Guest Release and Capture by Hemicarcerands Introduces the Phenomenon of Constrictive Binding[1-3]

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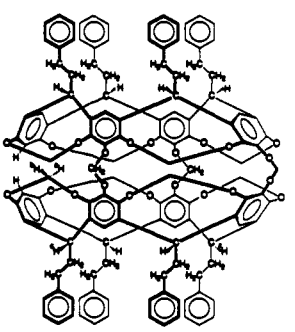
Abstract: Two rigidly hemispherical cavitands containing three out of four possible phenolic hydroxyl groups regularly spaced on their rims were shell closed by their reactions with three molecules of CH_2BrCl and K_2CO_3 in $(CH_3)_2NCHO$, $(CH_3)_2NCOCH_3$, or $(CH_3)_2SO$ to give hemicarceplexes **1**·$(CH_3)_2NCHO$ (20%), **1**·$(CH_3)_2NCOCH_3$ (42%), or **1**·$(CH_3)_2SO$ (51%), respectively. The crystal structure of **1**·$(CH_3)_2NCHO$·$2CH_3CN$·$2CHCl_3$ shows the $(CH_3)_2NCHO$ guest to be firmly lodged within the cavity, the other molecules acting as solvates. The guest's carbonyl group is pointed toward the portal connecting the inner and outer phases. Upon heating in solvents too large to occupy the cavity, these complexes released their guests to give free hemicarcerand **1**. The $t_{1/2}$ values for decomplexation in 1,2,4-$Cl_3C_6H_3$ at 140 °C for **1**·$(CH_3)_2NCHO$ and **1**·$(CH_3)_2NCOCH_3$ were 14 and 34 h, respectively, and for **1**·$(CH_3)_2SO$ at 195 °C, 24 h. When **1** was dissolved in the presence of small molecules such as CH_3CN, CS_2, CH_2Cl_2, or CH_2Br_2, new hemicarcerands **1**·CH_3CN, **1**·CS_2, **1**·CH_2Cl_2, and **1**·CH_2Br_2, respectively, were formed, isolated, and characterized. Complexes **1**·O_2, **1**·N_2, **1**·H_2O, and **1**·Xe in $CDCl_3$ solution were prepared and detected by the effect of guest on the ^1H NMR signals of the host. Only **1**·Xe was kinetically stable and subject to isolation and characterization. The association constant of **1** with N_2 in $CDCl_3$ at 22 °C was estimated to be ~180 M^{-1}, with O_2 to be ~44 M^{-1}, and with Xe to be ~200 M^{-1}. The $t_{1/2}$ value for **1**·Xe dissociating in $CDCl_3$ at 22 °C was 47 h. Formation of **1**·C_6H_6, **1**·$(CH_2)_4O$, and **1**·C_5H_5N required days of refluxing **1** in guest as solvent, and proceeded to 80, 100, and 100% completion, respectively. Heating **1** in a 5:1 solution of C_6H_5Cl–Et_2NH at 65 °C (4 h) gave a 70% conversion to **1**·Et_2NH. Heating **1** in 4:1 solutions of C_6H_5Cl–$CH_3(CH_2)_3NH_2$ at 105 °C (24 h) gave a 90% conversion to **1**·$CH_3(CH_2)_3NH_2$. No hemicarceplexes were formed when **1** was heated at reflux in $CHCl_3$, C_6H_5Cl, $C_6H_5CH_3$, $(CH_3)_2CHC_6H_5$, or 1,2,4-$Cl_3C_6H_3$. The ^1H NMR signals of incarcerated guests were moved upfield by 1-4 ppm while the ^{129}Xe signal of **1**·Xe was moved upfield 101 ppm compared to free guest dissolved in $CDCl_3$. We suggest the term *constrictive binding* to describe the steric forces that must be overcome for decomplexation of hemicarceplexes whose guest cross sectional sizes exceed those of the host's portals.

In prior papers of this series, we have reported studies of host–guest complexes bound to one another by polar attractions (e.g., hydrogen bonding, ion pairing, ion dipole, dipole–dipole, metal ligating),[4] and by steric repulsions in which guests are fully incarcerated in rigidly hollow hosts (carceplexes).[5] Here we report the syntheses of the new host **1**, the first hemicarcerand, whose rigidly hollow shell contains a portal through which guests can enter and depart the inner phase by thermally overcoming the steric constraints imposed by the size and shape of the guest, and those of the portal and the attractions of the inner phase. We propose the term *constrictive binding* to apply to the steric repulsions that must be overcome for dissociation of a hemicarceplex.

