Synthetic and Computational Studies of Silametacyclophanes: Macrocyclic Cage Compounds

William R. Kwochka,† Robert Damrauer,*,† Michael W. Schmidt,‡ and Mark S. Gordon‡

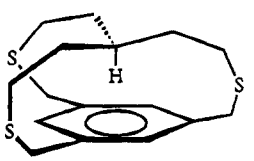
Chemistry Department, University of Colorado at Denver, P.O. Box 173364, Denver, Colorado 80217-3364, and Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

Received June 24, 1994®

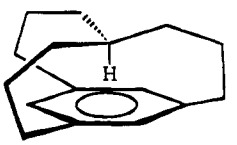
Multiple Pd(0)-catalyzed coupling reactions of 9-borabicyclo[3.3.1]nonane (9-BBN) adducts of allylsilanes and bromobenzenes are used to prepare several unusual silametacyclophanes. Reaction of the 9-BBN adduct of dimethyldiallylsilane and 1,3-dibromobenzene gives 4-dimethyl-4-sila[7]metacyclophane in 32% yield, while reaction of the 9-BBN adduct of methyltriallylsilane and 1,3,5-tribromobenzene leads to 4-methyl-4-sila[$3^{4,10}$][7]metacyclophane in 4% yield. NMR data are presented to help characterize these compounds. Computational studies of the cyclophanes HE[$-$Y$-$(CH$_2$)$_n-$]$_3$C$_6$H$_3$ for E = C, Si, Y = CH$_2$, O, and n = 2, 3 reveal various important factors in stabilizing compounds with H at E inside the cage. These include that the macrocycle be large enough to accommodate the EH bond and that the EH bond be polarized so that its H atom is positive when directed toward the π cloud of the benzene ring. Even the small n = 2 macrocycles are only moderately strained at both E and the benzene base.

Introduction

Ricci and co-workers reported the synthesis of several novel sulfur-containing macrocycles in 1976.[1] In 1987, Pascal and co-workers reported NMR studies demonstrating clearly that one of these, compound **1**, had a



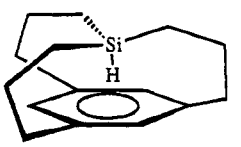
1



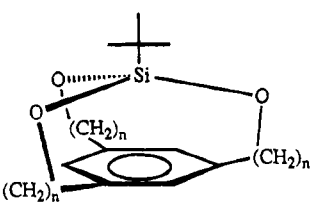
2

hydrogen located inside the cage structure (^{1}H NMR signal of the methine H at δ -1.68).[2a] X-ray analysis of the trisulfone corresponding to **1** shows that its hydrogen is located inside the macrocycle as well.[2b] Hydrocarbon **2**, which was prepared by thermal SO$_2$ extrusion from this trisulfone, has a proton NMR signal at δ -4.03. Its methine CH stretching frequency is increased about 400 cm^{-1} due to its inside location. Molecular mechanics calculations (MM2)[2c] on **2** confirm an energetic preference (of an unspecified magnitude) for hydrogen in the interior of the cage. Sulfur-containing macrocycles with fewer methylenes than **1** can also be prepared by direct ring closure, indicating that these smaller macrocycles also have an energetic preference for the inside hydrogen isomer.[2d]

We have been interested in whether silicon analogs of cage structures such as **2** will prefer hydrogen on the inside or the outside of the cage.[3] This paper reports on synthetic studies directed toward the preparation of **3** (H on Si in or out) and on a computational study that



3 (H on Si can be in or out)



4 (where n = 2, 3, 9)

addresses the in–out isomerization question more generally. The synthetic work builds on previous studies in which we were able to prepare the silicon-containing cages **4** with n = 2, 3, or 9.[3]

Results and Discussion

Synthetic Studies. The preparation of cages **4** with n = 2, 3, and 9 was carried out by metal-catalyzed cyclotrimerization of various tripod triynes, *i*-Bu$-$Si[$-$O$-$(CH$_2$)$_n-$C$\equiv$CH]$_3$.[3] One of the unfavorable consequences of this synthetic approach was that the cyclotrimerization gave both 1,2,4- and 1,3,5-isomers of benzene. Not only were these difficult to separate but

† University of Colorado at Denver.
‡ Iowa State University.
® Abstract published in *Advance ACS Abstracts,* August 15, 1994.

(1) Ricci, A.; Danieli, R.; Rossini, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1691–1693.

