Table III. Summary of Crystallographic Data for 1 and 2

	1	2
empirical formula	$C_{40}H_{37}P_2ReS \cdot C_7H_8$	$C_{30}H_{50}P_5Re$
cryst syst	monoclinic	monoclinic
space group	*Pn* (No. 7)	$P2_1/n$ (No. 14)
Z	2	4
a, Å	10.300 (2)	10.868 (6)
b, Å	13.584 (4)	17.543 (5)
c, Å	13.913 (2)	17.564 (3)
β, deg	92.32 (1)	100.67 (3)
V, Å^3	1945 (1)	3291 (4)
d_{calcd}, g/cm^3	1.516	1.517
t, °C	-50	-20
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
$\lambda_{Mo K\alpha}$ (graphite monochr)	0.71069	0.71069
scan type	$2\theta/\omega$	$2\theta/\omega$
scan rate, deg/min	2-16.5	2-16.5
tot background time	scan time/2	scan time/2
take-off angle, deg	2.6	2.6
scan range, deg	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
2θ range, deg	2-25	2-22
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of data collected	3577	4192
no. of unique data $>3\sigma$	2122	2436
no. of parameters varied	362	320
abs coeff, cm^{-1}	33.294	39.997
systematic absences	*h*0*l*, *l* odd	0*k*0, *k* odd *h*0*l*, *l* odd
abs correction	differential	differential
range of transm factors	0.97-1.01	0.94-1.11
equivalent data	$0kl$, $0k\bar{l}$	$0kl$, $0k\bar{l}$
agreement of equiv data (F_o)	0.103	0.065
R_1	0.052	0.037
R_2	0.051	0.037
goodness of fit	1.216	1.073
largest peak in final *E* map	1.090	0.643

0.15 × 0.19 mm^3 was mounted on a glass fiber and placed on the diffractometer under a stream of nitrogen at -50 °C. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction revealed a primitive monoclinic crystal system. Data were collected in accord with the parameters in Table III. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection, indicating crystal stability. The space group was assigned as *Pn* (*P*2/*n* also possible), and the correctness of this choice was confirmed by the successful solution of the Patterson map, showing the Re atom. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure. The location of the sulfur atom could not be determined as the peak intensities of the positions α to the methylene group in the difference Fourier map were similar, suggesting S/CH disorder in the α position. The disorder was modeled by placing an individual sulfur atom at each position (S1A and S1B) and then constraining the coordinates of the carbon atoms (C39B and C39A, respectively) to those of the sulfur atoms. The B_{eq} values of the sulfur atoms were constrained together, as were those of the carbon atoms. The population was then varied to convergence, giving values of 0.61 and 0.39 for the population of the disordered molecules. Attempts to vary the coordinates of all four atoms independently led to divergence. A toluene solvent molecule of crystallization was also located in a difference Fourier map. The solvent molecule was refined isotropically as a group. An empirical absorption correction was applied after isotropic refinement of all non-hydrogen atoms by using the program DIFABS. Anisotropic refinement of all remaining non-hydrogen atoms allowed for the use of a difference Fourier map for the location of the hydrogen atoms. Four carbon atoms were refined isotropically, since anisotropic refinement led to nonpositive definite values. The hydrogens attached to the Re atom were not located. The coordinates of the remaining hydrogen atoms were subsequently idealized. The largest residual peaks in the final E-map were located in the vicinity of the solvent molecule. Selected bond distances and angles are given in Table I.

$\overline{Re(PMe_3)_4(PPh_2C_6H_4)}$ (2). An orange crystal of **2** with approximate dimensions 0.19 × 0.15 × 0.15 mm^3 was mounted on a glass fiber and placed on the diffractometer under a stream of nitrogen at -20 °C. Data collection was as for **1** with a monoclinic crystal system. Data were collected in accord with the parameters in Table III. The space group was uniquely assigned as $P2_1/n$, and the correctness of this choice was confirmed by the successful solution of the Patterson map, showing the Re atom. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure. An empirical absorption correction was applied after isotropic refinement of all non-hydrogen atoms by using the program DIFABS. After anisotropic refinement of all non-hydrogen atoms, the coordinates of the hydrogen atoms were idealized. Selected bond distances and angles are given in Table II.

Acknowledgment is made to the National Science Foundation, grant CHE9102318, for support of this work. W.D.J. also thanks NATO for a travel grant.

Supplementary Material Available: Tables of fractional atomic coordinates, thermal parameters, and bond distances and angles for complexes **1** and **2** (21 pages); calculated and observed structure factors for complexes **1** and **2** (32 pages). Ordering information is given on any current masthead page.

Six New Saddle-Shaped Hosts Based on Fused Dibenzofuran Units[1,2]

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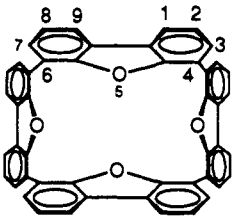
Contribution from the Department of Chemistry and Biochemistry of the University of California at Los Angeles, Los Angeles, California 90024. *Received June 29, 1992*

Abstract: The syntheses of six new host systems are reported whose semirigid, saddle-shaped structures are based on incorporation of three to four dibenzofuran units into a macroring (**4**-**9**). The two clefts in **4** have long axes mutually perpendicular to one another, each of which is structurally complementary to molecules such as dibenzofuran. The single clefts of **5**-**9** have a similar long axis. The width of their clefts varies with connecting groups A, which provide potential binding or catalytic sites on the floor of each cleft. Crystal structures are reported for **4**, **6**, and **8**. A survey of potential guests for binding **4** revealed weak binding to occur between **4** and 1,3-$(NC)_2C_6H_4$ and 1,3-$(O_2N)_2C_6H_4$ in $CDCl_3$. Host **8** was found to complex guanine in CD_3OD as solvent.

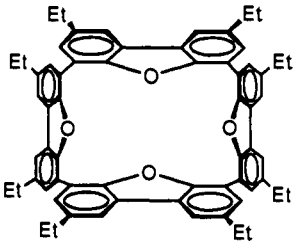
The dibenzofuran unit is attractive for use in assembling cavitands with large interiors. It possesses two large flat surfaces, undergoes metalation readily in its 4- and 6-positions, and undergoes electrophilic substitution in its 2- and 8-positions.[3] We

0002-7863/92/1514-10775$03.00/0

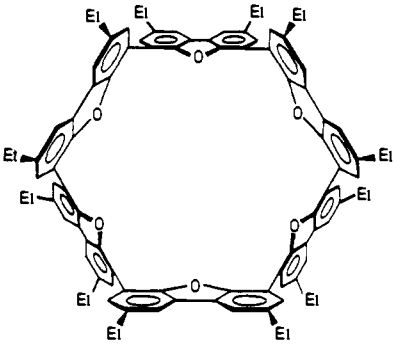
communicated the synthesis of **1**, but found it too insoluble to characterize except by mass spectra. Accordingly, **2** and **3** were prepared whose ethyl groups both extended the cavities and solubilized the compounds in organic media.[4] Molecular models (CPK) of **2** indicate the compound is free of strain, possesses D_{2d} symmetry, and contains two cleft-shaped cavities approximately 12 Å long, 3.4 Å deep, and 4.3 Å wide. Its four oxygens are nearly coplanar. Models of 4,4′-disubstituted 1,1′-biphenyl compounds are complementary to each of the cavities of **2**. Models of **3** indicate the compound is free of strain, possesses D_{3d} symmetry, and contains a single large cavity of dimensions ca. 11 × 7 × 7 Å. The six oxygens of **3** lie approximately in one plane and are beautifully complementary to a model of benzene occupying the same plane, which divides the cavity into halves, within each of which can be stacked three additional benzene models in planes perpendicular to the benzene occupying the oxygen's plane. The ethyl groups of **3** almost close the gaps on the cylindrical surfaces of the collar-shaped cavity.[4]



1



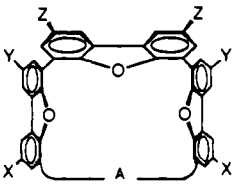
2

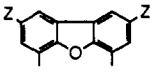


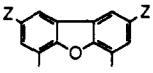
3

This paper reports the syntheses and characterizations of a group of six relatives of **2**. One of these **4**, like **2**, contains four bonded dibenzofuran units, the other five (**5–9**) being composed of three bonded dibenzofuran units whose terminal aryls are bridged by A groups of differing lengths and containing potential catalytic and binding functional groups. In molecular models, the enforced cavities of **4–9** resemble those of **1** and **2**. Hosts **4–9** possess the same attractive structural potentials for locating functional groups in X-positions, which allow them to act cooperatively in binding and(or) catalyzing the reactions of appropriate guests. Remote substituents Y and Z might be employed for extending the cavities and controlling the hydrophilic–lipophilic balance of the hosts.

Compounds **4–9** were selected for initial study to determine the synthetic viability of the systems to see if their crystal structures corresponded to expectations based on CPK model examination. We also wished to carry out exploratory binding studies on one of the hosts. The trimethylsilyl group of **4** and of **7–9** was selected because it survives the reaction conditions needed to construct the cycles and yet can be converted into a large number of functional groups after the macrocycle is closed.[5,6]



2, A =  , X = Y = Z = CH_3CH_2

4, A =  , X = Y = Z = $(CH_3)_3Si$

5, A = $CH_2N(Ts)CH_2$, X = Y = Z = H

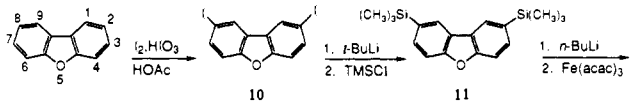
6, A = CH_2COCH_2, X = Y = Z = H

7, A = $CH_2N(Ts)CH_2$, X = Y = H, Z = $(CH_3)_3Si$

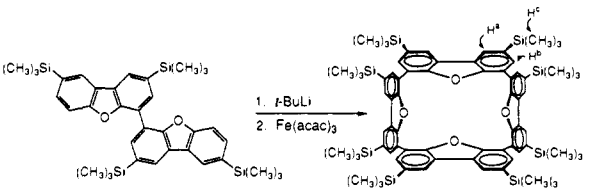
8, A = $CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2$, X = Y = H, Z = $(CH_3)_3Si$

9, A = $CH_2N(CH_3)CON(CH_3)CH_2$, X = Y = H, Z = $(CH_3)_3Si$

Syntheses. In the synthesis of **4**, dibenzofuran was iodinated in its 2- and 8-positions with I_2–HIO_4–AcOH to give **10**[7] (46%), which was dilithiated with $(CH_3)_3CLi$. The organometallic compound produced was treated with $(CH_3)_3SiCl$ to provide **11** (99%) as white needles. Carefully dried **11** was lithiated with BuLi, and the organometallic product was cannulated into a refluxing solution of dry $Fe(acac)_3$ in benzene to provide **12** (80%).[8] Thoroughly dried **12** was dilithiated with $(CH_3)_3CLi$, and the product was cannulated into a refluxing solution of $Fe(acac)_4$ in benzene to provide macrocycle **4** (7%).[8] Crystallization of **4** from C_6H_6 gave crystals suitable for crystal structure determination.