The first section describes the syntheses of hemicarceplexes **1**·guest (**1**·G) and **2**·$(CH_3)_2NCHO$, hemicarcerand **1**, and carceplexes **3**·$(CH_3)_2SO$ and **4**·$(CH_3)_2SO$. The second part reports the crystal structure of **1**·$(CH_3)_2NCHO$. The third section gives the characterization of the complexes. The fourth part details the decomplexation kinetics of **1**·$(CH_3)_2NCHO$, **1**·$(CH_3)_2NCOCH_3$, and **1**·$(CH_3)_2SO$ to give **1** and free guest. Free **1** and its complexation with N_2, O_2, H_2O, and CO_2 are described in the fifth section. The sixth part deals with hemicarceplexes formable at ambient temperature, and the seventh with hemicarceplexes formable at only elevated temperatures. The eighth part lists molecules too large to serve as guests. The last section describes the protonation and isotopic exchange of incarcerated amines.



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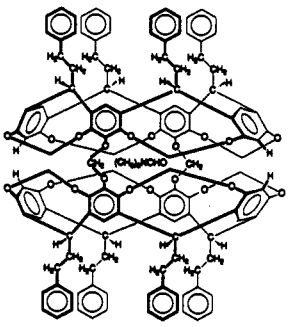
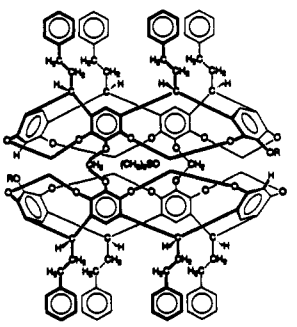


2·$(CH_3)_2NCHO$



3·$(CH_3)_2SO$, R = H; **4**·$(CH_3)_2SO$, R = CH_3

Results and Discussion

Syntheses. The triol **6** was initially isolated as a byproduct (23%) in the synthesis of tetrol **5**, needed as an intermediate in the synthesis of carceplexes **8**·G.[5d] In an attempt to increase the yield of triol **6** and obtain diol **7** as well, the readily available octol **9**[6] was brominated with only three moles of *N*-bromosuccinimide

(1) Host–Guest Complexation. 58.

(2) We warmly thank the National Science Foundation for supporting Grant NSF CHE 8802800.

(3) A preliminary account of a fraction of these results has appeared: Tanner, M. E.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 1659–1660.

(4) (a) Cram, D. J. *Science* **1988**, *240*, 760–767. (b) Cram, D. J. *Chemtracts* **1988**, *1*, 89–101.

(5) (a) Cram, D. J.; Karbach, S.; Kim, Y. H.; Baczynskyj, L.; Marti, K. J.; Sampson, R. M.; Kalleymeyn, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 2554–2560. (b) Sherman, J. C.; Cram, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 4527–4528. (c) Bryant, J. A.; Blanda, M. T.; Vincenti, M.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, *112*, 1403–1405. (d) Sherman, J. C.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 2167–2172. (e) Bryant, J. A.; Blanda, M. T.; Vincenti, M.; Cram, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 2194–2204.

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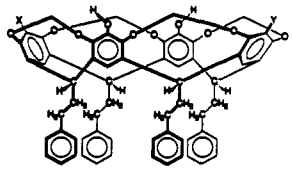
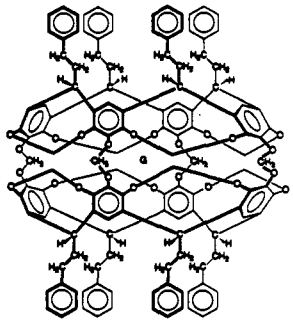
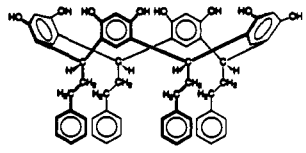
to give a statistical mixture of mono-, di-, tri-, and tetrabrominated octols. The tetrabrominated material precipitated from the reaction mixture, and the three soluble bromides were carried through the following steps without separation. The four sets of hydroxyl groups were bridged (excess CH_2BrCl–$(CH_3)_2NCHO$–K_2CO_3) by four methylenes. The resulting mixture of four bromides was lithiated (*n*-BuLi–$(CH_2)_4O$ at −78 °C), and the organometallics produced were quenched with $(CH_3O)_3B$. The aryl borate mixture was oxidized with basic H_2O_2 to produce a mixture of the four phenols, which were separated by chromatography (silica gel). The overall yield of triol **6** based on **9** was 5%, not far from the 7% reported in the original synthesis.[5d] The diols (8%) were obtained as a 2:1 mixture of **7** (the A,C-isomer) and the A,B-diol, which were separated through their dibenzoate esters to provide an overall yield of 2% for **7**.