(2) (a) Pascal, R. A., Jr.; Grossman, R. B. *J. Org. Chem.* **1987**, *52*, 4616–4617. (b) Pascal, R. A., Jr.; Grossman, R. B.; Van Engen, D. *J. Am. Chem. Soc.* **1987**, *109*, 6878–6880. (c) Pascal, R. A., Jr.; Winans, C. G.; Van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 3007–3010. (d) L'Esperance, R. P.; West, A. P.; Van Engen, D.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 2672–2676.

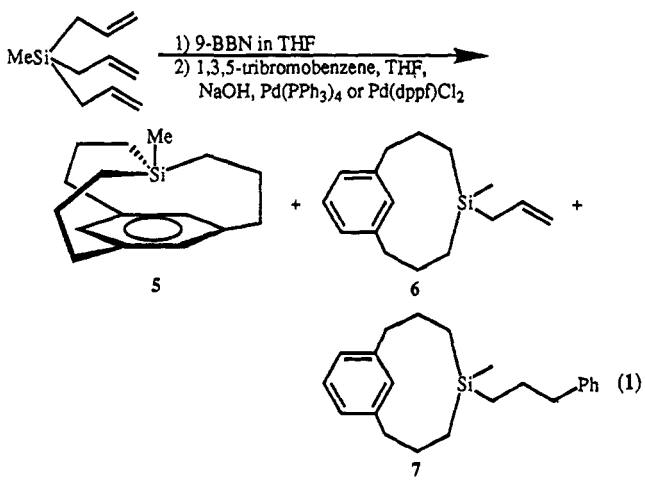
(3) (a) Damrauer, R.; Hankin, J. A.; Haltiwanger, R. C. *Organometallics* **1991**, *10*, 3962–3964. (b) Hankin, J. A.; Howe, R. W.; Damrauer, N. H.; Peterson, K. A.; Bruner, S. J.; Damrauer, R. *Main Group Met. Chem.* **1994**, *17*, 391.

0276-7333/94/2313-3728$04.50/0

the desired 1,3,5-isomers were obtained in low yields. As a result we have undertaken a different synthetic approach in which the cage structure is closed from a fragment already possessing a 1,3,5 benzene orientation. Our approach is the first application of multiple Pd(0)-catalyzed coupling reactions of silicon-containing boranes and aryl bromides (Suzuki coupling[4]) for the preparation of silametacyclophane ring structures.

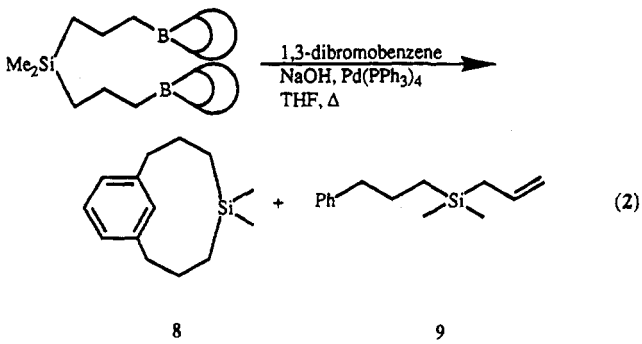
The synthesis of small, strained cyclophanes has intrigued chemists for many years because the forced proximity of atoms leads to unusual chemical and physical properties.[5] We have been interested in the effect of placing silicon atoms in strained cyclic molecules for some time.[6] The synthetic approach reported here seeks to use the Suzuki reaction[4] to couple a three-legged borane intermediate derived from a triallylsilane to 1,3,5-tribromobenzene to form a silicon analog of Pascal's hydrocarbon **2**[2b] in a single step. By having the reactive electrophilic centers already in place, we seek to maintain absolute regiocontrol of addition, thereby avoiding formation of 1,2,4-isomers, which were so problematic in the cyclotrimerization reactions.[3]

This strategy has been successfully applied to the synthesis of **5** from the tris(9-borabicyclo[3.3.1]nonane) (9-BBN) adduct of methyltriallylsilane and 1,3,5-tribromobenzene (eq 1). Competing with formation of cage



5 are **6** (1–2%), which results from an intramolecular coupling of two legs of the silane and a β-elimination of the third leg, and **7** (5%), whose origin is unknown. A number of attempts were made to vary conditions to increase the yield of **5**. The only effect on its yield came by undertaking coupling reactions using $Pd(dppf)Cl_2$, a Pd(0) catalyst that has been reported to minimize β-elimination.[7] The yield of **5** could be increased from 1 to 4% without appreciably affecting that of **6** or **7**. In these attempts, no other products in appreciable amounts could be detected by gas or flash chromatography. It is likely that large amounts of polymers formed in these reactions, but no attempt was made to isolate or characterize these.

