phenyl–ethynyl "single-bond" connection is 1.434 Å with a standard deviation of 0.009 Å, and the average triple-bond length is 1.192 Å ± 0.011 Å. The comparable bonds in **12a**, **15**, **16**, and **18** all fall within these ranges.

The experimental values of the extremal distances of alkynylcubane rods were compared (Table 1) with the values obtained from MM2 calculations. The agreement is good. Module values (Table 2) were obtained by averaging, for each bond, the experimental values available for alkynylcubanes and other cubane derivatives. These module values should prove useful in estimating the lengths of new and longer rods.

Rearrangement of Alkynylcubanes to Alkynylcyclooctatetraenes. Halpern, Cassar, and Eaton showed years ago that the cubane skeleton is readily invaded by Rh(I).[29] Oxidative addition is followed by rapid ring opening to the *syn*-tricyclooctadiene. The process is second-order and usually catalytic in Rh(I). In a subsequent step, independent of Rh(I), thermal rearrangement

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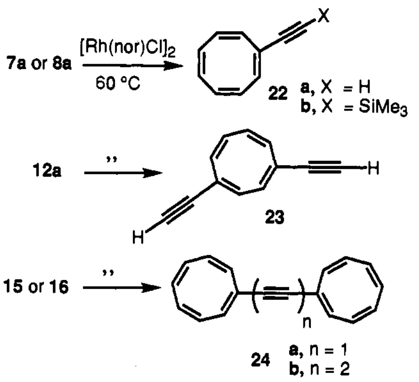
(27) $C_{30}H_{30}Si_2$; FW = 446.7; monoclinic space group *C*2/*m*; *a* = 21.069(5), *b* = 28.505(9), *c* = 6.690(2) Å; β = 95.52(2)°; *V* = 3999(2) Å^3; *Z* = 6; ρ_{calcd} = 1.113 mg mm^{-3}; μ = 1.299 mm^{-1}; *F*(000) = 1428. A clear, colorless, lath-shaped (0.03 × 0.04 × 0.46 mm^3) crystal was used. There were 2132 unique reflections, and 939 were observed with $F_o > 3\sigma(F_o)$. *R* = 0.085 and R_w = 0.076.

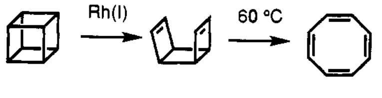
(28) Kennard, O.; Watson, D.; Allen, F.; Motherwell, W.; Town, W.; Rodgers, J. *J. Chem. Brit.* **1975**, *11*, 213.

(29) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515.

Scheme 9



of the tricyclooctadiene to the cyclooctatetraene occurs readily at 50–60 °C (eq 2).



This process has been shown to apply to numerous cubane derivatives.[5b,29] We have now found that it can be extended even to the opening of alkynylcubanes without disruption of the acetylene subunits. Treatment of alkynylcubanes **7a**, **8a**, **12a**, **15**, and **16** with $[Rh(norbornadiene)Cl]_2$ gave, ultimately, the alkynylcyclooctatetraenes **22a**,[9] **22b**,[9] **23**, **24a**,[9] and **24b**, respectively (Scheme 9). In a typical experiment $[Rh(norbornadiene)Cl]_2$ (2.5 mol %) was added to a solution of the alkynylcubane in $CDCl_3$ at room temperature, and the course of reaction was followed by NMR. Over time, the cubyl proton resonances at 4 ppm were replaced by absorptions at 2.8–3.6 and 6.0–6.7 ppm, characteristic of *syn*-tricyclooctadienes.[30] The rates of ring opening varied with substrate; 6–12 h were usually required for complete conversion at the concentrations employed.

As tricyclooctadienes are thermally labile, no attempt was made to characterize them further. Instead, their conversion to the corresponding cyclooctatetraenes was brought about by heating the solutions at 60 °C. Over a few hours, the proton signals at 2.8–3.6 and 6.0–6.7 ppm disappeared and were replaced by broad, diffuse resonances around 6 ppm, characteristic of cyclooctatetraenes (COTs). In most cases, the solutions turned dark and some brown precipitate formed. This might be a COT–rhodium complex(es).[31] Column chromatography afforded **22a**[9] (30%), **22b**[9] (88%), **23** (45%), **24a**[9] (62%), and **24b** (80%) as yellow oils that slowly decomposed. The spectroscopic data obtained for **22b** and **24a** are in agreement with the published data. Note that when ((trimethylsilyl)ethynyl)cubane (**8a**) was used as starting material, the reaction occurred without formation of a precipitate, and ((trimethylsilyl)ethynyl)cyclooctatetraene (**22b**) was obtained in particularly good yield. As with the ethynylcubanes, the trimethylsilyl derivatives of the ethynylcyclooctatetraenes are more stable than the corresponding terminal alkynes.

Such conversions of alkynylcubanes to alkynylcyclooctatetraenes complement the work of Eaton and Stössel and give access to alkynyl-bridged cyclooctatetraenes, for which there is precedent only in the Staley and Siesel synthesis.[9]

Experimental Section

Caution. *Most cubanes are quite stable kinetically. Nonetheless, as they are high-energy materials, it is prudent to run reactions thereof behind safety shields. Crude reaction mixtures should not be concentrated at elevated temperature, particularly in the presence of acidic or metallic contaminants.*