5, X = Y = OH; **6**, X = H, Y = OH; **7**, X = Y = H



8•G



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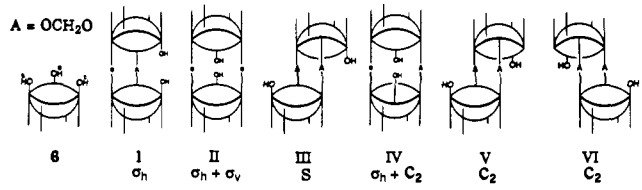
The shell closures were conducted by procedures similar to those which led to carceplexes **8**•G. Solutions of triol **6** and CH_2ClBr were added over several hours to suspensions of Cs_2CO_3 in pure, dry $(CH_3)_2NCHO$, $(CH_3)_2NCOCH_3$, or $(CH_3)_2SO$ stirred at 60 °C. The temperature was raised to 100 °C for 24 h, and the products were isolated by evaporation, extraction, and chromatography to give **1**•$(CH_3)_2NCHO$ (20%), **1**•$(CH_3)_2NCOCH_3$ (42%), and **1**•$(CH_3)_2SO$ (51%), respectively. These yields are remarkably high, and compare well with the yields of the corresponding carceplexes, **8**•$(CH_3)_2NCHO$ (49%), **8**•$(CH_3)_2NCOCH_3$ (51%), and **8**•$(CH_3)_2SO$ (61%).[5d] Hemicarceplex **3**•$(CH_3)_2SO$ was isolated as a byproduct (5%) and converted to its bismethyl derivative, **4**•$(CH_3)_2SO$ (>80%), with CH_3I–NaH in refluxing tetrahydrofuran.

Interesting questions arise concerning the numbers of different reaction pathways that are formally available for arriving at **1**•G and **3**•G and their isomers from triol **6**. In this analysis, we make the following assumptions: (1) that the final partitioning of intermediates between polymer and **1**•G depends mainly on the relative amounts of I–VI (the compounds are intermediates envisioned as formed by the first ring closures); (2) that $ArOCH_2Cl$ intermediates are formed at rates much slower than they react with ArOH to give $ArOCH_2OAr$;[7] (3) that both kinds of hydroxyl groups (a and c on the one hand, and b on the other) are of equal reactivity; (4) that their $ArOCH_2Cl$ derivatives are of equal reactivity; (5) that structurally feasible ring closures occur faster than competing oligomerization reactions; and (6) that competing ring closures (e.g., those leading to I and III) go at the same rate. There are sixteen different ways of assembling I–VI taken in sum, four of which lead to I (limiting yield, 25%), two leading to II (limiting yield, 12.5%), four leading to III (limiting yield, 25%), two leading to IV (limiting yield, 12.5%), two leading to V (limiting yield, 12.5%), and two leading to VI (limiting yield, 12.5%). Intermediates I and II can lead to shell-closed product **1**, whereas further reactions of III–VI can lead only to polymer. Notice that IV is only a different way of representing the host of isolated diol **3**•$(CH_3)_2SO$. Thus, subject to the validity of the assumptions, a statistical yield of **1**•G is only 37.5%. The interesting symmetry properties of I–VI are listed below their formulas.



The yields of **1**•G were 42 and 51%, respectively, when the solvents employed were $(CH_3)_2NCOCH_3$ and $(CH_3)_2SO$, somewhat in excess of the statistical yield of 37.5%. We attribute the excess yields of shell-closed product to a special role played by solvent, which favors forming I, II, and IV over III, V, and VI. The transition state for forging the last O–CH_2 link leading to I, II, and IV is highly polar, and must be solvated by the solvent molecule eventually found incarcerated in the interiors of **1**•G, **2**•G, and **3**•G. Molecular models (CPK) of I, II, and IV show that *1 mol* of any of the three solvents used is well accommodated in these interiors. In contrast, the transition states leading to III, V, and VI must involve 2 mol of solvent, one in each bowl, which means 1 mol more of solvent must be collected and oriented in these transition states than in those leading to I, II, and IV. Thus, assumption 6 is probably invalid. Another feature that might favor ring closures leading to I and II is the proximity of the two nonreacting hydroxyl groups, which are within hydrogen-bonding distances of one another in their CPK models, and probably so in their transition states as well. In this connection, it should be noted that the isolated 5% yield of **3**•$(CH_3)_2SO$ is 40% of that predicted by the statistical model. The two hydroxyls cannot hydrogen bond one another in **3**. Inasmuch as some **3**•$(CH_3)_2SO$ must have reacted further to give oligomer, this 40% is only part of that which formed.