Coupling of the bis-9-BBN adduct of diallyldimethylsilane and 1,3-dibromobenzene in the presence of $Pd(PPh_3)_4$ and K_3PO_4 produced the 10-membered silametacyclophane **8** in 10% isolated yield.[8] Replacing K_3PO_4 by NaOH increased the yield of **8** to 32% (eq 2).



Compound **9** (4%) (resulting from β-elimination) also was isolated from the reaction mixture. Surprisingly, neither 1,2- nor 1,4-dibromobenzene yielded the corresponding silacyclophanes under similar conditions.

Compounds **5** and **8**, which were characterized by ^1H, ^{13}C, and ^{29}Si NMR, mass spectral, ultraviolet, infrared, and elemental analysis, show some of the expected NMR diamagnetic anisotropic effects caused by benzene ring currents but by no means present a clear picture.[5,9] In cage molecule **5**, we observe that its Si–CH_2's are shifted upfield relative to those of **8** (Si–CH_2: **5**, ^1H 0.25 ppm, ^{13}C 10.8 ppm; **8**, ^1H 0.81 ppm, ^{13}C 16.6 ppm), although the ^{29}Si shift in **5** is only 1.61 ppm upfield of that in **8** (**5**, ^{29}Si 1.93 ppm; **8**, ^{29}Si 3.54 ppm). The CH_3 in **5**, which is outside the cage (it will not fit inside) and far from the π-electron density of the ring, exhibits a larger than expected upfield ^1H shift but no discernible upfield ^{13}C shift (Si–CH_3: **5**, ^1H −0.41 ppm, ^{13}C 9.9 ppm; **8**, ^1H −0.71 ppm, ^{13}C −0.80 ppm). The silametacyclophane **8** has ^1H and ^{13}C chemical shifts at −0.71 and −0.80 ppm, respectively, for its Si–CH_3 group. The center methylene protons in the closely related [7]-metacyclophane have a −0.18 ppm ^1H chemical shift (no ^{13}C results have been reported), which is believed to result from facile dynamic conformational processes that place these hydrogens in "averaged environments" above the benzene π cloud.[5,8] In the silametacyclophane **8**, the ^1H and ^{13}C shifts are also likely to be the result of such dynamic effects. Thus, although we expected that compound **5**, because it is more constrained than **8**,

(4) (a) Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419–422. (b) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314–321. (c) Miyaura, N.; Ishiyama, T.; Suzuki, A. *Tetrahedron Lett.* **1986**, *27*, 6369–6372.

(5) (a) *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vols. I, II. This is a fine general reference for a variety of aspects of cyclophane chemistry. (b) Vögtle, F. *Cyclophane Chemistry: Synthesis, Structures, and Reactions*; Wiley: Chichester, U.K., 1993. This is a new work encompassing both older and recent cyclophane chemistry. (c) Diederich, F. *Cyclophanes*; Monograph in Supramolecular Chemistry; Royal Society of Chemistry: Cambridge, U.K., 1991. This monograph concentrates on guest–cyclophane complexation and molecular recognition.

(6) (a) Damrauer, R. *Organomet. Chem. Rev. A* **1972**, *8*, 67–133. (b) Damrauer, R.; Davis, R. A.; Burke, M. T.; Karn, R. A.; Goodman, G. T. *Organomet. Chem.* **1972**, *43*, 121–125. (c) Damrauer, R.; Burke, M. T.; Karn, R. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1068–69. (d) Damrauer, R.; Simon, R.; Laporterie, A.; Manuel, G.; Part, Y. T.; Weber, W. P. *J. Organomet. Chem.* **1990**, *391*, 7–12.

(7) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158–163.

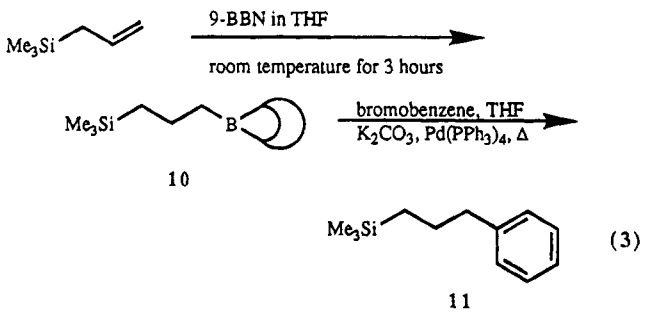
(8) For a discussion of carbon [*n*]cyclophanes closely related to **8**, see: Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219–2227. See also ref 5.