General Methods. NMR spectra were run in chloroform-*d* at ambient probe temperature unless otherwise noted: ^1H NMR at 400 MHz and referenced to internal tetramethylsilane (the spectra of trimethylsilyl derivatives were referenced to residual chloroform); ^{13}C NMR spectra at 100.6 MHz and referenced to the central line of the solvent. Proton chemical shifts are reported to a precision of ±0.01 ppm; coupling constants, to a precision of ±0.1 Hz. Carbon chemical shifts are reported to a precision of ±0.1 ppm. FT-IR spectra were obtained at a digital resolution of 1 cm^{-1}. Low-resolution mass spectra (70 eV, EI) were obtained on eluates from a OV-17-coated (0.25-mm film) capillary column; major ions are reported to unit mass (intensity parenthetically as a percentage of the strongest peak above m/z 40). High resolution mass spectra were recorded on a VG Analytical 70-70E double-focusing mass spectrometer. Thin-layer chromatography was carried out on 0.25-mm Polygram silica gel plates using UV light and/or 10% ethanolic phosphomolybdic acid as developing agents. Merck silica gel 60 (230–400 mesh) was used for column chromatography. THF was distilled from sodium benzophenone ketyl; CH_2Cl_2, pyridine, and triethylamine, from CaH_2 under nitrogen. 2-Cyclohexen-1-one was dried over molecular sieves and fractionally distilled. Dry DMSO (Aldrich) was used without further purification. CBr_4 was sublimed. *N*-bromosuccinimide was crystallized from water and dried under vacuum. Air- and/or moisture-sensitive reactions were performed under nitrogen or argon using glassware flamed under vacuum. "Standard workup" refers to extraction with an organic solvent, washing of the extract with saturated brine, drying over Na_2SO_4, and removal of solvents *in vacuo* on a rotary evaporator. The bath was kept at room temperature.

Iodocubane (1).[32] Ethylmagnesium bromide (24 mmol, 8 mL of a 3 M solution in ether) was added to a solution of 1,4-diiodocubane[33a] (2.1 g, 6.1 mmol) in THF (100 mL). This solution was cooled to −78 °C (dry ice/acetone bath), whereupon a large amount of precipitate appeared. *n*-Butyllithium (25 mmol, 10 mL of a 2.5 M solution in hexane) was added dropwise. The reaction mixture turned into a clear, yellow solution. The solution was stirred at −78 °C for 5 min; then the reaction was quenched with MeOH (20 mL). The cooling bath was removed. The solution was refluxed with NaOMe (15 mL of a 25% solution in MeOH) for 2 h, then cooled with an ice bath, diluted with pentane, and acidified with 1 N HCl. After standard workup with pentane, column chromatography with pentane afforded **1** (1.2 g, 91%) as colorless low-melting crystals. The spectroscopic data of **1** are in agreement with the values reported in literature.[33b]

3-Cubylcyclohexanone (3a). The reaction was run under argon. The temperature was monitored using a glass-enclosed thermocouple in the solution. *tert*-Butyllithium (0.5 mmol, 0.3 mL of a 1.7 M solution in pentane) was added dropwise to a stirred solution of iodocubane[32] (54 mg, 0.2 mmol) in THF (4 mL) at −75 °C (dry ice/acetone bath) and the mixture stirred at −75 °C for 30 min. Lithium 2-thienylcyanocuprate[12] (0.2 mmol, 0.9 mL of a 0.25 M solution in THF, Aldrich) was added dropwise. The temperature was held between −72 and −75 °C. The orange solution so obtained was stirred for 10 min, and then 2-cyclohexen-1-one (0.2 mmol, 21 mg) in THF (1 mL) was added dropwise. The mixture was stirred at −78 °C for 30 min, and then, while the solution was cold, the reaction was quenched with MeOH. The cooling bath was removed, and saturated aqueous NH_4Cl (ca. 50 mL) was added. After standard workup using ether, column chromatography (ether/pentane, 1/1 v/v) afforded **3a**, which crystallized on evaporation of the solvent (42 mg, 91%). Crystallization from ether/hexanes afforded white, flat crystals: mp 95–97 °C; ^1H NMR δ 4.04 (m, 1H, cubyl), 3.84 (m, 6H), 2.30 (m, 3H), 2.10 (m, 1H), 2.00 (m, 2H), 1.8 (m, 1H), 1.3 (m, 1H) ppm; ^{13}C NMR δ 212.4, 61.5, 48.5, 46.4, 43.9, 41.5, 41.4, 41.0, 25.2, 24.6 ppm; IR ν (KBr) 2970, 2945, 2930, 2849, 1710 cm^{-1}; MS m/z 200 (M^+, 1),

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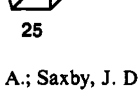
[30] Two isomers, **25** and **26**, can arise from rearrangement of **7a**; only one was found. It was isolated and identified as **25**, as its ^1H NMR spectrum shows only three olefinic protons and the ^{13}C DEPT spectrum shows that only one of the four vinyl carbons is quaternary.



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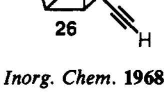

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[31] Bennett, M. A.; Saxby, J. D. *Inorg. Chem.* **1968**, *7*, 321.

[32] This procedure was developed in this laboratory by Y. S. Xiong.

[33] (a) Eaton, P. E.; Tsanaktsidis, J. *Tetrahedron Lett.* **1989**, *30*, 6967. (b) Moriarty, R. M.; Khosronshahi, J. S.; Penmasta, R. *Tetrahedron Lett.* **1989**, *30*, 791.

171 (4), 167 (2), 141 (35), 129 (100), 115 (65), 103 (61), 91 (63), 78 (65); HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1180.