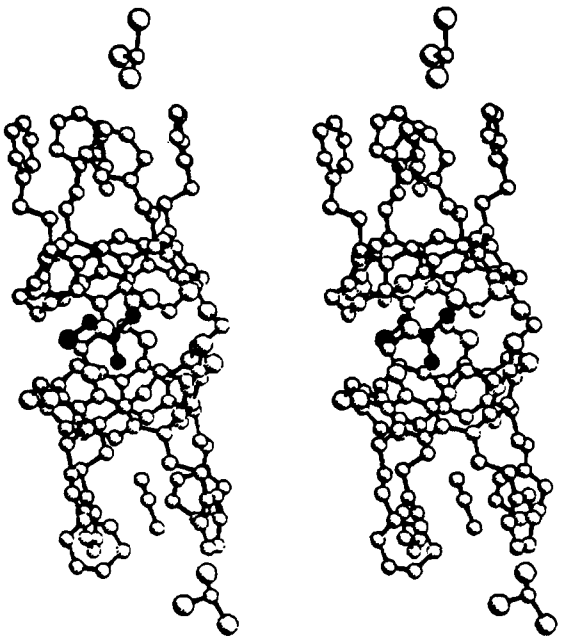
Diol **7**, when subjected to the same shell-closing conditions in $(CH_3)_2NCHO$–$CsCO_3$ gave **2**•$(CH_3)_2NCHO$ in 22% yield, not far from the 20% observed for **1**•$(CH_3)_2NCHO$ from tiol **6**. Here again, nonreacting but intramolecularly hydrogen-bonding hydroxyls were absent in this shell closure. It is noteworthy that the guest molecule in **2**•$(CH_3)_2NCHO$, **3**•$(CH_3)_2SO$, and **4**•$(CH_3)_2SO$ did not escape or undergo solvent exchange reactions during their isolations. In CPK models, the maximum portal size of the four hosts decreases in the order **2** > **1** > **3** > **4**. Guest exchange rates of **2**–**4** will be examined in the future.

As hoped, heating **1**•$(CH_3)_2NCHO$, **1**•$(CH_3)_2NCOCH_3$, or **1**•$(CH_3)_2SO$ in solvents whose molecules are too large to enter the hemicarcerand resulted in expulsion of the guest and production of the free host **1**. When heated at 165 °C in mesitylene, **1**•$(CH_3)_2NCHO$ produced **1** within 12 h and **1**•$(CH_3)_2NCOCH_3$ gave **1** within 24 h, whereas **1**•$(CH_3)_2SO$ remained unchanged even after the extended periods of time. Decomplexation of **1**•$(CH_3)_2SO$ required heating in 1,2,4-$C_6H_3Cl_3$ at 214 °C for 48 h.

Crystal Structure of 1•$(CH_3)_2NCHO$•$2CH_3CN$•$2CHCl_3$. A sample of **1**•$(CH_3)_2NCHO$ was recrystallized from CH_3CN–$CHCl_3$ to give **1**•$(CH_3)_2NCHO$•$2CH_3CN$•$2CHCl_3$, whose crystal structure (R = 0.168) is portrayed in stereoview **10**. The molecule has C_2 symmetry. The $(CH_3)_2NCHO$ guest is fully incarcerated, with its carbonyl group pointing toward the portal. It is disordered about the crystallographic C_2 axis, which is an axis that passes through the oxygen and nitrogen of the guest, the middle interhemisphere's bridging methylene, and the middle of the host's

(6) Tunstad, L. M.; Tucker, J. A.; Dalcanale, E.; Weiser, J.; Bryant, J. A.; Sherman, J. C.; Helgeson, R. C.; Knobler, C. B.; Cram, D. J. *J. Org. Chem.* **1989**, *54*, 1305–1312.