10 **11**

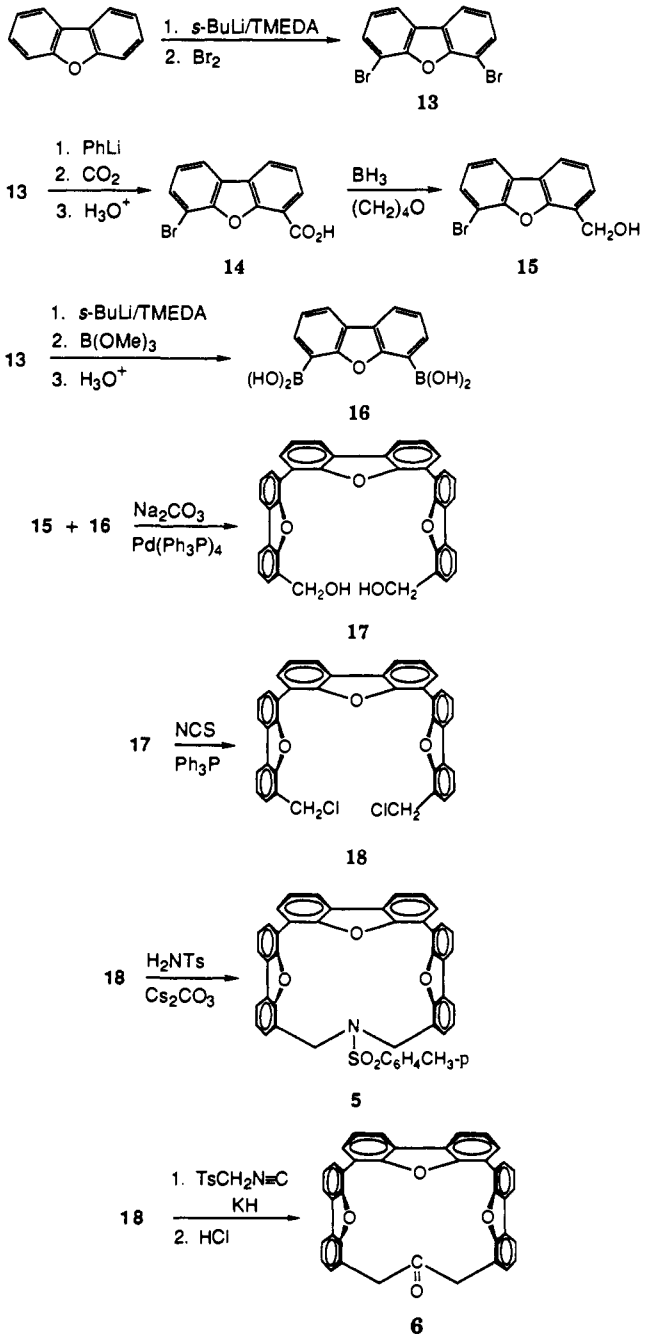


12 **4**

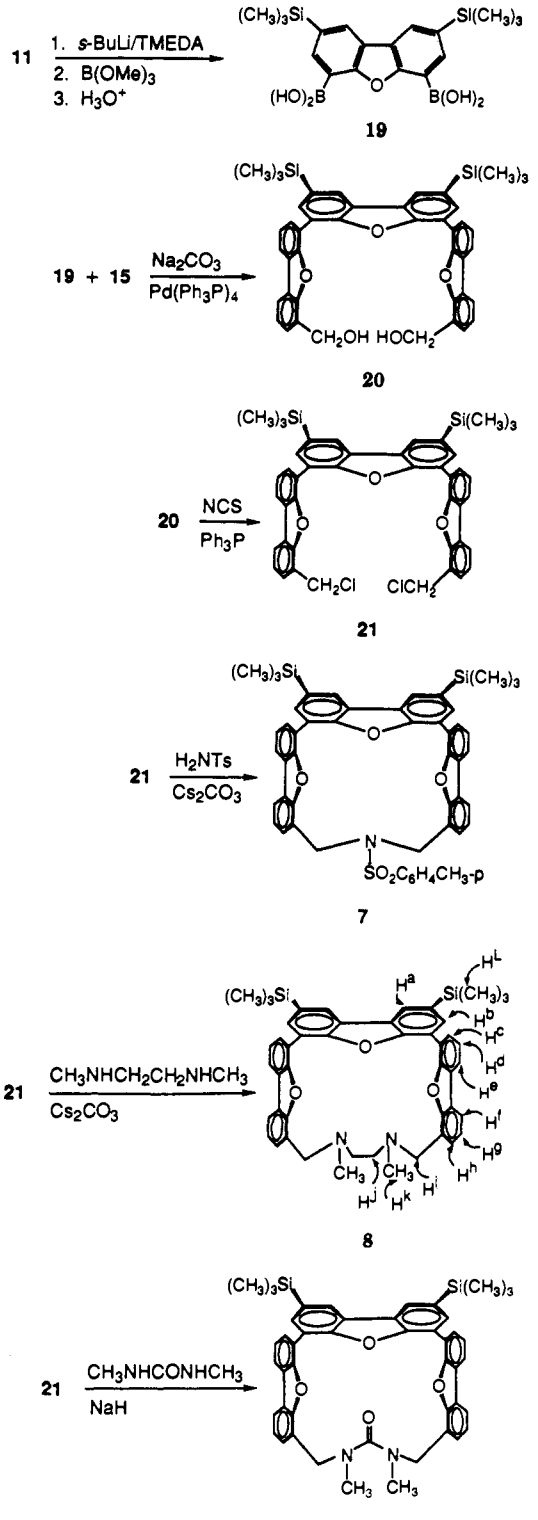
In the syntheses of **5** and **6**, dichloride **18** was the key intermediate for ring closures. It was prepared as follows. Dibenzofuran was dilithiated with 2-butyllithium in Et_2O–tetramethylethylenediamine (TMEDA), and the organometallic compound formed was treated with bromine to give dibromide **13** (65%). Lithiation of **13** in Et_2O–$(CH_2)_4O$ and PhLi at −78 °C gave monometalated material which then stirred with CO_2 produced bromoacid **14** (95%). The carboxyl group of **14** was reduced with $H_3B{\cdot}O(CH_2)_4$ to provide bromoalcohol **15** (91%). Dimetalation of **13** with *sec*-BuLi–TMEDA, boronation of the organometallic compound with $B(OMe)_3$, and hydrolysis of the bisboronic ester formed gave diboronic acid **16** (65%) as a dihydrate, whose elemental analysis suggested it to be inhomogeneous. Bromoalcohol **15** and diboronic acid **16** were subjected

(1) Host–Guest Complexation. 65.
(2) We warmly thank the U.S. Public Health Service for supporting Grant GM-12640.
(3) (a) Sargent, M. V.; Stransky, P. O. *Adv. Heterocycl. Chem.* **1984**, *35*, 1–75. (b) Parham, W. E. *Heterocycl. Compds.* **1951**, *2*, 123–144.
(4) Helgeson, R. C.; Lauer, M.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1983**, 101–103.
(5) (a) Sargent, M. V.; Stransky, P. O. *Adv. Heterocycl. Chem.* **1984**, *35*, 1–80. (b) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761–786.
(6) Diaz, H.; Kelly, J. W. *Tetrahedron Lett.* **1991**, *32*, 5725–5728.
(7) Gilman, H.; Brown, G. E.; Bywater, W. G.; Kirkpatrick, W. H. *J. Am. Chem. Soc.* **1934**, *56*, 2473–2477.
(8) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Brown, S. B.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 3645–3657.

to a Suzuki coupling[9] with a $Pd(Ph_3P)_4$ catalyst in an EtOH–C_6H_6–H_2O–Na_2CO_3 mixture to give diol **17**. Diol **17** was converted to dichloride **18** (70%) with *N*-chlorosuccinimide and $P(Ph)_3$ in $(CH_2)_4O$. Dichloride **18** reacted with *p*-$CH_3C_6H_4SO_2NH_2$ in $(CH_3)_2NCOCH_3$–Cs_2CO_3 to produce macrocycle **5** (76%). Dichloride **18** was also treated with *p*-$CH_3C_6H_4SO_2CH_2NC$ in $(CH_2)_4O$. The initially formed cyclic isocyanide intermediate was hydrolyzed with C_6H_6–H_3OCl to give macrocyclic ketone **6** (7%). Elemental analyses of **6** showed the compound contained three water molecules of crystallization, less than one of which was lost when the sample was dried at 100 °C and 10^{-5} mm of Hg. Crystallization of ketone **6** from CH_2Cl_2 provided crystals suitable for crystal structure determination.

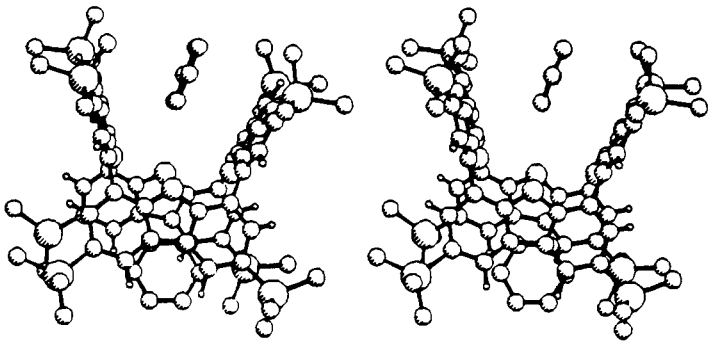


Dichloride **21** was the key intermediate in the syntheses of macrocycles **7–9**. In its preparation, bistrimethylsilyl substituted dibenzofuran compound **11** was dilithiated with *sec*-BuLi–TMEDA, the dilithium compound produced was diboronated with $B(OCH_3)_3$, and the diboronate ester formed was hydrolyzed with H_3OCl to give diboronic acid **19** (92%). One mole of this diacid was Suzuki coupled with 2 mol of bromoalcohol **15** with $Pd(Ph_3P)_4$ catalyst in EtOH–C_6H_6–H_2O–Na_2CO_3 to give diol **20** (60%), which when treated with *N*-chlorosuccinimide in $(CH_2)_4O$ and $P(Ph)_3$ gave dichloride **21** (71%). This compound was subjected to macrocyclic ring closure through its reaction with *p*-$CH_3C_6H_4SO_2NH_2$–Cs_2CO_3 in $(CH_3)_2NCOCH_3$ to give **7** (74%). The reaction between **21** and $CH_3NHCH_2CH_2NHCH_3$ in $(CH_3)_2NCOCH_3$–Cs_2CO_3 gave macrocyclic diamine **8** (12%). X-ray quality crystals of **8** were grown from CH_2Cl_2–CH_3OH. Treatment of dichloride **21** with $CH_3NHCONHCH_3$–NaH–$(CH_2)_4O$ gave macrocyclic urea compound **9** (6%).