((Trimethylsilyl)ethynyl)cubane (3b). The reaction was run under argon. The temperature was monitored using an internal thermocouple. *tert*-Butyllithium (0.51 mmol, 0.30 mL of a 1.7 M solution in pentane) was added dropwise to a stirred solution of iodocubane (58 mg, 0.2 mmol) in THF (5 mL) at –78 °C (dry ice/acetone bath) and the mixture stirred at this temperature for 20 min. The temperature was kept between –72 and –75 °C as lithium 2-thienylcyanocuprate (0.2 mmol, 1.0 mL of a 0.25 M solution in THF, Aldrich) was added dropwise. Solid phenyl((trimethylsilyl)ethynyl)iodonium triflate[14] (**2**, 120 mg, 0.2 mmol) was added in one portion (the temperature rose to –68 °C). The mixture was stirred at –78 °C for 2 h, and then, while the mixture was still cold, the reaction was quenched with MeOH. The cooling bath was removed, and saturated aqueous NH_4Cl (ca. 50 mL) was added. After standard workup with ether, column chromatography (ether/pentane, 15/85 v/v) afforded **3b**, which was crystallized from pentane to give small white needles (15 mg, 30%): mp 98–100 °C; ^{1}H NMR δ 4.09 (m, 3H, cubyl), 3.95 (m, 4H, cubyl), 0.17 (s, 9H, Me_3Si) ppm; ^{13}C NMR δ 106.5, 93.0, 51.8, 47.9, 44.9, 0.2 ppm; IR ν (KBr) 2954, 2918, 2850, 2149, 1462, 1373, 1265, 854, 842 cm^{-1}; MS *m/z* 200 (M$^+$, 4), 185 (78), 170 (33), 159 (79), 155 (33), 141 (30), 131 (34), 127 (5), 107 (100), 78 (67), 73 (22). Anal. Calcd for $C_{13}H_{16}Si$: C, 77.93; H, 8.05. Found: C, 78.13; H, 8.09.

Cubanecarboxaldehyde (5a). This procedure is a modification of the procedure reported in literature.[34] Dry DMSO (3.5 mL, 50 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a stirred solution of oxalyl chloride (2.3 mL, 25 mmol) in CH_2Cl_2 (20 mL) at –78 °C. A solution of cubanecarbinol[34] (2.8 g, 21 mmol) in CH_2Cl_2 (30 mL) was added slowly with stirring. The mixture was stirred at –78 °C for 1.5 h. Triethylamine (13 mL, 92 mmol) was added dropwise. The cooling bath was removed; the mixture, once at room temperature, was stirred for 10 min, and then the reaction was quenched with water (30 mL). After standard workup with CH_2Cl_2 the crude was transferred to the top of a silica column. Elution with CH_2Cl_2 gave an oil, which was further purified by column chromatography (pentane/CH_2Cl_2, 50/50 v/v) to afford **5a**, sufficiently pure that it crystallized when the solvent was removed (1.9 g, 69%): ^{1}H NMR δ 9.72 (s, 1H, C(O)H), 4.39 (m, 3H, cubyl), 4.03 (m, 4H, cubyl) ppm; ^{13}C NMR δ 198.29, 62.62, 48.13, 47.66, 45.25 ppm; IR ν (NaCl) 2986, 2799, 2707, 1698; MS *m/z* 131 (5), 105 (10), 103 (100), 77 (70).

Cubane-1,4-dicarboxaldehyde (10). The reaction was run in a flask equipped with a mechanical stirrer. DMSO (2.0 mL, 28 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a solution of oxalyl chloride (0.58 mL, 6.6 mmol) in CH_2Cl_2 (7 mL) at –78 °C. 1,4-Bis(hydroxymethyl)cubane[34] (0.50 g, 3.0 mmol), dissolved in 7 mL of a mixture of DMSO and THF (1/6 v/v), was added slowly. The reaction mixture was stirred for 1.5 h at –15 to –20 °C (ice/acetone bath) and then cooled to –78 °C; triethylamine (2.8 mL, 20 mmol) was added dropwise. The cooling bath was removed. The mixture was stirred at room temperature for 10 min, and then the reaction was quenched with water (10 mL). After standard workup with CH_2Cl_2 column chromatography (pentane/ether, 60/40 v/v) followed by crystallization from hexanes afforded **10** as white crystals (0.32 g, 65%): mp 133–135 °C; ^{1}H NMR δ 9.76 (s, 2H, C(O)H), 4.40 (s, 6H, cubyl) ppm; ^{13}C NMR δ 197.2, 62.7, 45.9 ppm; IR ν (NaCl) 2991, 2914, 2843, 1686 cm^{-1}; MS *m/z* 160 (M$^+$, 2), 131 (11), 103 (100), 77 (94). Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.74; H, 5.04.

1-Iodo-4-(hydroxymethyl)cubane (4b). BH_3·THF complex (16 mmol, 16 mL of a 1.0 M THF solution) was added dropwise at room temperature to a stirred solution of 4-iodo-1-carbomethoxycubane[32] (1.0 g, 3.6 mmol) in THF (10 mL) under nitrogen. The solution was stirred for 5 h and then cooled to 0 °C, and the reaction was quenched cautiously with water. After standard workup with AcOEt the white solid obtained was crystallized from hexanes to afford **4b** as white crystals (0.8 g, 87%): mp 108–110 °C; ^{1}H NMR δ 4.22 (m, 3H, cubyl), 4.06 (m, 3H, cubyl), 3.79 (s, 2H, CH_2), 1.18 (s, 1H, OH) ppm; ^{13}C NMR δ 63.2, 59.0, 54.7, 47.8, 38.8 ppm; IR ν (NaCl) 3321(b), 2991, 2974, 2913, 1191, 1029 cm^{-1}; MS *m/z* 260 (M$^+$, 2), 204 (7), 165 (21), 152 (30), 127 (10), 115 (39), 103 (80), 77 (100).

1-Iodocubane-4-carboxaldehyde (5b). This was prepared as described using 1-iodo-4-(hydroxymethyl)cubane (**4b**, 1.3 g, 5.0 mmol), oxalyl chloride (0.55 mL, 6.0 mmol), dry DMSO (3.0 mL, 42 mmol), and triethylamine (6.0 mL, 43 mmol). Purification by column chromatography (CH_2Cl_2) and crystallization from hexanes afforded 1.0 g of **5b** as white crystals and a second crop of 90 mg (84% total): dec above 130 °C; ^{1}H NMR δ 9.75 (s, 1H, C(O)H), 4.52 (m, 3H, cubyl), 4.30 (m, 3H, cubyl) ppm; ^{13}C NMR δ 197.0, 62.7, 54.8, 49.0, 35.6 ppm; IR ν (NaCl) 2996, 2842, 1679 cm^{-1}; MS *m/z* 258 (M$^+$, 36), 231 (28), 204 (57), 152 (16), 130 (21), 103 (80), 77 (100).