(9) General comments about diamagnetic anisotropic effects in silametacyclophanes are difficult to make since the silametacyclophane reported by Pascal and co-workers in ref 3d and those reported by Sekiguchi and co-workers (Sekiguchi, A.; Yatabe, T.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 757–758) are structurally more complex than **5**.

would exhibit more pronounced ring current effects at room temperature, we find that the NMR behavior of the two compounds is not simply interpreted.

Ultraviolet spectra of [*n*]meta- and [*n*]paracyclophanes have revealed that bathchromic shifts and loss of fine structure accompany decreasing *n*.[5,8] These effects are believed to result from distortions from benzene planarity as the ring size decreases. A comparison of the ultraviolet spectral characteristics of **5** and **8** may suggest some distortion in benzene planarity in **5**. Thus, although the 13 nm difference between these compounds may be nothing more than an alkyl-substitution effect, the dramatic lack of fine structure of the shoulder peaks of **5** is consistent with a more distorted benzene ring. We would like to confirm this by single-crystal X-ray analysis but have thus far been unable to grow suitable crystals of **5**.

Prior to the work reported in eqs 1 and 2, we studied the efficiency of Suzuki coupling for simpler silane model systems by forming **10**, as illustrated in eq 3. Its



(3)

introduction into a solution of bromobenzene, K_3PO_4, and $Pd(PPh_3)_4$ in refluxing THF provided **11** in 74% yield. A similar coupling with the 9-BBN adduct of allyldimethylsilane failed, presumably because of Pd(0) insertion into the Si—H bond.[10] Thus, a direct synthesis of the silicon analog **3** (in or out) cannot be carried out from triallylsilane. Work is in progress to prepare the unsubstituted isomer(s?) **3**.

We have also demonstrated that 1,3,5-tribromobenzene can be alkylated with 3 equiv of the alkylborane **10** to give a mixture of compounds closely related to the triply substituted aromatic compound 1,3,5-tris(3-(trimethylsilyl)propyl)benzene. We believe that this compound is initially formed but is unstable to the reaction conditions, undergoing a series of trimethylsilyl group migrations along the alkyl chain (elimination of $(CH_3)_3SiH$ followed by hydrosilylation)[11] to give a 36% yield of five quite similar isomers, which have identical molecular ions and nearly identical fragmentation patterns by GCMS analysis.

Computational Studies. The purpose of our computational study is twofold: (1) to confirm by *ab initio* calculation the remarkable structure of compound **2** and (2) to examine the factors that control the preference of hydrogen for inside versus outside orientation.

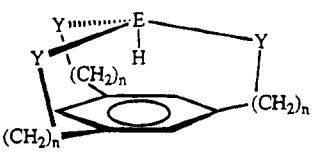
Table 1 presents the results of the computations on compounds **12** for E = C, Si, Y = CH_2, O, and *n* = 2, 3. The first line in this table corresponds to Pascal's hydrocarbon **2**. The computations agree with experiment, the inside isomer being preferred by about 13 kcal/mol. Replacement of E = C by Si, however, causes the hydrogen to prefer an outside orientation by a large amount, 43 kcal/mol. The well-studied silatranes[11] differ from the outside isomer with E = Si, Y = O, and *n* = 2 only in that the basal benzene ring is replaced by a nitrogen atom. This suggested that we replace the methylenes adjacent to silicon in the silacyclophane by oxygens. Indeed, we have prepared E = Si, Y = O, *n* = 2 and determined the X-ray structure of this compound with an outside *tert*-butyl group.[3b] However, oxygen substitution destabilizes both E = C and Si inside isomers by about 29 kcal/mol. This is sufficient to make even the E = C isomer prefer an outside geometry. Consideration of the Si—H bond lengths and the geometry changes caused by using the slightly smaller oxygen atom suggested that increasing the macrocycle's size might afford more room for the long Si—H bond. Accordingly, we expanded the rings by adding one methylene group so that *n* = 3. The hydrocarbon (E = C) prefers the inside orientation position by 18 kcal/mol, 5 kcal/mol more than for **2**. Ring expansion has a much larger effect on the silacyclophane. Although the outside geometry is still preferred, the inside isomer is predicted to be only about 3 kcal/mol less stable. Thus,