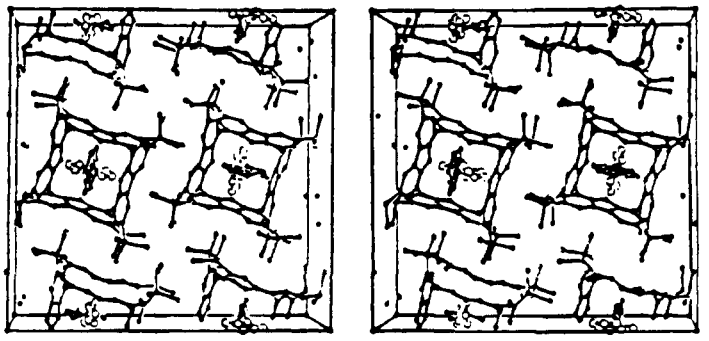


(9) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513–519.

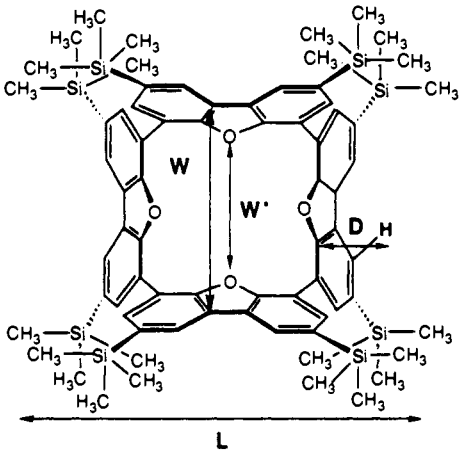
Chart I



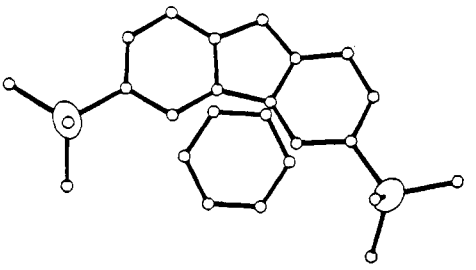
4a



4b



4c



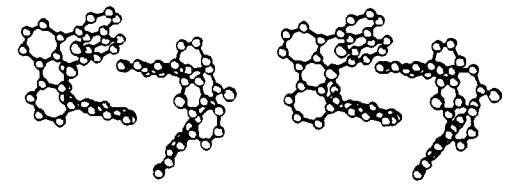
4d

The solubility properties of the five trisdibenzofuranyl macrocycles **5–9** correlate with the complementarity of the host cavities and the solvent on the one hand and with the presence or absence of the trimethylsilyl groups on the other. In CPK models, all of these hosts have cleft-shaped cavities complementary to C_6H_6, but the clefts in **5–7** are too narrow to accommodate models of CH_2Cl_2, $CHCl_3$, $(CH_3)_2CO$, or $(CH_3)_2SO$. Cycles **5** and **6** are soluble and **7** is very soluble in C_6H_6, but **5–7** are only sparingly soluble in CH_2Cl_2, $CHCl_3$, $(CH_3)_2CO$, or $(CH_3)_2SO$ and are insoluble in CH_3OH. In CPK models, **8** and **9** have much wider clefts due to their longer bridges and nicely accommodate all of the above solvents in their clefts. Hosts **8** and **9** are very soluble in benzene, **9** is soluble and **8** is very soluble in CH_2Cl_2 and $CHCl_3$, **9** is slightly soluble and **8** is soluble in $(CH_3)_2CO$, both are soluble in $(CH_3)_2SO$, but only **8** is soluble in CH_3OH. Thus the solubilities of **8** and **9** appear to correlate with the abilities of their functional groups to generate attractive pole–dipole interactions.

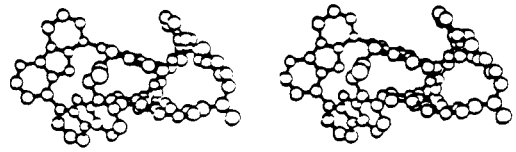
Crystal Structures. Cavitand **4** crystallized from benzene–*p*-xylene with 2 mol of benzene per host molecule, one benzene being located inside of each of the two clefts, as shown in stereoview **4a** of Chart I. This structure belongs to the four-bar crystallographic point group (S_4). Within the unit cell, each complex is related to the next by a 4-fold screw axis, as shown in stereoview **4b** of Chart I.

Each cleft is defined by two facing bistrimethylsilyldibenzofuran walls separated by two rigid spacer (also bistrimethylsilyldibenzofuran) units. The facing subunits are splayed outward, each wall lying 68° from a plane perpendicular to the best plane of the four oxygens. The benzene guests are not centered in the cleft in two respects: the benzene is 0.2 Å closer to one end of the long axis of the cleft than the other; the benzene is closer to one of the dibenzofuran units than the other (see **4d** of Chart I). Accordingly, the guests are disordered. The best plane of the benzene guest is very roughly parallel to the best plane of the dibenzofuran unit to which it is closest (see **4b**), the distances between these two planes ranging from 3.43–3.82 Å. The host–guest binding

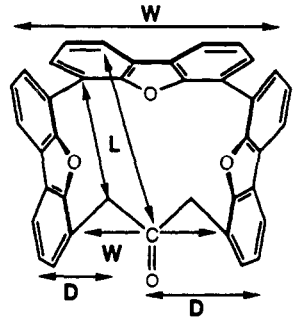
Chart II



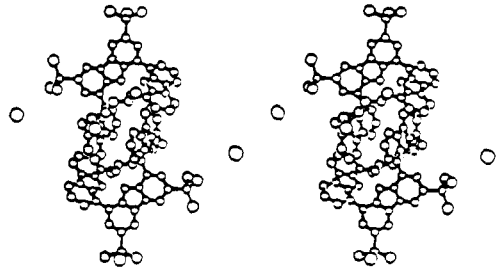
6a



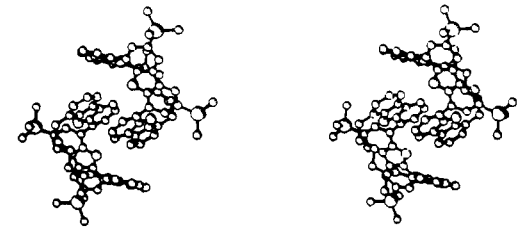
6b



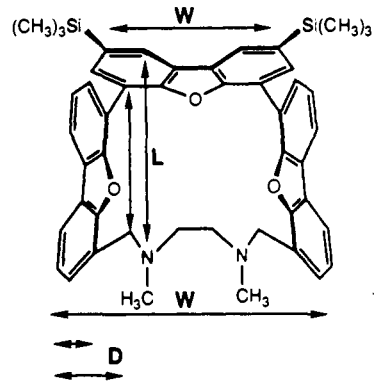
6c



8a



8b



8c

appears to be of the $\pi-\pi$ attraction variety.[5a,11] The benzene guests extend fairly deeply into the cavities. The distance between the most deeply penetrating carbon atom of the benzene guest and the best plane defined by the four oxygens of the dibenzofuran units is 2.92 Å.

The dimensions of the cleft are defined from atom center to atom center, as illustrated in **4c** of Chart I. The length (*L*) of the cleft is defined as the distance between the silyl*methyl carbon* at the 2-position and the silyl*methyl carbon* at the 8-position on one dibenzofuran unit. The length of the cleft is 12.17 Å. Because the cleft walls are splayed, the width is measured at two limits. At the upper limit, the width (*W*) of the cleft is defined by the distance between the 9c-carbon of one dibenzofuran unit and the 9c-carbon directly across on the facing dibenzofuran unit. The upper limit width is 6.69 Å. At the lower limit, the width (*W'*) is defined by the distance between the 5-oxygen of one dibenzofuran unit and the 5-oxygen of the parallel dibenzofuran unit. The lower limit width is 5.08 Å. The depth (*D*) of the cleft is defined by the distance between the 4-carbon and the hydrogen on the 1-carbon on one dibenzofuran unit. The depth is 3.43 Å. These dimensions indicate each host contains two cavities of substantial size, which are roughly complementary to aromatic guest molecules.

The near planar array of oxygens (±0.35 Å) in the depths of the cavities is interesting in terms of a potential cation ligating site. The distances between oxygens on parallel dibenzofuran units (5.08 Å) and oxygens on perpendicular dibenzofuran units (3.66 Å) indicate a possible size compatibility with fairly large cations. Although the hole defined by the four oxygens is geometrically complementary to Cs^+ and Rb^+, a 50 mM solution of **4** in $CDCl_3$ failed to extract either cesium or rubidium picrate from a 50 mM solution of these salts in water. The contribution of the unshared electrons of dibenzofuran oxygens to the aromatic character of the system appears to make them poor ligands for alkali metal ions.

Chart II provides two stereoviews of each of the crystal structures of hosts **6** (**6a** and **6b**) and **8** (**8a** and **8b**). In both cases, the hosts were devoid of solvent molecule guests. In each crystal structure, two molecules dimerize, each molecule providing one filled cleft and one inserted dibenzofuran unit. This unique feature illustrates the complementarity of this host type to aromatic guests. Molecular models (CPK) of **4** show it to be impossible for dimerization to occur due to the steric requirements of the trimethylsilyl groups. The cleft of **4** is too narrow to accommodate

(10) (a) Possel, O.; van Leusen, A. M. *Tetrahedron Lett.* **1977**, 4229–4232. (b) Frazza, M. S.; Roberts, B. W. *Tetrahedron Lett.* **1981**, 4193–4196.
(11) Taylor, R. *J. Chem. Soc. B* **1968**, 1559–1562.

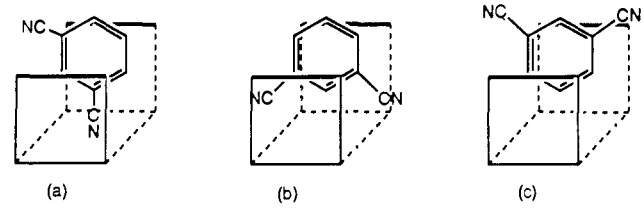
$ArSi(CH_3)_3$ moieties, unlike the benzene that is the guest in the crystal structure of **4**.

The crystal structure of cyclic ketone (**6**) is characterized by the $P2_1/n$ crystallographic space group. Host **6** possesses a narrow cleft-like cavity. The cleft is defined by two facing dibenzofuran units separated by one rigid dibenzofuran spacer group and a somewhat flexible CH_2COCH_2 bridge. The facing dibenzofuran subunits are splayed outward somewhat and are not parallel to each other. One dibenzofuran unit of one molecule is arranged within the cleft of a second molecule in a manner which should provide attractive π–π interactions, which we postulate reside in the two "benzene" portions of each dibenzofuran unit.[5a] The inserted dibenzofuran moiety resides closer to one of the two facing dibenzofuran units of the cleft than the other, in a nearly parallel fashion. The distances between the best plane of the inserted dibenzofuran and the best plane of the closest dibenzofuran of the cleft vary from 3.34–3.75 Å. The dibenzofuran unit does not fill the cleft entirely but extends as far as the short aliphatic carbonyl bridge at the base of the cleft will allow. The distance between the deepest atom of the inserted dibenzofuran and the plane defined by the three oxygens of the cleft at its lowest point is 3.49 Å. The keto oxygen of the inserted dibenzofuran host is oriented in an "anti" orientation with respect to the ether oxygens of the two facing dibenzofuran units of the cleft-providing host. In CPK molecular models, the carbonyl group can be made to partially fill the cleft or point away from the cleft. The crystal structure shows the carbonyl group pointing away from the cleft, providing room for the "dibenzofuran" unit of the second molecule. Structure **6c** of Scheme II illustrates the length "*L*" (5.16–7.02 Å), width "*W*" (3.59–7.51 Å), and depth "*D*" (3.77–5.25 Å) dimensions of host **6**.