(2,2-Dibromovinyl)cubane (6a). Triphenylphosphine (1.2 g, 4.5 mmol) was added in small portions to a solution of CBr_4 (0.76 g, 2.3 mmol) in CH_2Cl_2 (10 mL) at room temperature; the orange solution was stirred for 15 min, and then a solution of **5a** (0.28 g, 2.1 mmol) in CH_2Cl_2 (6 mL) was added dropwise. The reaction, monitored by TLC (CH_2Cl_2), was complete after 10 min. Water (10 mL) was added, the organic layer was separated, and after standard workup with CH_2Cl_2 (3 × 10 mL) the solid residue was transferred to the top of a silica gel chromatography column. Elution with pentane/CH_2Cl_2 (50/50 v/v) afforded a beige solid, which was further purified by column chromatography (pentane) to afford **6a** (0.55 g, 82%) as a colorless solid: mp 31–32 °C; ^{1}H NMR δ 6.77 (s, 1H, $CH{=}BR_2$), 4.19 (m, 3H, cubyl), 3.97 (m, 4H, cubyl) ppm; ^{13}C NMR δ 139.3, 88.3, 58.1, 51.1, 47.3, 44.8 ppm; IR ν (NaCl) 2981, 1572, 804 cm^{-1}; MS *m/z* 290 (1), 288 (M$^+$, 2), 286 (1), 209 (12), 207 (12), 128 (100), 102 (13), 78 (10); HRMS calcd for $C_{10}H_8Br_2$ (^{79}Br^{81}Br) 287.8972, found 287.8966. As the compound is labile, it was stored in the refrigerator in pentane solution.

1,4-Bis(2,2-dibromovinyl)cubane (11). This was prepared as described using **10** (0.30 g, 1.9 mmol), triphenylphosphine (2.2 g, 8.4 mmol), and CBr_4 (1.3 g, 4.0 mmol). The crude was transferred to the top of a silica gel chromatography column. Elution with CH_2Cl_2 afforded a beige solid. Further chromatography (CH_2Cl_2/pentane, 20/80 v/v) followed by crystallization from hexanes afforded **11** as thick, colorless, square crystals (0.74 g, 84%): dec above 125 °C; ^{1}H NMR δ 6.77 (s, 2H, $CH{=}CBr_2$), 4.14 (s, 6H, cubyl) ppm; ^{13}C NMR δ 138.6, 89.1, 57.7, 48.3 ppm; IR ν (NaCl) 3020, 2981, 807 cm^{-1}; MS *m/z* 474 (1), 472 (M$^+$, 2), 470 (1), 393 (13), 312 (31), 262 (10), 231 (20), 195 (5), 152 (100), 115 (10); HRMS calcd for $C_{12}H_8Br_4$ (^{79}Br^{81}Br) 471.7319, found 471.7329. Anal. Found: C, 31.22; H, 1.62; Br, 67.11.

1-Iodo-4-(2,2-dibromovinyl)cubane (6b). This was prepared as described using **5b** (0.88 g, 3.4 mmol), triphenylphosphine (1.7 g, 5.0 mmol), and CBr_4 (0.45 g, 1.3 mmol). The crude was transferred to the top of a silica gel chromatography column. Elution with CH_2Cl_2 afforded an off-white solid. Further chromatography (CH_2Cl_2/pentane, 50/50 v/v) gave pale-yellow crystals. Crystallization from hexanes afforded **6b** (0.95 g, 67%) as white crystals: mp 118–120 °C; ^{1}H NMR δ 6.77 (s, 1H, $CH{=}Br_2$), 4.33 (m, 3H, cubyl), 4.26 (m, 4H, cubyl) ppm; ^{13}C NMR δ 137.6, 89.9, 58.6, 54.8, 51.7, 36.7; IR ν (KBr) 3022, 3005, 2981, 1192, 1023, 788 cm^{-1}; MS *m/z* 415 (42), 414 (M$^+$, 8), 413 (100), 287 (33), 208 (11), 127 (67), 101 (21).

Ethynylcubane (7a). *n*-Butyllithium (0.7 mmol, 0.3 mL of a 2.5 M solution in hexanes) was added dropwise under nitrogen to a solution of (2,2-dibromovinyl)cubane (**6a**, 0.11 g, 0.3 mmol) in THF (5 mL) cooled at –78 °C. The mixture was stirred at –78 °C for 1 h, then the mixture was quenched with MeOH, and the solution was warmed to room temperature. Afterward, 4 mL of 5% hydrochloric acid was added, the organic layer was separated, and the aqueous layer was extracted with pentane (2 × 10 mL). The organic extract was washed with 5% hydrochloric acid and then with brine, and the solvent was removed *in vacuo* by flash distillation. Column chromatography (pentane) afforded **7a** as colorless crystals (37 mg, 85%): mp 43–45 °C; ^{1}H NMR δ 4.09 (m, 3H, cubyl), 3.98 (m, 4H, cubyl), 2.80 (s, 1H $\equiv$CH) ppm; ^{13}C NMR δ 84.4, 76.6, 51.3, 48.0, 45.1 ppm; IR ν (NaCl) 3294, 2986, 2925, 2855, 2100 cm^{-1}; MS *m/z* 128 (M$^+$, 13), 127 (100), 102 (90), 78 (75). Anal. Calcd for $C_{10}H_8$: C, 93.71; H, 6.29. Found: C, 93.26; H, 6.35.