Table 1. Total (hartree) and Relative Energies (kcal/mol) for the Cyclophanes 12, with Geometric Data[a]

E	Y	*n*	hydrogen	6-31G(d) energy, hartree	Δ*E*, kcal/mol 6-31G(d)	Δ*E*, kcal/mol AM1
C	CH_2	2	inside	−618.640 736	−12.9	−3.3
C	CH_2	2	outside	−618.620 189	0	0
Si	CH_2	2	inside	−869.664 674	+42.8	+36.1
Si	CH_2	2	outside	−869.732 914	0	0
C	CH_2	3	inside	−735.790 035	−18.4	−13.6
C	CH_2	3	outside	−735.760 694	0	0
Si	CH_2	3	inside	−986.837 533	+2.6	+2.1
Si	CH_2	3	outside	−986.841 742	0	0
C	O	2	inside	−726.077 388	+16.5	+23.7
C	O	2	outside	−726.103 618	0	0
Si	O	2	inside	−977.217 362	+71.4	+55.3
Si	O	2	outside	−977.331 071	0	0

E	Y	*n*	hydrogen	*r*(EH), Å	Δz, Å	HEY angle, deg	YEY angle, deg	opb, deg
C	CH_2	2	inside	1.044	1.703	103.9	114.4	22.5
C	CH_2	2	outside	1.080		100.6	116.7	20.3
Si	CH_2	2	inside	1.381	1.661	97.1	118.5	20.0
Si	CH_2	2	outside	1.495		100.9	116.5	16.0
C	CH_2	3	inside	1.071	2.116	108.2	110.7	8.5
C	CH_2	3	outside	1.086		104.2	114.2	15.6
Si	CH_2	3	inside	1.445	2.128	104.6	113.8	10.1
Si	CH_2	3	outside	1.491		107.5	111.4	12.8
Si	O	2	inside	1.350	1.546	101.4	116.2	24.9
Si	O	2	outside	1.470		107.5	111.4	21.1
***t*-BuSi**	**O**	**2**	**outside**			**108.9**	**109.9**	**24**
C	O	2	inside	1.030	1.585	107.6	111.3	27.1
C	O	2	outside	1.084		107.8	111.1	25.8

[a] Δz is the distance from H to the ring center, and opb is an out-of-plane bend, described in the text.



12 (H on E can be in or out) (n = 2, 3)

(10) Ojima, I. In *The Chemistry of Functional Groups: The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25.
(11) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1–147.

expanding the ring size by one methylene per methylene chain stabilizes the inside isomer by 40 kcal/mol. The relative energies computed using the semiempirical AM1 method are presented in Table 1. They demonstrate that the simple AM1 model is capable of qualitatively reproducing the RHF/6-31G(d) energetics.

Table 1 also contains the RHF/6-31G(d) structural results. The most important geometric parameter is of course the location of the hydrogen inside the macrocycle. In **2** this hydrogen lies 1.70 Å from the center of the benzene ring (given by Δz in Table 1). This C—H bond is compressed 3.3% relative to the outside isomer. Replacement of E = C by Si gives a structure in which the H is pushed slightly closer to the ring (1.66 Å) and has its Si—H bond compressed 0.11 Å (7.6%) compared to that of the outside isomer. Use of the smaller Y = O instead of Y = CH_2 gives even shorter distances to the ring center (Δz = 1.6 Å). This is no doubt too close and results in the 29 kcal/mol destabilization of the inside isomer noted above. Expansion of the ring to n = 3 places the hydrogen about 2.1 Å above the benzene for E = C or Si. Note that in the n = 3 compound the inside Si—H bond is compressed only 0.05 Å (3.1%) compared to the outside orientation.

Although the expansion of the macrocycle affords sufficient room to accommodate an inside hydrogen, the E = Si, Y = CH_2, n = 3 system still prefers an outside geometry. A simple explanation of this is based on the relative electronegativities of C and Si. The C—H bond is ordinarily polarized so that the H is slightly positive, whereas the reverse is true of the Si—H bond. Thus, it is energetically preferable for the hydrogen lying above the benzene π cloud to be slightly positive. The present computations show that relief of ring strain alone, via adoption of four-atom side chains, gives an inside isomer only 2.6 kcal/mol less stable than the outside form. It is thus possible that a synthesis of this system would yield a mixture of isomers.