Host **8** possesses a wide cleft-like cavity, defined by two facing dibenzofuran units separated by one rigid dibenzofuran spacer group and a flexible aliphatic diamine bridge. The facing dibenzofuran subunits are splayed outward but not as much as in structure **6**. Again, each host molecule possesses as its guest a dibenzofuran group of a second molecule of host. In the "dimer," the two amine bridges are remote from one another. The dibenzofuran units are arranged within the clefts in a manner which allows effective π–π interactions. Each inserted dibenzofuran unit resides closer to one facing dibenzofuran unit of the cleft than the other, in a nearly parallel fashion. The distances between the best plane of the inserted dibenzofuran and the best plane of the closest dibenzofuran unit of the cleft vary from 3.40–3.80 Å. The dibenzofuran units fill much of the clefts, extending as deeply as the diamine bridge of the guest will allow. The distance between the deepest atom of the inserted dibenzofuran unit and the plane defined by the three oxygens of the lowest point of each cleft is 2.29 Å. In CPK molecular models, the methyl groups on the two nitrogens of the diamine bridge can be made to partially fill the cleft or point away from the cleft. The crystal structure shows these methyl groups pointing away from the clefts oriented at a maximum distance from each other, providing room for the inserted dibenzofuran unit. Two interstitial water molecules reside between each dimer in **8a** and **8b**. Structure **8c** of Chart II provides the length "*L*" (5.10–7.15 Å), width "*W*" (5.76–8.57 Å), and depth "*D*" (2.88–4.41 Å) dimensions of the cleft of **8**.

Binding Properties of Octa(trimethylsilyl) System 4. The association of host **4** in $CDCl_3$ at 25 °C was investigated through changes in the 200 MHz ^1H NMR spectra of **4** (at 4 mM concentration, referenced to the residual $CHCl_3$ peak) in the presence of incremental additions of $CDCl_3$ solutions of guests at [H]:[G] ratios of 1:20 to 1:60. Of the potential guests examined, only π-acids 1,3-$(NC)_2C_6H_4$ and 1,3-$(O_2N)_2C_6H_4$ provided strong enough binding for detection. Fluorene, dibenzofuran, 2,4,6-trinito-9-fluorenone, 1,3-dimethoxybenzene, 3-cyanopyridine, cyanobenzene, chlorobenzene, nitrobenzene, toluene, benzene, acetonitrile, and carbon disulfide failed to give detectable binding. Host dimerization is impossible for steric reasons. Protic and aprotic dipolar solvents could not be used for solubility reasons.

The high symmetry (D_{2d}) of **4** provided two sharp singlets in its ^1H NMR spectrum at δ 7.91 and 7.51 (respectively, Ar-H^a and Ar-H^b) whose changes of $\Delta\delta$ in the presence of changing guest concentrations allowed the application[12] of the Benesi–Hildebrand method in determination of K_a and $\Delta G°$ values. The $SiCH_3^c$ peak at δ 0.19 was insensitive to complexation. The peak at 7.91 changed from δ 7.676 at 40.3 mM of 1,3-$(NC)_2C_6H_4$ concentration to 7.581 at 278 mM to give (11 points) a $K_a = 1.45 \pm 0.88$ M^{-1}, while that at δ 7.51 changed from 7.316 to 7.238 to provide a $K_a = 2.10 \pm 0.46$ M^{-1}, whose r values were 0.997 and 0.993, respectively. The average K_a value is 1.96 ± 0.41 M^{-1}, which gives $\Delta G° = -0.40$ kcal mol^{-1} binding free energy. As a control, acyclic precursor **12** of **4** was subjected to a similar ^1H NMR titration. No changes in δ values of the protons of **12** were observed. Although the upfield shift of the aryl protons of the host are consistent with insertion of the dicyanoaryl guest in the cleft of the host, no evidence is available to differentiate between the three possible ways this can be accomplished (see a, b, and c).



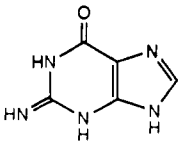
When a similar titration was performed with 1,3-$(O_2N)_2C_6H_4$ as guest (7.92–133 mM, 11 points, H^a ranged from δ 7.688 to 7.450 and H^b from 7.319 to 7.194), Ar-H^a provided $K_a = 8.40 \pm 1.22$ M^{-1} ($r = 0.997$) and Ar-H^b, 2.99 ± 0.48 M^{-1} ($r = 0.999$). An averaged $K_a = 3.72 \pm 0.45$ M^{-1} gave $\Delta G° = -0.80$ kcal mol^{-1} of binding. When $(O_2N)_2C_6H_4$ was similarly added to $CDCl_3$ solutions of precursor **12**, shifts in δ on the order of 2–6 Hz were observed. Even **11**, when treated with this guest, provided small changes in δ. Thus the binding between 1,3-$(O_2N)_2C_6H_4$ and **4** could represent a sum of contributions from guest inserted into the cleft of **4**, and some in which guest bound the outer faces of the host.

Binding Properties of Diamine Host 8. The ^1H NMR spectra of diamine host **8** were taken at 25 °C in $CDCl_3$, CD_2ClCD_2Cl, $(CD_3)_2CO$, and $(CD_3)_2SO$. In all spectra the signals were very broad, unlike those of **5**–**7**. The peak assignments for the protons of **8** were determined by COSY 2D NMR at 200 MHz. When the 360 MHz ^1H NMR spectra of **8** in CD_2ClCD_2Cl at 103 °C and 33 °C were compared, the signals of the higher temperature spectra were sharp compared to those at the lower temperature, probably due to conformational reorganizations becoming fast on the ^1H NMR time scale at the higher temperature. Although it is possible that **8** dimerizes weakly in solution as well as in its crystal structure, we do not think dimerization a likely explanation for the observed peak broadening.

In CPK models, guanine (**22**) appeared to be a possible guest that is complementary to host **8**. A 0.003 M solution of **8** in CD_3OD was prepared and sonicated with solid guanine. The resulting filtered solution at 25 °C gave a 200 MHz ^1H NMR spectrum with much sharper peaks than that of the host taken alone. The broad "benzyl" doublet of doublets (H^i) was resolved into a fairly sharp doublet of doublets, and one of the doublets was shifted upfield from δ 3.85 to δ 3.65. There was an upfield shift of the N-CH_3 protons (H^k) from δ 2.38 to δ 2.23, and the singlet H^k also sharpened. Small upfield shifts were observed in aromatic protons H^a-H^g. There was one significant change in the host's aromatic protons. The multiplet between δ 7.24 and 7.40 was resolved with proton H^h shifting upfield from δ 7.33 to 7.18. The remote trimethylsilyl protons H^L did not shift under these conditions. Guanine **22** is completely insoluble in CD_3OD. Even with heating and sonication, no ^1H NMR spectrum could be obtained of **22**. Although no peaks corresponding to guanine could be assigned in the spectrum of the complex, there are a few possibilities among the peaks unaccounted for in the aromatic region.

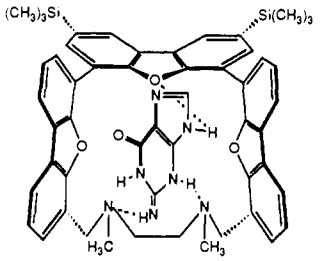
These results suggest that host **8** complexes **22** in CD_3OD. For guanine to fit into the cleft of **8**, the CH_3^k groups attached to the

nitrogens must reorient themselves to point away from the cavity and move into a shielding region of the aryl group, resulting in their $\Delta\delta = 0.15$ upfield shift (CPK molecular model examination).



22

Formula **23** represents the structure of the **8·22** complex suggested by CPK model examination. Three hydrogen bonds and π-acid to π-base attractions between host and guest acting simultaneously are postulated as the binding forces in **23**.



23

The low solubility in organic solvents coupled with the narrowing of their cavities at their three atom bridge made **5–7** unattractive for binding studies. The low yield in the synthesis of **9** limited its study.

Summary. Syntheses are reported for six new macrocyclic ring systems (**4–9**) composed of three or four dibenzofuran systems attached to one another or to a bridging unit at their two positions adjacent to their oxygens. These potential hosts possess saddle-shaped, semirigid structures. Crystal structures are reported for **4**, **6**, and **8**, which conform to expectations based on CPK molecular model examination. The clefts of **4–9** in models are complementary to those of aromatic compounds, e.g., dibenzofuran. Macrocycles **5–9** contain clefts whose floors contain functional groups. A survey of potential guests for host **4** dissolved in $CDCl_3$ revealed weak binding to occur between **4** and 1,3-$(NC)_2C_6H_4$ or 1,3-$(O_2N)_2C_6H_4$. Host **8** was found to complex and solubilize guanine in CD_3OD, which is insoluble in CD_3OD in the absence of **8**.

Experimental Section

General Methods. Dibenzofuran was purified according to Perrin and Perrin.[13] All alkyllithium reagents were titrated with diphenylacetic acid before use. Et_2O and THF were distilled from sodium benzophenone ketyl before use. Both *N*-formylpiperidine and tetramethylenediamine (TMEDA) were dried over 4 Å molecular sieves. Flash chromatography was performed as described by Still.[14a] Thin-layer chromatography (TLC) involved glass-backed and plastic-backed 0.25 mm thick silica gel 60 F-254 plates (E. Merck, Inc.). Melting points were obtained on a Mel-Temp apparatus in open capillaries and are uncorrected. The 60 MHz ^1H NMR spectra were obtained on a Varian T-60 instrument and the 200 MHz spectra on a Bruker WP-200 spectrometer. Mass spectra were obtained on a AEI-MS-9 spectrometer, whereas FAB MS were run on a VG Analytical ZAB-XE instrument fitted with a saddle-field FAB gun with *m*-nitrobenzyl alcohol (NOBA) as a matrix. Reverse-phase thin-layer chromatography (RPTLC) involved Whatman C_{18} glass-backed plates. Semipreparative chromatography was performed on a Harrison Research Chromatotron Model 7924. Silica gel rotors were homemade. Flash reverse-phase chromatography required homemade C_{18} silica.[14b]

2,8-Diiododibenzofuran (10). A mixture of dibenzofuran (16.8 g, 0.10 mol), iodine (19.7 g, 0.078 mol, finely divided), iodic acid (7.7 g, 0.044 mol), 200 mL of glacial acetic acid, 15 mL of water, 2 mL of concentrated H_2SO_4, and 5 mL of CCl_4 was stirred vigorously. The brown heterogeneous mixture was heated to 65 °C for 3 days. A cream-colored solution with voluminous precipitate formed which was filtered, and the solid was washed with 500 mL of water and air dried. Recrystallization of the solid from benzene/petroleum ether (30–60 °C) and drying the product under high vacuum gave diiodide **10** (19.44 g, 0.0463 mol, 46%), a shiny, grey-white solid: mp 172–173 °C (lit.[7] 177 °C); ^1H NMR (200 MHz, $CDCl_3$) 7.32 (d, J = 8.0, 2 H, Ar-*H*), 7.74 (d, J = 8.8, 2 H, Ar-*H*), 8.20 (s, 2 H, Ar-*H*); MS (100 °C, 70 eV, *m/e*) 421 (24.1, M + 1), 420 (100.0, M^+). Anal. Calcd for $C_{12}H_6I_2O$: C, 34.32; H, 1.44. Found: C, 34.42; H, 1.34.