1,4-Diethynylcubane (12a).[8] This was prepared as described using **11** (0.24 g, 0.5 mmol) and *n*-butyllithium (2.0 mmol, 0.8 mL of a 2.5 M solution in hexanes). Purification by column chromatography (CH_2Cl_2) afforded **12a** as a white solid (73 mg, 95%). Crystallization from hexanes afforded **12a** as colorless, thick needles which decompose without melting above 160 °C: ^{1}H NMR δ 4.05 (s, 6H, cubyl), 2.81 (s, 2H $\equiv$CH) ppm; ^{13}C NMR δ 83.3, 77.4, 48.7, 45.8 ppm; IR ν (NaCl) 3292, 3282, 3007, 2987, 2096, 1203 cm^{-1}; MS *m/z* 152 (M$^+$, 14), 151 (87), 126 (29), 102 (100), 76 (27); HRMS calcd for $C_{12}H_8$ 152.0626, found 152.0604. Anal. Calcd for $C_{12}H_8$: C, 94.70; H, 5.30. Found: C, 94.21; H, 5.45.

(4-Iodocubyl)acetylene (7b). This was prepared as described using **6b** (0.63 g, 1.5 mmol) and methyllithium (5.2 mmol, 3.70 mL of a 1.4 M solution in ether). Column chromatography (CH_2Cl_2/pentane, 50/50 v/v) and crystallization from pentane afforded **7b** as thick colorless crystals

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(34) Chen, N.; Jones, M., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981.

(35) Eaton, P. E.; Yip, Y. C. *J. Am. Chem. Soc.* **1991**, *113*, 7692.

(0.35 g, 90%) which decompose without melting above 125 °C: ^{1}H NMR δ 4.24 (m, 6H, cubyl), 2.86 (s, 1H ≡CH) ppm; ^{13}C NMR δ 82.63, 78.56, 54.86, 51.97, 46.19, 36.40 ppm; IR ν (KBr) 3288, 2988, 2985, 2101, 1195, 1031 cm^{-1}; MS *m/z* 254 (M$^+$, 2), 228 (6), 204 (19), 127 (100), 126 (84), 102 (21), 101 (31), 77 (69). Particular care should be taken with this compound; a crude sample detonated when touched with a spatula.

((Trimethylsilyl)ethynyl)cubane (8a = 3b). The glassware was flame-heated under vacuum. The reaction was run under nitrogen. *n*-Butyllithium (2.7 mmol, 1.1 mL of a 2.5 M solution in hexanes) was added dropwise to a solution of **6a** (0.39 g, 1.4 mmol) in THF (3 mL) cooled at −78 °C. The mixture was stirred at −78 °C for 1 h, and then Me$_3$SiCl (0.2 mL, 1.5 mmol) was added. The cooling bath was removed, and the solution was stirred at −10 to −15 °C (ice/acetone bath) for 15 min. Afterward, 20 mL of 2 N hydrochloric acid was added along with pentane. After standard workup with pentane and column chromatography (pentane), crystallization from pentane afforded white crystals (25 mg, 91%). The spectroscopic data are identical to those of an authentic sample of **3b** (see above).

1,4-Bis((trimethylsilyl)ethynyl)cubane (12b).[8] This was prepared as described using 1,4-bis(2,2-dibromovinyl)cubane (**11**, 1.0 g, 2.2 mmol), *n*-butyllithium (5.1 mmol, 4.0 mL of a 2.5 M solution in hexanes), and Me$_3$SiCl (0.6 mL, 5.1 mmol). Column chromatography (CH$_2$Cl$_2$/pentane, 30/70 v/v) and crystallization (ether/pentane) afforded thin, flat colorless crystals of **12b** (60 mg, 92%): mp 174–175 °C; ^{1}H NMR δ 4.02 (s, 6H, cubyl), 0.16 (s, 18H, Me$_3$Si) ppm; ^{13}C NMR δ 105.42, 93.85, 49.16, 10.11, 0.15 ppm; IR ν (NaCl) 2996, 2963, 2145, 1249, 838 cm^{-1}; MS *m/z* 296 (M$^+$, 34), 281 (43), 265 (11), 223 (15), 207 (17), 183 (15), 159 (58), 107 (14), 73 (100).

1-(4-Iodocubyl)-2-(trimethylsilyl)acetylene (8b).[8] This was prepared as described using 4-iodo-1-(2,2-dibromovinyl)cubane (**6b**, 0.7 g, 1.7 mmol), methyllithium (3.5 mmol, 2.5 mL of a 1.4 M solution in ether), and Me$_3$SiCl (0.7 mL, excess). Column chromatography (CH$_2$Cl$_2$/pentane, 40/60 v/v) and crystallization (hexanes) afforded **8b** (0.46 g, 82%): mp 168–170 °C; ^{1}H NMR δ 4.23 (s, 6H, cubyl), 0.17 (s, 9H, Me$_3$Si) ppm; ^{13}C NMR δ 104.4, 95, 54.8, 52.5, 46.9, 36.6, 0.09 ppm; IR ν (NaCl) 2998, 2949, 2154, 1249, 1200, 840 cm^{-1}; MS *m/z* 326 (M$^+$, 14), 311 (14), 265 (8), 263 (8), 204 (50), 199 (63), 183 (73), 169 (61), 159 (100), 115 (28), 73 (71); HRMS calcd for C$_{13}$H$_{15}$SiI 325.9988, found 325.9990.