The strain in these cyclophanes is illustrated by the final three columns of Table 1. For two of the E = C cases, the angles around E show that the inside isomers more nearly achieve the ideal tetrahedral angles, while both Y = O isomers deviate equally from tetrahedral geometry. For E = Si, the outside isomers are more nearly tetrahedral at E. However, the angles at E are not as revealing with regard to the macrocycle's strain as the column labeled "opb" in Table 1. This angle is the out-of-plane angle between the methylene carbon bonded to the benzene and the plane of the three closest carbons in the benzene. It would be 0° in an unstrained benzene but is as large as 27° in the smallest macrocycle. We have obtained[3a] X-ray structures for the outside isomers E = Si, Y = O, n = 2, 3. The angles between methylene and the average benzene plane are 24 and 6°, respectively. The first value is in good agreement with the opb value found here and is presented in Table 1 as well. Note that the decrease in opb as the side-chain length is increased is much larger for the inside than for the outside isomers, whether E = C or Si. This out-of-plane bend and the angles at E are surprising, in that they show less strain than we might intuitively expect. In fact, the n = 3 hydrocarbon's inside orientation is nearly strain free, as shown by r(CH), the angles at E, and the angles at the benzene base.

Pascal and co-workers have reported a silacyclophane with an inside hydrogen.[2d] It has a complex structure with four atoms in each side chain, including sulfur atoms located as in **1**. The two carbon atoms between sulfur and the capping silicon in each chain are members of benzene rings. Of course, their steric bulk forces these benzene rings outside the macrocycle, in turn forcing the hydrogen to adopt an inside orientation. The calculations presented here imply that the use of four-atom side chains to provide space for the Si—H bond as well as the large bulk of these external benzenes to ensure overcoming the unfavorable dipole interactions are important in producing this type of compound.

Experimental and Computational Methods

All reagents were purified prior to use. Pd(dppf)Cl_2 was prepared by a known route.[7] Alkylchlorosilanes were distilled from CaH_2. Anhydrous THF was obtained by distillation from Na/benzophenone. 9-BBN was titrated using Brown's method.[12] All reactions were performed in flame-dried glassware under an inert atmosphere of argon. ^{1}H and ^{13}C NMR were obtained on either an IBM NR 80 MHz or a Bruker 400 MHz NMR, and ^{29}Si NMR, on a Varian VXR 300S. Infrared spectra were obtained on a Beckman IR-33. Ultraviolet spectra were recorded on a Perkin-Elmer Model 552A UV—visible spectrophotometer. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph using a 30 m J + W Scientific SE-30 fused silica capillary column. GCMS analyses were carried out on a Hewlett-Packard 5895B GCMS system. Flash chromatography was performed on silica gel 60 (230—400 mesh ASTM) obtained from Baxter Scientific. The aluminum-backed TLC plates used were cut from sheets of Whatman AL AIL G/UV plates. Visualization of the TLC plates was done by dipping the plate in 10% phosphomolybdic acid/ethanol and heating with a heat gun. Melting points were taken using a Laboratory Devices MEL-TEMP apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

Preparation of Triallylmethylsilane. This compound was prepared in 88% isolated yield by a known procedure.[13,14] ^{1}H NMR (80 MHz, acetone-d_6): δ 6.34 (m, 3 H), 5.64 (m, 6 H), 2.34 (m, 6 H), 0.69 (s, 3 H). ^{13}C NMR (20 MHz, acetone-d_6): δ 135.7, 114.2, 21.8, −5.7.

General Preparation of 9-Borabicyclo[3.3.1]nonane (9-BBN) Adducts of Allylsilanes. To a 50 mL round-bottom flask was added 25 mL of 0.3 M 9-BBN (7.51 mmol) in THF. The solution was stirred at room temperature for a short time before the appropriate allylsilane (2.42 mmol for triallylsilane) was rapidly added. The reaction mixture was stirred at room temperature for 3—4 h before use.