2,8-Dibenzofurandiylbis[trimethyl]silane (11). Under dry conditions in an Ar atmosphere, 2,8-diiododibenzofuran **10** (4.49 g, 0.0107 mol) was dissolved in 30 mL of dry THF and 90 mL of dry Et_2O. The solution was cooled to −78 °C, and *tert*-butyllithium (25.2 mL, 0.0428 mol, 1.7 M in pentane) was added via syringe. A bright yellow solution and voluminous white precipitate were produced. The reaction mixture was warmed slowly to 0 °C over a 2-h period. The reaction mixture was cooled to −10 °C, and chlorotrimethylsilane (9.0 mL, 0.0709 mol) was added rapidly via syringe. A cloudy white solution was produced. After the solution had been stirred at 25 °C for 12 h, 50 mL of water was added, and the organic solvents were removed under vacuum. The residue was extracted with 500 mL of CH_2Cl_2. The extract was washed with 100 mL of 30% aqueous $NaHSO_3$ and 100 mL of brine, dried ($MgSO_4$), and concentrated in vacuo to give a yellow semisolid. Recrystallization of the solid from methanol yielded pure **11** (3.30 g, 0.0106 mol, 99%), as long, colorless needles: mp 92–99 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 0.37 (s, 9 H, $Si(CH_3)_3$), 7.58 (dd, 4 H, Ar-*H*), 8.14 (s, 2 H, Ar-*H*); MS (170 °C, 16 eV, *m/e*) 313 (26.0, M + 1), 312 (100.0, M^+). Anal. Calcd for $C_{18}H_{24}OSi_2$: C, 69.17; H, 7.74. Found: C, 69.09; H, 7.77.

[4,4′-bidibenzofuran]-2,2′,8,8′-tetrayltetrakis[trimethyl]silane (12). Under dry conditions in an Ar atmosphere, disilane **11** (4.49 g, 0.0144 mol, azeotroped with benzene, and dried under high vacuum) was dissolved in 100 mL of dry THF. The solution was cooled to −78 °C, and *n*-butyllithium (6.7 mL, 0.0151 mol, 2.25 M in hexanes) was added via syringe. A dark-colored solution formed. After the reaction mixture had stirred at 25 °C for 5 h, the lithiate was cooled to −78 °C and cannulated into a refluxing solution of $Fe(acac)_3$ (7.20 g, 0.0204 mol, activated at 100 °C under high vacuum) in 100 mL of benzene (dried over activated 3 Å molecular sieves). The red $Fe(acac)_3$ solution turned brown and a precipitate formed. The mixture was refluxed for 2 h. At 25 °C, 400 mL of 2 N aqueous HCl was added to the reaction mixture. Four hours later, the organic solvents were removed under vacuum, and the residue was extracted with 700 mL of CH_2Cl_2. The organic extract was washed with 350 mL of 2 N aqueous HCl and 350 mL of water, dried ($MgSO_4$), and concentrated. Flash chromatography (150 g of silica gel, 85:15 hexanes/CH_2Cl_2, R_f 0.45) of the residue and concentration of the product under high vacuum produced **12** (3.60 g, 5.79 mmol, 80%) as a white foam: mp 196–198 °C; ^1H NMR (200 MHz, $CDCl_3$) 0.38 (s, 18 H, $Si(CH_3)_3$), 0.43 (s, 18 H, $Si(CH_3)_3$), 7.49 (d, J = 8.0, 4 H, Ar-*H*), 7.60 (d, J = 8.0, 4 H, Ar-*H*), 8.04 (s, 2 H, Ar-*H*), 8.21 (s, 4 H, Ar-*H*); MS (20 eV, *m/e*) 624 (30.0), 623 (59.0, M + 1), 622 (100.0, M^+). Anal. Calcd for $C_{36}H_{46}O_2Si_4$: C, 69.39; H, 7.44. Found: C, 69.48; H, 7.56.

11,8,10:18,15,17:25,22,24:26,1,27-Tetra[1,3]butadien[1]yl[4]ylidenetetrabenzo[*b*,*d*,*i*,*n*][1,6,11,16]tetraoxacycloeicosin-3,6,13,20,31,34,38,42-octayloctakis[trimethyl]silane (4). Under dry conditions under an Ar atmosphere, **12** (2.01 g, 0.00323 mol, azeotroped with benzene and dried under high vacuum) was dissolved in 50 mL of dry Et_2O. The solution was cooled to −78 °C and *tert*-butyllithium (5.7 mL, 0.00969 mol, 1.7 M in pentane) was added via syringe. The reaction mixture was warmed to 0 °C over 90 min, and the lithiate became dark red. The lithiate was then cooled to −78 °C and cannulated over 10 min into a refluxing solution of $Fe(acac)_3$ (3.42 g, 0.009 69 mol, activated at 110 °C under high vacuum) in 1.5 L of dry benzene (dried over activated 3 Å molecular sieves). The red-colored solution became brown and a tan precipitate formed. The reaction mixture was refluxed for 1 h, then cooled to 25 °C, and allowed to stand for 12 h. To the mixture was added 100 mL of 2 N aqueous HCl, and the organic solvents were removed under vacuum. The residue was extracted with 800 mL of CH_2Cl_2, and the organic extract was washed with 800 mL of water, dried ($MgSO_4$), and concentrated to give a pale yellow semisolid. Trituration of the semisolid with 20 mL of Et_2O, filtration of the precipitate, and drying the product

(12) (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707. (b) Bergeron, R. J.; Roberts, W. P. *Anal. Biochem.* **1978**, *90*, 844–848. (c) Cram, D. J.; Stewart, K. D.; Goldberg, I.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2574–2575.

(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1980; p 196.

(14) (a) Still, W. C.; Kahn, M.; Maitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925. (b) Kuhler, T. C.; Lindsten, G. R. *J. Org. Chem.* **1983**, *48*, 3589–3591.

under high vacuum gave pure **4** (85.3 mg, 0.0688 mmol). The filtrate from the Et_2O trituration was concentrated to 5 mL, and a white solid was isolated. Preparative thin-layer chromatography (2.0 mm SiO_2, hexanes, R_f 0.2) of the solid gave more **4** (49.5 mg, 0.0399 mol), total yield, 6.7%: mp > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$) 0.19 (s, 72 H, $Si(CH_3)_3$), 7.51 (s, 8 H, Ar-*H*), 7.91 (s, 8 H, Ar-*H*); ^{13}C NMR (200 MHz, $CDCl_3$) −0.78, 120.14, 123.70, 124.84, 131.46, 133.48, 154.54; FAB MS ($CHCl_3$/NOBA, *I* = 2.7 v, *m/e*) 1242 (42.0, M^+), 1169 (38.0), 1083 (36.0), 677 (100.0), 460 (52.0). Anal. Calcd for $C_{72}H_{88}O_4Si_8$: C, 69.62; H, 7.14. Found (dried at 150 °C at 10^{-5} mmHg): C, 69.29; H, 7.11.

4,6-Dibromodibenzofuran (13). Under dry conditions under an Ar atmosphere, a solution of dibenzofuran (24.08 g, 0.1433 mol), TMEDA (64 mL, 0.42 mol), and 1400 mL of dry Et_2O was cooled to −78 °C. To the solution was added via syringe *sec*-butyllithium (331 mL, 0.42 mol, 1.3 M in cyclohexane), and the reaction mixture was warmed to 25 °C for 20 h. The mixture was cooled to −78 °C, and bromine (25 mL, 0.48 mol) in 25 mL of pentane was added. The mixture was warmed to 25 °C for 18 h, and 500 mL of 30% aqueous $NaHSO_3$ was added to the solution. The two phases were separated, and the aqueous phase was extracted with 400 mL of Et_2O. The ether extract was combined with the organic phase from the reaction, and the solution was washed with 400 mL of 30% aqueous $NaHSO_3$ and 800 mL of water, dried ($MgSO_4$), and concentrated. The residue was recrystallized from cyclohexane, and the product was dried under high vacuum to give dibromide **13** (30.37 g, 0.0931 mol, 65%), a pale yellow crystalline solid: mp 146–148 °C; ^{1}H NMR (200 MHz, $CDCl_3$) 7.25 (dd, *J* = 7.9, 2 H, Ar-*H*), 7.65 (d, *J* = 7.9, 2 H, Ar-*H*), 7.86 (d, *J* = 7.9, 2 H, Ar-*H*); MS (180 °C, 70 eV, *m/e*) 328 (48.0, M^+), 326 (100.0, M^+), 324 (47.0, M^+). Anal. Calcd for $C_{12}H_6Br_2O$: C, 44.21; H, 1.86. Found: C, 44.43; H, 1.89.

6-Bromo-4-dibenzofurancarboxylic Acid (14). Under dry conditions under an Ar atmosphere, a solution of dibromide **13** (10.0 g, 0.0307 mol) in 80 mL of dry THF and 270 mL of dry Et_2O was cooled to −78 °C. To the heterogeneous solution, phenyllithium (15.3 mL, 0.0306 mol, 2.0 M in cyclohexane) was added via syringe to produce a yellow heterogeneous solution. After 50 min at −78 °C, CO_2 was bubbled into the lithiate at a very rapid rate. When the yellow solution color faded, the flow of CO_2 was halted, and the quenched mixture was warmed to 25 °C and allowed to stand for 18 h. After 200 mL of 2 N aqueous HCl had been added to the mixture, the organic solvents were removed under vacuum. The white precipitate was filtered, washed with water, and recrystallized from benzene. The product was dried under high vacuum to give pure **14** (8.45 g, 0.029 mol, SiO_2, R_f 0.5: 5% CH_3OH/CH_2Cl_2, 95%) as a white powder: mp 274–275 °C; ^{1}H NMR (200 MHz, acetone-d_6) 7.38 (t, *J* = 8.0, 1 H, Ar-*H*), 7.56 (t, *J* = 8.0, 1 H, Ar-*H*), 7.76 (d, *J* = 8.0, 1 H, Ar-*H*), 8.17 (d, *J* = 8.0, 2 H, Ar-*H*), 8.40 (d, *J* = 8.0, 1 H, Ar-*H*); MS (130 °C, 70 eV, *m/e*) 292 (97.6, M^+), 290 (100.0, M^+). Anal. Calcd for $C_{13}H_7BrO_3$: C, 53.62; H, 2.42. Found: C, 53.64; H, 2.35.