Dicubyl Ketone (14). A solution of cubyllithium in THF was prepared in advance by adding *tert*-butyllithium (10 mmol, 5.8 mL of 1.8 M solution in pentane) to a solution of cubyl iodide (1.2 g, 5.0 mmol) in THF (20 mL) cooled at −78 °C. Separately, EtMgBr (4 mmol, 1.3 mL of a 3.0 M solution in THF) was added to a stirred solution of cubanecarboxylic acid (**13**, 0.6 g, 4.0 mmol) in THF (20 mL) cooled to −10 to −15 °C (ice/acetone bath). The solution was stirred for 30 min at −10 to −15 °C. Then the previously prepared solution of cubyllithium was added by cannula. The resulting solution was kept at 0 °C overnight, then cooled at −78 °C, and poured over finely crushed dry ice. After the dry ice had evaporated, 3 N hydrochloric acid (20 mL) was added to the remaining solid. The aqueous layer was extracted with CH$_2$Cl$_2$ (4 × 20 mL). The organics were combined and extracted with aqueous 10% NaOH (4 × 20 mL). The organic layer was dried over MgSO$_4$, and the solvent was removed *in vacuo*. Column chromatography (CHCl$_3$) afforded **14** (0.77 g, 82% yield) as a white solid: mp 175–177 °C; ^{1}H NMR δ 4.31 (m, 6H), 4.02 (m, 8H) ppm; ^{13}C NMR δ 206.2, 62.6, 49.6, 47.7, 45.1 ppm; IR ν (NaCl) 2980, 1643, 1219 cm^{-1}; MS *m/z* 234 (5), 215 (7), 202 (11), 191 (14), 178 (13), 165 (15), 152 (6), 141 (9), 128 (20), 115 (14), 103 (100), 77 (98). Anal. Calcd for C$_{17}$H$_{14}$: C, 87.15; H, 6.02. Found: C, 86.94; H, 5.97.

Dicubylacetylene (15). *n*-Butyllithium (2.1 mmol, 0.8 mL of a 2.5 M solution in hexanes) was added dropwise to a stirred solution of (trimethylsilyl)diazomethane (2.1 mmol, 1.0 mL of a 2.0 M solution in hexanes, Aldrich) in THF (7 mL) cooled at −78 °C. The solution was stirred for 5 min, and then dicubyl ketone (**14**, 0.33 g, 1.4 mmol) in THF was added dropwise at −78 °C. The mixture was stirred at −78 °C for 1.5 h, and then the reaction was quenched with MeOH. The cooling bath was removed, and the mixture was allowed to warm to room temperature and then filtered. The off-white solid so collected was washed with pentane, then dissolved in hot chloroform, and crystallized by slow cooling to room temperature over 24 h to afford **15** as flat, light, colorless crystals (0.17 g, 52%) which decompose above 180 °C: ^{1}H NMR δ 4.07 (m, 6H), 3.95 (m, 8H) ppm; ^{13}C NMR δ 89.4, 52.3, 48.3, 46.7, 44.9 ppm; IR ν (KBr) 3001, 2993, 2983, 1218, 842 cm^{-1}; MS *m/z* 230 (M$^+$, 49), 228 (75), 202 (67), 152 (100), 115 (28); HRMS calcd for C$_{18}$H$_{14}$ 230.1095, found 230.1039. Anal. Calcd for C$_{18}$H$_{14}$: C, 93.87; H, 6.13. Found: C, 93.12; H, 6.18.

1,4-Dicubyl-1,3-butadiyne (16). DBU (3 μL, 5 mol %) and CuBr (3 mg, 5 mol %) were added to a stirred solution of ethynylcubane (**7a**, 53 mg, 0.41 mmol) in pyridine (3 mL). Oxygen was bubbled into the mixture for 2 h. Ice-cold 6 N hydrochloric acid was added. A standard workup with chloroform was used, but the extract was boiled with decolorizing charcoal and then filtered through a short pad of silica gel before the solvent was removed *in vacuo*. This gave **16** (40 mg, 75%) as a white solid which decomposes above 140 °C: ^{1}H NMR δ 4.10 (m, 3H), 3.96 (m, 4H) ppm; ^{13}C NMR δ 80.7, 73.4, 51.6, 48.1, 45.9, 45.2 ppm; IR ν (KBr) 2976, 2141, 1959, 1215, 842 cm^{-1}; MS *m/z* 254 (M$^+$, 37), 252 (100), 226 (21), 176 (71), 150 (33), 126 (30), 77 (17); HRMS calcd for C$_{20}$H$_{14}$ 254.1095, found 254.1055. Anal. Calcd for C$_{20}$H$_{14}$: C, 94.45; H, 5.55. Found: C, 93.90; H, 5.59.

1-((Trimethylsilyl)ethynyl)-4-ethynylcubane (17). MeLi·LiBr complex (1.4 mmol, 1.0 mL of a 1.5 M solution in ether, Aldrich) was added over 20 min to a stirred solution of 1,4-bis((trimethylsilyl)ethynyl)cubane (**12b**, 0.40 g, 1.3 mmol) in THF (7 mL) at 5–10 °C. The mixture was stirred at that temperature for 5 more min and then was poured into ice-cold 3 N hydrochloric acid (100 mL). After standard workup with CH$_2$Cl$_2$ column chromatography (CH$_2$Cl$_2$/pentane, 10/90 v/v) afforded **17** (0.10 g, 33%) as a white solid: mp 153–154 °C; ^{1}H NMR δ 4.01 (m, 6H, cubyl), 2.77 (s, 1H, ≡CH), 0.14 (s, 9H, Me$_3$Si) ppm; ^{13}C NMR δ 105.3, 93.9, 83.4, 77.2, 49.3, 48.6, 46.7, 45.7 ppm; IR ν (NaCl) 3288, 2988, 2149, 1251, 838 cm^{-1}; MS *m/z* 224 (M$^+$, 2), 209 (14), 193 (15), 183 (21), 181 (19), 165 (43), 159 (100), 155 (21), 129 (10), 102 (78), 77 (19). Some starting material (44%) and 1,4-diethynylcubane (7%) were also isolated from the chromatography.