Preparation of 4-Methyl-4-sila[3^{4,10}][7]metacyclophane (5), 4-(2-Propenyl)-4-methyl-4-sila[7]metacyclophane (6), and 4-(3-Phenylpropyl)-4-methyl-4-sila[7]metacyclophane (7). The alkylborane above was cannulated into a 250 mL, three-necked round-bottom flask equipped with a condenser which contained 0.76 g of 1,3,5-tribromobenzene (2.42 mmol), 53 mg of Pd(dppf)Cl_2 (0.073 mmol), and 0.24 g of dry NaOH pellets (6.05 mmol) in 100 mL of THF, and this mixture was refluxed for a period of 8—12 h. The mixture was poured into 100 mL of hexanes and extracted with 1 M HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). Following drying ($MgSO_4$) and solvent removal, the crude material was filtered through a plug of silica gel with hexanes.

(12) Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.
(13) Grummitt, O.; Budewitz, E. P.; Chudd, C. C. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, pp 748—752.
(14) Zhun', V. I.; Tsvetkov, A. L.; Sheludyakov, V. D.; Lavygin, I. A.; Leitan, O. V.; Chalbysheva, N. V.; Bochkarev, V. N.; Slyusarenko, T. F. *Zh. Obshch. Khim.* **1988**, *58*, 1599—1606.

The products were isolated by flash column chromatography on 10% $AgNO_3$-impregnated silica gel with 2% Et_2O/98% hexanes. The chromatographic separation was followed by TLC. After concentration, the products were dissolved in hexanes, filtered through a plug of Florisil to remove silver salts, and isolated by solvent removal.

4-Methyl-4-sila[3^{4,10}][7]metacyclophane (5) was obtained as a white solid in 4% isolated yield (mp (uncorrected) 120–122 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 [s, 3 H], 2.50 [br s, 6 H], 1.68 [br s, 6 H], 0.25 [Br s, 6H], −0.41 [s, 3 H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 143.4, 127.6, 36.7, 26.1, 10.8, 9.9. ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ 1.93. IR (CCl_4): 3110, 3060, 2969, 2820, 1600 (s), 1560, 1450, 1400, 1155 cm^{-1}. UV (hexanes): λ_{max} (log ϵ) 190 (3.89), 251 nm (2.82). MS: *m/z* 229 (M − CH_3, 28%), 216 (M − C_2H_4, 100%). Anal. Calcd for $C_{16}H_{24}Si$: C, 78.61; H, 9.89. Found: C, 78.43; H, 10.04.

4-(2-Propenyl)-4-methyl-4-sila[7]metacyclophane (6) was obtained as an oil in 1–2% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 [m, 2 H], 6.95 [dd, J = 7.47, 1.45 Hz, 2 H], 5.62 [m, 1 H], 4.70 [m, 2 H], 2.73 [ddd, J = 12.82, 5.63, 3.33, 2 H], 2.54 [dt, J = 12.35, 3.57, 2 H], 2.00 [m, 2 H], 1.45 [m, 2 H], 1.07 [d, J = 8.10 Hz, 2 H], 0.92 [dd, J = 15.45, 9.52 Hz, 2 H], 0.68 [ddd, J = 15.57, 11.58, 1.37 Hz, 2 H], 0.11 [s, 3 H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 141.7, 135.9, 129.7, 129.5, 125.6, 112.4, 37.9, 27.4, 26.8, 14.6, −7.1. IR (neat): 3020, 2970, 2870, 2800, 1570, 1370, 1350, 1185 cm^{-1}. UV (hexanes): λ_{max} (log ϵ) 194 (3.73), 253 (2.69), 261 (2.61), 271 nm (2.23). MS: *m/z* 229 (M − CH_3, 100%), 203 (M − allyl, 91%).

4-(3-Phenylpropyl)-4-methyl-4-sila[7]metacyclophane (7) was obtained as an oil in 5% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.17 [m, 7 H], 6.99 [dd, J = 7.45, 1.22 Hz, 2 H], 2.77 [ddd, J = 12.84, 5.99, 3.40 Hz, 2 H], 2.64–2.54 [m, 4 H], 2.01 [m, 2 H], 1.57–1.46 [m, 4 H], 0.92 [dd, J = 15.29, 9.39 Hz, 2 H], 0.75 [dd, J = 14.49, 11.32 Hz, 2 H], 0.14 [m, 2 H], −0.96 [s, 3 H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.8, 141.6, 129.6, 129.3, 128.4, 128.1, 125.5, 125.4, 40.0, 37.8, 26.6, 26.1, 18.7, 14.8, −6.6. IR (neat): 3040, 3000, 2920, 2890, 2790, 1560, 1435, 1395, 1190, 1100 cm^{-1}. UV (hexanes): λ_{max} (log ϵ) 193 (3.93), 253 (3.05), 264 (3.02), 278 nm (2.93). MS: *m/z* 322 (M$^+$, 1%), 307 (M − CH_3, 15%), 203 (M − $CH_2)_3$Ph, 100%).