6-Bromo-4-dibenzofuranmethanol (15). Under dry conditions under an Ar atmosphere, borane (27 mL, 0.027 mol, 1 M in THF) was added carefully via syringe to a solution of carboxylic acid **14** (3.17 g, 0.0109 mol) in 25 mL of dry THF. The reaction mixture was heated to reflux for 18 h. The solution was cooled to 25 °C, and an aqueous solution of Na_2CO_3 (3.0 g in 50 mL of H_2O) was added very slowly to the reaction mixture until gas evolution ceased. The THF was removed under vacuum, and the residue was extracted with 300 mL of CH_2Cl_2. The extract was washed with 200 mL of 6 M NaOH and 300 mL of water, dried ($MgSO_4$), and concentrated. The residue was recrystallized from methanol and hexanes. The product was dried under high vacuum to give alcohol **15** (2.78 g, 0.0100 mol, 92%) as a white crystalline solid: mp 132–134 °C; ^{1}H NMR (200 MHz, $CDCl_3$) 2.05 (t, *J* = 6.4, 1 H, −O*H*), 5.12 (d, *J* = 6.4, 2 H, Ar-CH_2), 7.22 (t, *J* = 7.6, 1 H, Ar-*H*), 7.37 (t, *J* = 7.6, 1 H, Ar-*H*), 7.52 (d, *J* = 7.9, 1 H, Ar-*H*), 7.59 (d, *J* = 7.9, 1 H, Ar-*H*), 7.87 (d, *J* = 7.6, 2 H, Ar-*H*); MS (200 °C, 16 eV, *m/e*) 278 (96.3, M^+), 276 (100.0, M^+). Anal. Calcd for $C_{13}H_9BrO_2$: C, 56.35; H, 3.27. Found: C, 56.47; H, 3.39.

4,6-Dibenzofuranylbisboronic Acid (16). Under dry conditions under an Ar atmosphere, a solution of dibenzofuran (13.36 g, 0.0795 mol), TMEDA (36 mL, 0.239 mol), and 500 mL of dry Et_2O was cooled to −78 °C. To the solution, *sec*-butyllithium (184 mL, 0.239 mol, 1.3 M in cyclohexane) was added via syringe. The reaction mixture was warmed to 25 °C for 25 h. After the solution was cooled to −78 °C, $(CH_3O)_3B$ (90 mL, 0.792 mol) was added quickly via syringe. The quenched mixture was warmed to 25 °C for 12 h. Following the addition of 500 mL of 6 N aqueous HCl to the mixture, the two layers were separated. The aqueous phase was extracted with 1 L of Et_2O, and the extract was combined with the ether phase from the reaction. The ether solution was basified with 6 N NaOH to pH 13. After stirring for 1 h, the two phases of the solution were separated. The aqueous phase was acidified to pH 1 with concentrated HCl to produce a white precipitate. The solid was filtered, washed with water, and dissolved in acetone. The acetone solution was dried ($MgSO_4$) and concentrated. The product was dried under high vacuum to give bisboronic acid **16** (13.23 g, 0.0517 mol, 65%) as a white solid. The product was stored in the refrigerator in the presence of moisture to prevent anhydride formation. Prior to use in a reaction, the bisboronic acid was dried under high vacuum to enable an accurate weight determination: mp > 300 °C; ^{1}H NMR (200 MHz, DMSO-d_6) 3.35 (b s, 4 H, $-B(OH)_2$), 7.38 (t, *J* = 7.3, 2 H, Ar-*H*), 7.78 (d, *J* = 7.3, 2 H, Ar-*H*), 8.19 (d, *J* = 7.3, 1 H, Ar-*H*); MS (270 °C, 16 eV, *m/e*) 256 (71.7, M^+), 255 (30.7), 238 (12.7), 212 (4.4). Anal. Calcd for $C_{12}H_{10}B_2O_5 \cdot 2H_2O$: C, 49.38; H, 4.83. Found: C, 48.98; H, 4.12.

[4,4′:6′,4″-Terdibenzofuran]-6,6″-dimethanol (17). Under dry conditions under an Ar atmosphere, a mixture of alcohol **15** (1.24 g, 0.00448 mol), 40 mL of benzene, 20 mL of 2 M aqueous Na_2CO_3, bisboronic acid **16** (1.10 g, 0.0043 mol), 30 mL of 95% ethanol, and $Pd(Ph_3P)_4$ (52 mg, 0.045 mmol) was heated to reflux for 23 h. The reaction mixture was cooled to 25 °C, and 50 mL of water was added. The white precipitate that formed was filtered, washed with water, CH_2Cl_2, and methanol, and dried under high vacuum to give pure diol **17** (0.997 g, 0.00178 mol, 80%): mp > 300 °C; ^{1}H NMR (500 MHz, DMSO-d_6) 4.68 (d, *J* = 5.2, 4 H, Ar-CH_2-OH), 5.26 (t, *J* = 5.2, 2 H, CH_2-OH), 6.94 (t, *J* = 7.7, 2 H, Ar-*H*), 7.45 (t, *J* = 7.7, 2 H, Ar-*H*), 7.56 (d, *J* = 7.7, 2 H, Ar-*H*), 7.69 (t, *J* = 7.7, 2 H, Ar-*H*), 7.88 (d, *J* = 7.7, 2 H, Ar-*H*), 8.05–8.08 (m, 2 H, Ar-*H*), 8.10 (d, *J* = 7.7, 2 H, Ar-*H*), 8.38 (d, *J* = 7.7, 2 H, Ar-*H*); MS (280 °C, 70 eV, *m/e*) 560 (10.4, M^+), 558 (10.3), 544 (16.6), 543 (38.2), 542 (100.0). Anal. Calcd for $C_{38}H_{24}O_5 \cdot Na_2CO_3 \cdot H_2O$: C, 68.42; H, 3.83. Found: C, 68.51; H, 3.62.

6,6″-Bis(chloromethyl)[4,4′:6′,4″-terdibenzofuran] (18). Under dry conditions under an Ar atmosphere, $(Ph)_3P$ (307 mg, 1.17 mmol) in 15 mL of dry THF was added via syringe to a solution of bisalcohol **17** (305 mg, 0.545 mmol), *N*-chlorosuccinimide (156 mg, 1.17 mmol, recrystallized from benzene), and 50 mL of dry THF. The reaction mixture was stirred at 25 °C for 18 h. To the solution, 50 mL of water was added and a white precipitate formed. The THF was removed under vacuum, and the residue was extracted with 300 mL of CH_2Cl_2. The extract was washed with 300 mL of water, dried ($MgSO_4$), and concentrated. Flash chromatography (30 g of SiO_2, 1:1 CH_2Cl_2/hexanes, R_f 0.7) of the residue and concentration of the product under high vacuum gave bischloride **18** (227 mg, 0.38 mmol, 70%): mp 252–254 °C; ^{1}H NMR (500 MHz, DMSO-d_6) 4.74 (s, 4 H, Ar-CH_2-Cl), 7.14 (t, *J* = 7.5, 2 H, Ar-*H*), 7.42 (t, *J* = 7.7, 2 H, Ar-*H*), 7.56 (d, *J* = 7.0, 2 H, Ar-*H*), 7.69 (t, *J* = 7.7, 2 H, Ar-*H*), 7.93 (d, *J* = 7.7, 2 H, Ar-*H*), 8.08–8.13 (m, 6 H, Ar-*H*), 8.39 (d, *J* = 7.7, 2 H, Ar-*H*); MS (210 °C, 70 eV, *m/e*) 600 (12.2), 599 (27.4, M^+), 598 (68.2, M^+), 597 (39.3, M^+), 596 (100.0, M^+). Anal. Calcd for $C_{38}H_{22}Cl_2O_3$: C, 76.39; H, 3.71. Found: C, 76.26; H, 3.83.

9,10-Dihydro-9-[(4-methylpheny l)sulfonyl] 7,4,6:11,12,14:18,19,21-tri[1,3]butadien[1]yl[4]ylidene-8*H*-tribenzo[*j*,*l*,*q*][1,9,14,5]trioxazacyclooctadecine (5). Under dry conditions under an Ar atmosphere, Cs_2CO_3 (1.53 g, 0.00469 mol) was suspended in 200 mL of dry DMA. To the mixture, a solution of bischloride **18** (280 mg, 0.47 mmol) in 42 mL of dry DMA and a solution of tosylamide (80 mg, 0.47 mmol) in 42 mL of dry DMA, each in a syringe, were added via syringe pump over 26 h at 25 °C. The reaction mixture was stirred at 25 °C for an additional 2 days. The reaction mixture was poured into 500 mL of water and acidified to pH 3 with 10 mL of 2 N aqueous HCl to precipitate a white solid. The solid was filtered and dissolved in 100 mL of CH_2Cl_2. The solution was washed with 100 mL of water and 100 mL of brine, dried ($MgSO_4$), and concentrated. Flash chromatography (50 g of SiO_2, CH_2Cl_2, R_f 0.7) of the residue and concentration of the product under high vacuum gave **5** (248 mg, 0.357 mmol, 76%). The white crystalline solid, cycle **5**, is slightly soluble in chlorinated hydrocarbon solvents and very soluble in aromatic solvents. Crystallization of **5** from a variety of solvent mixtures (e.g., $HCCl_3$/hexanes, benzene/cyclohexane, EtOAc/hexanes, $HCCl_3$/cyclohexane, benzene, toluene) yielded feather-like crystals, unsuitable for crystal structure determination: mp > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 2.46 (s, 3 H, Ar-CH_3), 4.42 (d, *J* = 15.3, 2 H, Ar-CH_2-N), 4.94 (d, *J* = 15.3, 2 H, Ar-CH_2-N), 7.15 (t, *J* = 8.0, 2 H, Ar-*H*), 7.25–7.30 (m, 6 H, Ar-*H*), 7.35 (d, *J* = 8.0, 2 H, Ar-*H*), 7.47 (d, *J* = 7.3, 2 H, Ar-*H*), 7.54 (t, *J* = 8.0, 2 H, Ar-*H*), 7.59 (d, *J* = 7.6, 2 H, Ar-*H*), 7.77–7.81 (m, 4 H, Ar-*H*), 8.16 (d, *J* = 7.8, 2 H, Ar-*H*); MS (280 °C, 16 eV, *m/e*) 697 (9.3), 696 (24.9), 695 (57.2, M^+), 542 (11.4), 541 (39.4), 540 (100.0), 539 (69.4). Anal. Calcd for $C_{45}H_{29}NO_5S$: C, 77.68; H, 4.20. Found: C, 77.62; H, 4.11.