1,4-Bis((trimethylsilyl)ethynyl)cubyl-1,3-butadiyne (18). DBU (3 μL, 5 mol %) and CuBr (1 mg, 2 mol %) were added to 1-((trimethylsilyl)ethynyl)-4-ethynylcubane (**17**, 85 mg, 0.38 mmol) dissolved in pyridine (2 mL). Oxygen was bubbled in; within minutes an abundant precipitate formed. The mixture was stirred overnight at room temperature with continuing introduction of oxygen, and then the mixture was added to ice-cold 3 N hydrochloric acid. Standard workup with chloroform gave a beige solid, which was purified by column chromatography (CHCl$_3$/pentane, 60/40 v/v) to afford a white solid. Slow evaporation of a CHCl$_3$ solution thereof afforded light, thin, off-white needles (74 mg, 87% yield) of **18** which decompose slowly above 160 °C: ^{1}H NMR δ 4.01 (s, 12H, cubyl), 0.14 (s, 18H, Me$_3$Si) ppm; ^{13}C NMR δ 105.0, 94.0, 79.9, 73.6, 49.3, 48.9, 46.6, 0.1 ppm; IR ν (KBr) 2995, 2956, 2144, 1253, 839 cm^{-1}; HRMS calcd for C$_{30}$H$_{30}$Si$_2$ 446.1886, found 446.1881.

1-(Bromoethynyl)-4-((trimethylsilyl)ethynyl)cubane (19). MeLi·LiBr complex (0.93 mmol, 0.62 mL of a 1.5 M solution in ether, Aldrich) was added over 20 min to a stirred solution of 1,4-bis((trimethylsilyl)ethynyl)cubane (**12b**, 0.25 g, 0.9 mmol) in THF (4 mL) at 10–15 °C. The mixture was stirred at that temperature for 5 more min and then cooled to −78 °C, and NBS (0.34 g, 1.9 mmol) was added in one portion. The mixture was stirred at −78 °C for 30 min and at 0–4 °C for 16 h, and then the reaction was quenched with water. After standard workup with CH$_2$Cl$_2$ column chromatography (CH$_2$Cl$_2$/pentane, 10/90 v/v), followed by crystallization from hexanes afforded **19** as small white crystals (46 mg, 44%) which decompose above 145 °C: ^{1}H NMR δ 4.00 (s, 6H, cubyl), 0.14 (s, 9H, Me$_3$Si) ppm; ^{13}C NMR δ 105.2, 94.1, 79.3, 49.3, 48.6, 48.2, 46.9, 46.7, 0.14 ppm; IR ν (KBr) 2987, 2965, 2142, 1246, 845 cm^{-1}; HRMS calcd for C$_{15}$H$_{15}$Si^{79}Br 302.0126, found 302.0119, calcd for C$_{15}$H$_{15}$Si^{81}Br 304.0126, found 304.0108. On one occassion this material exploded; use shields! Some starting material (46%) and 1,4-bis(bromoethynyl)cubane (5%) were also isolated from the chromatography.

1-(4-((Trimethylsilyl)ethynyl)cubyl)-4-cubyl-1,3-butadiyne (21). *The ethynylcopper derivative of cubane **20** might be particularly hazardous. Use a shield*! *n*-Butyllithium (0.49 mmol, 0.19 mL of a 2.6 M solution in hexanes) was added to a stirred solution of ethynylcubane (63 mg, 0.49 mmol) in THF (5 mL) at −78 °C. The mixture was stirred for 20 min, and then the dry ice/acetone bath was replaced with an ice bath. CuBr (71 mg, 0.49 mmol) was added in one portion. The resulting mixture was stirred vigorously at room temperature in the dark for 20 min. A bright-yellow precipitate formed. Most of the volatiles were removed *in vacuo*, but complete dryness was carefully avoided (no heat!). The residue was taken up in pyridine (2 mL), and **19** (0.15 g, 0.49 mmol) was added in one portion at room temperature. The resulting mixture was stirred vigorously at 40–50 °C for 2.5 h and then cooled to room temperature, and the reaction was quenched by addition of ice-cold 6 N hydrochloric acid (50 mL). The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (3 × 5 mL). The organics were combined, washed with 6 N hydrochloric acid and then brine, and dried over $MgSO_4$. The solvents were removed *in vacuo*. Column chromatography (CH_2Cl_2/pentane, 15/85 v/v) afforded 67 mg of **21** and 33 mg of **18**. Crystallization from hexanes afforded **21** (50 mg, 30% from **19**) as white small crystals which slowly decompose above 150 °C: ^{1}H NMR δ 4.08 (m, 3H, cubyl), 4.01 (m, 6H, cubyl), 3.94 (m, 4H, cubyl), 0.14 (s, 9H, Me_3Si) ppm; ^{13}C NMR δ 105.1, 94.0, 81.0, 79.6, 74.0, 73.2, 51.6, 49.3, 49.0, 48.1, 46.7, 46.3, 45.8, 45.2, 0.1 ppm; IR ν (KBr) 2993, 2981, 2141, 1247, 840 cm^{-1}; HRMS calcd for $C_{25}H_{22}Si$ 350.1491, found 350.1479.

General Procedure for the Preparation of Alkynylcyclooctatetraenes (22a, 22b, 23, 24a, and 24b) from Alkynylcubanes (7a, 8a, 12a, 15, and 16). Norbornadienerhodium(I) chloride dimer ([Rh(nor)Cl]$_2$) was dissolved at room temperature in a stirred solution of the alkynylcubane in $CDCl_3$ (2 mL). The solution was deoxygenated by several freeze–pump–thaw cycles. The stirred solution, under nitrogen, was heated in an oil bath at 60 °C. When the signals of the starting material and disappeared (NMR monitoring of aliquots), the mixture was cooled to room temperature and then washed with CH_2Cl_2 through a pipet containing silica gel mixed with polymer-supported PPh_3 (Fluka, 200–300 mesh, 3 mmol of PPh_3/g of resin). The solvent was removed *in vacuo*, and the oily residue was purified by column chromatography (CH_2Cl_2/pentane, 50/50 v/v) to afford the product as a yellow oil. The ultraviolet absorption spectrum of each COT was obtained from the eluate of a high-performance liquid chromatographer monitored by a fast-response, diode spectrometer. The spectroscopic data of **22a**, **22b**, and **24a** are in agreement with the values reported by Staley and Siesel.[9]

Ethynyl-1,3,5,7-cyclooctatetraene (22a).[9] Thirty milligrams (33%) was obtained by the above procedure from 100 mg of **7a** and 5 mol % catalyst: ^{1}H NMR δ 6.35–6.00 (b, 1H, COT), 6.00–5.70 (b, 6H, COT), 2.73 (s, 1H, $\equiv$CH) ppm; ^{13}C NMR (−50 °C) δ 139.4, 132.8, 132.7, 131.7, 131.4, 130.7, 130.3, 123.6, 83.5, 75.1 ppm; IR ν (KBr) 3288, 3003, 2958, 2927, 2093, 1675, 1127–1001 cm^{-1}; UV λ 240, 300 nm; MS *m/z* 128 (M$^+$, 100), 102 (23), 78 (16); HRMS calcd for $C_{10}H_8$ 128.0626, found 128.0618.