Preparation of 4,4-Dimethyl-4-sila[7]metacyclophane (8) and 7-phenyl-4,4-dimethyl-4-silahept-1-ene (9). The metacyclophane **8** was prepared and isolated from diallyldimethylsilane and 1,3-dibromobenzene using the method reported above.

4,4-Dimethyl-4-sila[7]metacyclophane (8) was obtained as an oil in 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 [m, 2 H], 6.94 [dd, J = 1.7, 7.4 Hz, 2 H], 2.63 [m, 4 H], 1.74 [m, 4 H], 0.81 [m, 4 H], −0.71 [s, 6 H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 141.8, 129.7, 129.4, 125.6, 37.9, 26.8, 16.6, −0.8. ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ 3.54. IR (neat): 3120, 3090, 3010, 2980, 1620, 1590, 1560, 1490, 1470, 1260, 840 cm^{-1}. UV (log ϵ) λ_{max} (hexanes): 203 (3.33), 246 (2.63), 238 (2.62), 255 (2.60), 262 (2.52), 270 nm (2.21). MS: *m/z* 218 (M$^+$, 3%), 203 (M − CH_3, 100%), 190 (M − C_2H_4, 67%). Anal. Calcd for $C_{14}H_{22}Si$: C, 76.98; H, 10.16. Found: C, 77.00; H, 10.12.

7-Phenyl-4,4-dimethyl-4-silahept-1-ene (9) was obtained as an oil in 2% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 [m, 2 H], 7.34 [m, 3 H], 5.95 [m, 1 H], 5.02 [m, 2 H], 2.80 [t, J = 7.63 Hz, 2 H], 1.81 [m, 2 H], 1.69 [dd, J = 8.11, 0.95 Hz, 2 H], 1.18 [m, 2 H], 0.18 [s, 6 H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 141.8, 129.7, 129.4, 125.6, 142.7, 135.2, 128.7, 128.4, 125.9, 112.9, 40.1, 26.2, 23.4, 14.9, −3.5. ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ 1.61. IR (neat): 3080, 3020, 2960, 2920, 2860, 1560, 1440, 1400, 1185, 1095, 830, 770. UV (hexanes): λ_{max} (log ϵ) 192 (3.25), 243 (2.56), 224 (2.42), 231 (2.50), 236 (2.54), 251 (2.44), 255 nm (2.42). MS: *m/z* 203 (M − CH_3, 6%), 177 (M − allyl, 44%), 99 (M − $(CH_2)_3$Ph, 100%).

Computational Aspects. All computations were carried out with the GAMESS program, using its recently described parallel SCF capability.[15] Preliminary computations using the AM1 semiempirical model[16] gave good results for both structures and energetics; therefore, the latter were included in Table 1. The *ab initio* computations were performed at the closed-shell SCF (RHF) level, using the 6-31G(d) basis set,[17] accompanied by full geometry optimization, starting from AM1 structural and vibrational information. The assumption of C_3 symmetry for each molecule was verified by computation and diagonalization of the AM1 Hessian matrix, proving each to be a minimum energy conformation. All *ab initio* computations were carried out on the Touchstone Delta computer, typically using 256 compute nodes.

Acknowledgment. This research was supported by grants from the Camille and Henry Dreyfus Foundation (R.D. and W.R.K.) and the National Science Foundation (M.S.G., No. CHE-9313717; R.D., Nos. CHE-8921522 and CHE-9223037). The computations were made possible by the ARPA-sponsored access to the experimental Touchstone Delta parallel computer located at the California Institute of Technology. We also thank Professor John Soderquist of the University of Puerto Rico for first pointing out to us the importance of Suzuki coupling chemistry, Martin Ashley at the University of Colorado at Boulder for assistance with the high-field NMR work, Joe Hankin at the University of Colorado at Boulder for yeopersonly assistance with the ^{29}Si NMR work, and Professor Gary Molander of the University of Colorado at Boulder for providing us with a recipe for the preparation of $AgNO_3$-impregnated silica gel.

OM940500Z

(15) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(16) Stewart, J. P. *J. Comput.-Aided Mol. Des.* **1990**, *4*, 1–105.

(17) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. (b) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163–168.