7,4,6:11,12,14:18,19,21-Tri[1,3]butadien[1]yl[4]ylidene-8*H*-tribenzo[*b*,*d*,*i*][1,6,11]trioxacyclooctadecin-9(10*H*)-one (6). In a dry Ar atmosphere, KH (200 mg, 1.5 mmol, 24.4% suspension in oil) was suspended in 200 mL of dry THF. To the mixture were added a solution of bischloride **18** (220 mg, 0.368 mmol) in 42 mL of dry THF and a solution

of tosylmethyl isocyanide (72 mg, 0.37 mmol) in 42 mL of dry THF, each in a syringe, via syringe pump over 26 h at 25 °C. The reaction mixture was stirred at 25 °C for an additional 2 days. To the reaction mixture, 50 mL of water and 50 mL of brine were added, and the THF was removed under vacuum. The residue was extracted with 500 mL of CH_2Cl_2, and the extract was washed with 100 mL of water and 100 mL of brine, dried ($MgSO_4$), and concentrated. Flash chromatography (50 g of SiO_2, CH_2Cl_2, R_f 0.6) of the residue yielded 24 mg of the isocyanide intermediate. Treatment of the intermediate dissolved in 5 mL of benzene with 2 N aqueous HCl at 25 °C for 6 h, and concentration of the benzene phase under high vacuum gave ketone cycle **6** (14.7 mg, 0.026 mmol, 7.2%). The white crystalline solid (**6**) is slightly soluble in chlorinated hydrocarbon solvents and very soluble in aromatic solvents. Crystallization of **6** from CH_2Cl_2 and Et_2O yielded hexagonally-shaped crystals, suitable for crystal structure determination: mp > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 3.49 (d, J = 13.3, 2 H, Ar-CH_2), 4.50 (d, J = 13.3, 2 H, Ar-CH_2), 7.05 (d, J = 12.7, 4 H, Ar-*H*), 7.23–7.37 (m, 6 H, Ar-*H*), 7.50 (d, J = 7.2, 2 H, Ar-*H*), 7.55–7.60 (m, 4 H, Ar-*H*), 7.75 (d, J = 7.6, 2 H, Ar-*H*); MS (230 °C, 16 eV, m/e) 555 (40.6), 554 (100.0, M^+), 527 (11.9), 526 (34.7). Anal. Calcd for $C_{39}H_{22}O_4 \cdot 3H_2O$: C, 76.96; H, 4.64. Found (dried at 25 °C and 10^{-5} mmHg): C, 76.88; H, 5.07. Calcd for $C_{39}H_{22}O_4 \cdot 2H_2O$: C, 79.31; H, 4.44. Found (dried at 100 °C and 10^{-5} mmHg): C, 78.66; H, 4.94. Water appears to depart the crystal lattice very slowly and incompletely.

[2,8-Bis(trimethylsilyl)-4,6-dibenzofurandiyl]bisboronic Acid (19). In a dry Ar atmosphere, a solution of TMEDA (7.65 mL, 0.050 mol) in 125 mL of dry Et_2O was cooled to −78 °C. To the solution was added *sec*-butyllithium (39.0 mL, 0.050 mol, 1.3 M in cyclohexane) via syringe. After 10 min, a solution of silane **11** (5.28 g, 0.0169 mol, azeotroped with hexanes and dried under high vacuum for 1 day) in 35 mL of dry Et_2O at −78 °C was cannulated into the reaction medium. The reaction mixture was warmed to 25 °C for 18 h. The lithiate at −78 °C was cannulated into a solution of $(CH_3O)_3B$ (16 mL, 0.14 mol) in 50 mL of dry Et_2O at −78 °C, and the quenched mixture was warmed to 25 °C for 3 h. To the solution was added 50 mL of water. The aqueous phase was isolated and extracted with 300 mL of Et_2O. The organic phase from the reaction mixture was combined with the ether extracts. This solution was washed with 500 mL of water and 500 mL of brine, dried ($MgSO_4$), and concentrated under vacuum. The residue was dried under high vacuum to afford bisboronic acid **19** (6.21 g, 0.0155 mol, 92%) as a white foam: mp 233–237 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) 0.35 (s, 18 H, Si-CH_3), 8.01 (s, 2 H, Ar-*H*), 8.22 (s, 2 H, Ar-*H*); MS (280 °C, 70 eV, m/e) 400 (3.9, M^+), 399 (17.5), 398 (5.9).

2′,8′-Bis(trimethylsilyl)[4,4′:6′,4″-terdibenzofuran]-6,6″-dimethanol (20). In a dry Ar atmosphere, a mixture of alcohol **15** (2.90 g, 0.0105 mol), 100 mL of benzene, 30 mL of 2 M Na_2CO_3 (aqueous), bisboronic acid **19** (3.14 g, 0.0079 mol), 50 mL of 95% EtOH, and $Pd(Ph_3P)_4$ (200 mg, 0.17 mmol) was heated to reflux for 18 h. The reaction mixture was cooled to 25 °C, and 50 mL of water was added. The organic solvents were removed under vacuum, and the residue was extracted with 400 mL of CH_2Cl_2. The extract was washed with 400 mL of water, dried ($MgSO_4$), and concentrated. Flash chromatography (100 g of RP SiO_2, 3% H_2O/MeOH, R_f 0.25) of the residue and concentration of the product under high vacuum gave pure diol **20** (2.22 g, 0.00315 mol, 60%), a white solid: mp 180–184 °C; ^{1}H NMR (200 MHz, acetone-d_6) 0.48 (s, 18 H, Si-CH_3), 3.72 (b s, 4 H, Ar-CH_2), 4.94 (b s, 2 H, CH_2-O*H*), 7.08 (t, J = 7.3, 2 H, Ar-*H*), 7.42 (t, J = 7.3, 2 H, Ar-*H*), 7.62 (d, J = 6.6, 2 H, Ar-*H*), 8.02 (d, J = 7.3, 4 H, Ar-*H*), 8.35 (s, 2 H, Ar-*H*), 8.55 (s, 2 H, Ar-*H*); MS (230 °C, 16 eV, m/e) 706 (18.7), 705 (56.1), 704 (100.0, M^+). Anal. Calcd for $C_{44}H_{40}O_5Si_2 \cdot 0.5H_2O$: C, 74.02; H, 5.79. Found (dried at 100 °C and 10^{-5} mmHg): C, 74.26; H, 5.88.

6,6″-Bis(chloromethyl)-2′,8′-bis(trimethylsilyl)[4,4′:6′,4″-terdibenzofuran] (21). In a dry Ar atmosphere, Ph_3P (836 mg, 3.19 mmol) in 80 mL of dry THF was added via syringe to a solution of bisalcohol **20** (1.02 g, 1.45 mmol), *N*-chlorosuccinimide (426 mg, 3.19 mmol, recrystallized from benzene), and 50 mL of dry THF. The reaction mixture was stirred at 25 °C for 48 h. To the solution was added 50 mL of water and a white precipitate formed. The THF was removed under vacuum, and the residue was extracted with 300 mL of Et_2O. The extract was washed with 300 mL of water, dried ($MgSO_4$), and concentrated. Preparative chromatography (2 mm SiO_2 chromatotron rotor, 20:80 chloroform/hexanes, R_f 0.4) of the residue, utilizing a chromatotron, and concentration of the product under high vacuum afforded bischloride **21** (764 mg, 1.03 mmol, 71%): mp 274–275.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) 0.49 (s, 18 H, Si-CH_3), 4.65 (s, 4 H, Ar-CH_2-Cl), 7.16 (t, J = 8.0, 2 H, Ar-*H*), 7.25–7.37 (m, 4 H, Ar-*H*), 7.45 (d, J = 7.3, 2 H, Ar-*H*), 7.82–7.89 (m, 2 H, Ar-*H*), 7.97 (d, J = 8.0, 2 H, Ar-*H*), 8.29 (s, 2 H, Ar-*H*), 8.31 (s, 2 H, Ar-*H*); MS (230 °C, 70 eV, m/e) 744 (26.9, M^+), 743 (45.8, M^+), 742 (82.8, M^+), 741 (57.6, M^+), 740 (100.0, M^+), 708 (15.0), 707 (16.6), 706 (32.4). Anal. Calcd for $C_{44}H_{38}Cl_2O_3Si_2$: C, 71.24; H, 5.16. Found: C, 71.19; H, 5.21.

12,13,15,16-Tetrahydro-13,15-dimethyl-3,29-bis(trimethylsilyl) 11,8,10:23,20,22:24,1,25-tri[1,3]butadien[1]yl[4]ylidene-14*H*-tribenzo[*b*,*l*,*n*][1,11,16,5,7]trioxadiazacycloeicosin-14-one (9). In a dry Ar atmosphere, NaH (100 mg, 3.33 mmol, 80% dispersion in mineral oil) was suspended in 40 mL of dry THF, and the mixture was heated to reflux. To the mixture was added a solution of bischloride **21** (210 mg, 0.283 mmol) and 1,3-dimethyl urea (32 mg, 0.364 mmol) in 36 mL of dry DMA, in a syringe, via syringe pump over 20 h. The reaction mixture was stirred at reflux for 1 day and at 25 °C for 1 day. The THF was removed from the reaction mixture under vacuum, and the remaining mixture was poured into 75 mL of water. A white solid precipitated from the mixture. The solid was filtered and dissolved in 150 mL of CH_2Cl_2. The solution was washed with 100 mL of water and 100 mL of brine, dried ($MgSO_4$), and concentrated. Flash chromatography (30 g of SiO_2, 5% acetone/CH_2Cl_2, R_f 0.25) of the residue and concentration of the product under high vacuum afforded urea cycle **8** (13.5 mg, 0.018 mmol, 6.3%). This white crystalline solid is slightly soluble in chlorinated hydrocarbon solvents and soluble in aromatic solvents: mp > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$) 0.05 (s, 18 H, Si-CH_3), 2.63 (s, 6 H, N-CH_3), 4.10 (d, J = 16.1, 2 H, Ar-CH_2), 4.42 (d, J = 16.1, 2 H, Ar-CH_2), 6.84 (d, J = 7.3, 2 H, Ar-*H*), 6.98 (t, J = 8.7, 2 H, Ar-*H*), 7.17 (t, J = 8.7, 2 H, Ar-*H*), 7.34 (d, J = 8.7, 2 H, Ar-*H*), 7.53–7.57 (m, 4 H, Ar-*H*), 7.68 (d, J = 8.7, 2 H, Ar-*H*), 8.17 (d, J = 7.3, 2 H, Ar-*H*); FAB MS (70 eV, m/e) 612 (30.0, M − 2TMS), 555 (52.0, M − $CONCH_3$). Anal. Calcd for $C_{47}H_{44}N_2O_4Si_2$: C, 74.57; H, 5.86. Found (dried at 25 °C and 10^{-3} mmHg): C, 74.32; H, 5.69.