1-((Trimethylsilyl)ethynyl)-1,3,5,7-cyclooctatetraene (22b).[9] Forty-four milligrams (88%) was obtained by the above procedure from 50 mg of **8a** and 5 mol % catalyst: ^{1}H NMR δ 6.35–6.00 (b, 1H, COT), 6.00–5.70 (b, 6H, COT), 0.15 (s, 9H, Me_3Si) ppm; ^{13}C NMR (−50 °C) δ 138.9, 132.7, 132.5, 131.7, 131.5, 131.0, 130.5, 124.9, 104.6, 91.8, 0.2 ppm; IR ν (KBr) 3006, 2958, 2143, 1249, 1153, 1100–1001, 842, 659 cm^{-1}; UV λ 240, 300 nm; MS *m/z* 200 (M$^+$, 48), 185 (100), 169 (19), 159 (23), 141 (17), 129 (13), 115 (150), 107 (31), 77 (24). HRMS calcd for $C_{13}H_{16}Si$ 200.1021, found 200.1030.

1,4-Diethynyl-1,3,5,7-cyclooctatetraene (23). Forty-five milligrams (45%) was obtained by the above procedure from 100 mg of **12a** and 45 mg of catalyst (15 mol %): ^{1}H NMR δ 6.25–6.15 (b, 2H, COT), 6.00–5.75 (b, 4 H, COT), 2.86 (s, 2H, $\equiv$CH) ppm; ^{13}C NMR (−50 °C) δ 138.9, 137.4, 132.1, 131.4, 132.3, 130.6, 124.6, 123.4, 83.1, 83.0, 76.6, 75.9 ppm; IR ν (KBr) 3291, 3013, 2092, 1331–1140, 1143, 858, 653 cm^{-1}; UV λ 240, 310 nm; MS *m/z* 152 (M$^+$, 11), 151 (100), 126 (16), 102 (30), 87 (5), 76 (17); HRMS calcd for $C_{12}H_8$ 152.0626, found 152.0608.

Dicyclooctatetraenylacetylene (24a).[9] Twenty-five milligrams (62%a) was obtained by the above procedure from 40 mg of **15** and 2.5 mol % of catalyst: ^{1}H NMR δ 6.25–5.60 (b, 14H); ^{13}C NMR (−50 °C) δ 138.0, 137.9, 132.6, 132.3, 131.7, 131.4, 130.9, 130.6, 128.2, 124.6, 87.2; IR (KBr) 3005, 2961, 2924, 2850, 2178, 1726, 1674, 1261, 1100–976, 810, 659 cm^{-1}; UV λ 230, 260, 320 nm; MS *m/z* 228 (M$^+$, 99), 215 (36), 202 (36), 189 (15), 151 (100), 139 (7), 126 (22), 115 (32), 101 (18), 76 (13); HRMS calcd for $C_{18}H_{14}$ 230.1096, found 230.1089.

1,4-Dicyclooctatetraenyl-1,3-butadiyne (24b). Twenty-four milligrams (80%) was prepared by the above procedure from 30 mg of **1** and 2.0 mol % of catalyst: ^{1}H NMR δ 6.25–5.70 ppm (b, 14H); ^{13}C NMR (−50 °C) δ 140.89, 133.16, 133.09, 131.61, 131.46, 130.29, 129.83, 123.77, 81.29, 71.37 ppm; IR ν (KBr) 3006, 2962, 2925, 2202, 1725–1631, 1132–1023, 807, 657 cm^{-1}; UV λ 240, 340 nm; MS *m/z* 254 (M$^+$, 50), 252 (100), 250 (15), 239 (9), 176 (59), 150 (24), 126 (11), 115 (4), 76 (9); HRMS calcd for $C_{20}H_{14}$ 254.1095, found 254.1080.

1-Ethynyltricyclooctadiene (25). [Rh(nor)Cl]$_2$ (5 mol %) was added, under nitrogen, to a stirred room-temperature solution of ethynylcubane (0.21 g) in $CHCl_3$ (2 mL) which had been degassed by the freeze–pump–thaw technique. The solution was stirred at room temperature under nitrogen for 3 h, at which time the reaction was judged complete by NMR examination of an aliquot. The solution was washed through a pipet containing polymer-supported PPh_3 and silica gel using CH_2Cl_2. The solvent was removed *in vacuo*. The oily residue was purified by column chromatography (CH_2Cl_2/pentane, 50/50 v/v), affording a yellow oil (60 mg): ^{1}H NMR δ 6.31 (d, 1H, J = 2.4 Hz), 6.08 (t, 1H, J_1 = 2.4 Hz, J_2 = 0.8 Hz), 599 (t, 1H, J = 2.4 Hz), 3.19 (m, 2H), 3.13 (m, 1H), 2.98 (m, 1H), 2.97 (s, 1H) ppm; ^{13}C NMR δ 141.4, 136.4, 136.2, 126.8 (quaternary), 78.7 (quaternary), 78.2 (quaternary), 42.4, 39.7, 39.4, 36.7 ppm.

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Supplementary Material Available: Single-crystal X-ray experimental details, data, labeled drawing, coordinates, and bond lengths and angles for compounds **12a**, **15**, **16**, and **18** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.