12,13,14,15,16,17-Hexahydro-13,16-dimethyl-3,30-bis(trimethylsilyl) 11,8,10:24,21,23:25,1,26-tri[1,3]butadien[1]yl[4]ylidenetribenzo[*b*,*m*,*o*][1,12,17,5,8]trioxadiazacyclotrioxadiazacyclohexacosine (8). In a dry Ar atmosphere, Cs_2CO_3 (730 mg, 2.24 mmol) was suspended in 70 mL of dry DMA, and the mixture was heated to 65 °C. To the mixture were added a solution of bischloride **21** (165 mg, 0.223 mmol) in 15 mL of dry DMA and a solution of *N*,*N*-dimethylethylenediamine (39 mg, 0.443 mmol) in 31 mL of dry DMA, each in a syringe, via syringe pump over 24 h. The reaction mixture was stirred at 65 °C for 1 day and at 25 °C for 1 day. The reaction mixture was poured into 75 mL of water, and a beige solid precipitated from the mixture. The solid was filtered and dissolved in 150 mL of CH_2Cl_2. The solution was washed with 100 mL of water and 100 mL of brine, dried ($MgSO_4$), and concentrated. Flash chromatography (15 g of SiO_2, 4% MeOH/CH_2Cl_2, R_f 0.14) of the residue and concentration of the product under high vacuum afforded diamine cycle **8** (19.4 mg, 0.026 mmol, 11.5%). This white crystalline solid is soluble in methanol, acetone, chlorinated hydrocarbon solvents, and aromatic solvents. Host **8** was found "hard to burn" during elemental analysis: mp 238–256 °C dec; ^{1}H NMR (360 MHz, $ClCD_2CD_2Cl$, 356 K) 0.45 (s, 18 H, Si-CH_3), 2.05 (s, 3 H, N-CH_3), 2.12 (s, 3 H, N-CH_3), 2.54 (b s, 2 H, N-CH_2), 2.74 (b s, 2 H, N-CH_2), 3.49 (d, J = 13.3, 2 H, Ar-CH_2), 3.73 (d, J = 13.3, 2 H, Ar-CH_2), 7.20–7.27 (m, 6 H, Ar-*H*), 7.50 (d, J = 6.3, 2 H, Ar-*H*), 7.75 (d, J = 7.7, 2 H, Ar-*H*), 7.82–7.85 (m, 4 H, Ar-*H*), 8.29 (s, 2 H, Ar-*H*); FAB MS (25 °C, 5.5 kV, m/e) 759 (20.6), 758 (58.2), 757 (100.0, M^+ + 1), 756 (18.5), 755 (19.2), 727 (11.5), 713 (36.8), 700 (31.0). Anal. Calcd for $C_{48}H_{48}N_2O_3Si_2 \cdot CH_3OH$: C, 74.58; H, 6.64. Found (dried at 78 °C and 10^{-3} mmHg): C, 74.34; H, 6.64.

9,10-Dihydro-9-[(4-methylphenyl)sulfonyl]-23,27-bis(trimethylsilyl) 7,4,6:11,12,14:18,19,21-tri[1,3]butadien[1]yl[4]ylidene-8*H*-tribenzo[*j*,*l*,*q*][1,9,14,5]trioxaazacyclooctadecine (7). In a dry Ar atmosphere, Cs_2CO_3 (444 mg, 1.36 mmol) was suspended in 65 mL of dry DMA. To the mixture were added a solution of bischloride **21** (100.8 mg, 0.136 mmol) in 23 mL of dry DMA and a solution of tosylamide (23 mg, 0.136 mmol) in 23 mL of dry DMA, each in a syringe, via syringe pump over 26 h at 25 °C. The reaction mixture was stirred at 25 °C for an additional 3 days. The reaction mixture was poured into 200 mL of water and acidified to pH 3 with 5 mL of 2 N aqueous HCl. A white solid precipitated from the mixture. The solid was filtered and then dissolved in 150 mL of CH_2Cl_2. The solution was washed with 100 mL of water and 100 mL of brine, dried ($MgSO_4$), and concentrated. Preparative thin-layer chromatography (2 mm SiO_2, CH_2Cl_2, R_f 0.7) of the residue and concentration of the product under high vacuum gave tosylamide cycle **7** (84 mg, 0.100 mmol, 74%). This white crystalline solid is soluble in chlorinated hydrocarbon solvents and very soluble in aromatic solvents: mp > 280 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 0.46 (s, 18 H, Si-CH_3), 2.45 (s, 3 H, Ar-CH_3), 4.49 (d, J = 15.3, 2 H, Ar-CH_2), 4.97 (d, J = 15.3, 2 H, Ar-CH_2), 7.15–7.18 (m, 4 H, Ar-*H*), 7.25 (d, J = 6.3, 2 H, Ar-*H*), 7.34 (d, J = 8.0, 2 H, Ar-*H*), 7.52 (d, J = 7.1, 2 H, Ar-*H*), 7.59–7.64 (m, 6 H, Ar-*H*), 7.82 (d, J = 8.1, 2 H, Ar-*H*), 8.35 (s, 2 H, Ar-*H*); FAB MS (25 °C, 16 eV, m/e) 842 (27.5), 841 (54.7), 840 (100.0, M^+ + 1), 839 (39.1), 824 (16.5). Anal. Calcd for $C_{51}H_{45}NO_5SSi_2 \cdot H_2O$: C, 71.38; H, 5.52. Found (dried at 25 °C and 10^{-3} mmHg): C, 71.18; H, 5.57.

^{1}H NMR Binding Studies. In a typical experiment, a 4 mM solution of host **4** (2.5 mg in 500 μL of $CDCl_3$) was prepared, and the solution ^{1}H NMR spectrum was recorded. A small aliquot of potential guest in $CDCl_3$ was added via syringe to the host solution (overall guest concentration ranging from 40–400 mM), and the ^{1}H NMR spectrum was recorded. The process was repeated at least ten times in each case to generate enough points for a binding constant calculation. The spectra were taken at 200 MHz at 298 K and were referenced to the residual proton peak of 99.99% $CDCl_3$.

Crystal Structure Determination. Compound **4**·$2C_6H_6$ crystallizes from C_6H_6 as colorless plates in the tetragonal system $I4_1/a$. Unit cell dimensions are as follows: a = 25.147 (2), c = 14.972 (1) Å, v = 9468 Å^3, Z = 4 (each molecule has $\bar{4}$ (S_4) symmetry). This host has two clefts and each cleft contains a (disordered) benzene molecule. This benzene molecule has four C···C distances of 3.6 Å to one of the dibenzofuran fragments of the macrocycle and the plane of the benzene ring is nearly parallel to the plane of that dibenzofuran (within 8°). The crystal was examined on a modified Syntex $P\bar{1}$ diffractometer, Cu Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 167 parameters (1679 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.103. Details will be published elsewhere.

Compound **8** crystallizes from CH_2Cl_2/MeOH as colorless parallelepipeds in the triclinic system $P\bar{1}$. Unit cell dimensions are as follows: a = 11.1041 (9) Å, b = 13.083 (1) Å, c = 16.973 (2) Å, α = 78.047 (5)°, β = 85.090 (5)°, γ = 65.753 (5)°, v = 2180 Å^3, Z = 2. The crystal was examined on a modified Syntex $P\bar{1}$ diffractometer, Cu Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 259 parameters (3100 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.118. Details will be published elsewhere.

This molecule forms centrosymmetric dimers with the following short intermolecular contacts: H···H < 2.7 Å 6, C···H < 3.2 Å 24, C···C < 3.7 Å 24, and O···H < 3.0 Å 2.

Compound **6** crystallizes from $CH_2Cl_2/(C_2H_5)_2O$ as colorless parallelepipeds in the monoclinic system $P2_1/n$. Unit cell dimensions are as follows: a = 16.280 (2) Å, b = 23.417 (4) Å, c = 16.735 (2) Å, β = 102.715 (4)°, v = 6224 Å^3, Z = 8. The crystal was examined on a modified Picker FACS-1 diffractometer, Mo Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 377 parameters (2869 reflections with $I > 2\sigma(I)$) has an agreement value, R, currently at 0.15.

The crystal contains two independent macrocycles. These form dimers by close contacts between dibenzofuran units from each of the two cycles. There are nine C···C contacts between 3.4 and 3.6 Å and the two dibenzofurans are nearly parallel (within 14°) although only one benzene ring from each dibenzofuran nearly overlaps one from the other dibenzofuran. The crystal contains both solvents used in the crystallization. Details will be published elsewhere.

Supplementary Material Available: Experimental details of the crystal structure determination, atom positions and thermal parameters, and bond lengths and angles (26 pages). Ordering information is given on any current masthead page.

Exo-Selective Diels–Alder Reactions of Aminocarbene Complexes

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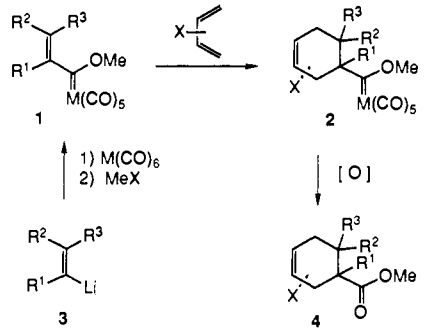
Abstract: The first examples of intermolecular Diels–Alder reactions of aminocarbene complexes are described. Various members of both the alkylamino and acylamino families of complexes are investigated. The E-isomer of [*trans*-propenyl(methylamino)methylene]pentacarbonyltungsten (**22**) will react with Danishefsky's diene and 1-methoxy-1,3-butadiene, but the *Z*-isomer will not. The yields are good only for the more reactive Danishefsky's diene, but all reactions with acyclic dienes are completely selective for the exo cycloadduct (≥96:4). The [*trans*-propenyl(*N*-methyl-*N*-benzoylamino)methylene]pentacarbonyltungsten(0) (**35**) is more reactive than **22**, and if it is converted into the chelated complex **42**, where the oxygen of the benzoyl group replaces a carbon monoxide ligand on the metal, a highly reactive dienophile is obtained. Complex **42** will react with Danishefsky's diene within minutes at room temperature, and although the yields are low (~30%) due to competing dinuclear carbene complex formation, the cycloaddition again occurs with complete exo selectivity (≥97:3). The cycloaddition of **42** with cyclopentadiene is not stereoselective and gives approximately a 1:1 mixture of endo and exo isomers. Possible sources of the unique reactivity and high exo selectivity of these complexes with acyclic dienes are discussed in terms of their solution spectra and the solid-state structures of complexes **22-E**, **22-Z**, and **34**.

Alkenyl alkoxycarbene Fischer carbene complexes of the type **1** were first identified as reactive Diels–Alder dienophiles in 1983.[2] The reaction rates, the endo/exo selectivities, and the regioselectivies were found to be comparable to Lewis acid catalyzed reactions of their corresponding esters.[2,3] Since the metal can be oxidatively removed from the product to give esters, these alkoxy carbene complexes can serve as synthons for esters in the Diels–Alder reaction (Scheme I). Furthermore, Fischer carbene complexes are compatible with sensitive diene functionalities that are not tolerated by the Lewis acidic conditions typically required for Diels–Alder reactions. Alkoxy-substituted Fischer carbene complexes, therefore, have real advantages to offer as synthons for the Diels–Alder reactions.

Scheme I



Although the preparation of alkenylaminocarbene complexes of the type **5** should be trivial (Scheme II), there are no reports

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