(7) Pappalardo, S.; Bottino, F.; Tringali, C. *J. Org. Chem.* **1987**, *52*, 405–412.



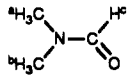
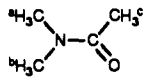
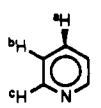
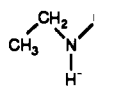
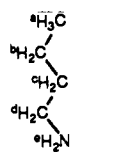
10 (guest heavy atoms darkened)

portal. The long axis of the cavity is 13.4 Å, and is the distance between the planes of the four aryl hydrogens of the northern and of the southern hemispheres. The short axis is 7.2 Å, and is defined as the distance between two interhemispheric bridging oxygens on the same hemisphere flanking the shell hole. Each CH_3CN is packed in a cave composed of four $CH_2CH_2C_6H_5$ groups, with its nitrogen atom directed inward. Each packet of $(CH_2CH_2C_6H_5)_4{\cdot}NCCH_3$ is capped with a $CHCl_3$ molecule, which is disordered about an inversion center. The five heavy atoms of the $(CH_3)_2NCHO$ guest are coplanar, with one methyl group oriented toward and occupying part of the northern hemisphere's cavity, and the other methyl group's axis being roughly coincident with the long hemicarceplex axis and its hydrogens occupying much of the southern hemisphere's cavity.

The planes of the two OCH_2O interhemispheric bridging groups that help define the portal extend the surface of the sphere, with their hydrogens pointing toward the portal, whereas the CH_2 of the third OCH_2O bridging group is oriented outward away from the cavity. As in the crystal structure of $8{\cdot}(CH_3)_2NCOCH_3$,[5d] the whole northern hemisphere is rotated around the long, rough axis of the whole complex by about 13° with respect to the southern hemisphere. This rotation diminishes the cavity and portal sizes somewhat, and allows the OCH_2O groups that define the rims of the two hemispheres to pack together in such a way as to have the hydrogens of the OCH_2O groups in the northern hemisphere pointing toward the oxygens of the OCH_2O groups in the southern hemisphere, and vice versa. Without this rotation, CPK model examination shows that four sets of $O_2CH_2\cdots H_2CO_2$ abut one another, one set bifurcating the portal. Model examination also shows an excellent correlation between structural expectations based on models and those observed in the crystal structure.

Characterization of the Hemicarceplexes. Axiomatic in science is the statement that "the more novel a phenomenon, the more completely documented should be its claims". We obtained a satisfactory analysis for each element present whose sums lay between 99.78 and 100.08% for $1{\cdot}(CH_3)_2NCHO$, $1{\cdot}(CH_3)_2NCOCH_3$, $1{\cdot}(CH_3)_2SO$, and **1**, and each element except oxygen for $2{\cdot}(CH_3)_2NCHO$ and $3{\cdot}(CH_3)_2SO$. These same complexes gave positive-mode FAB mass spectra, all but one of which gave major signals for the hemicarceplexes, the hemicarcerand, or both. In the case of $1{\cdot}(CH_3)_2NCHO$ and $1{\cdot}(CH_3)_2NCOCH_3$, the molecular ion, free **1**, was the parent ion. The spectrum of

Table I. Chemical Shifts (ppm) of Guest Signals in the 500-MHz ^1H NMR Spectra of G and $1{\cdot}G$ in $CDCl_3$ at 22 °C[a]

guest[b]	proton	δ of G in 1·G	δ of free G	Δδ
	[a]H	−0.43	2.86	−3.99
	[b]H	0.22	2.94	−2.73
	[c]H	4.04	7.99	−3.95
	[a]H	−1.43	2.94	−4.37
	[b]H	0.97	3.02	−2.05
	[c]H	−2.24	2.09	−4.33
$(CH_3)_2SO$		−1.20	2.61	−3.81
H_2O		−1.87	1.55	−3.42
CH_3CN		−2.42	2.00	−4.42
2 CH_3CN		−2.15	2.00	−4.15
CH_2Cl_2		2.64	5.30	−2.66
CH_2Br_2		~2.5	4.95	~−2.5
	[a]H	−2.2	1.85	−3.07
	[b]H	−0.23	3.75	−3.98
	[a]H	6.24	7.68	−1.44
	[b]H	2.84	7.30	−4.46
	[c]H	4.08	8.62	−4.54
C_6H_6		3.87	7.36	−3.49
	[a]H	−2.94	1.08	−4.02
	[b]H	−0.48	2.65	−3.13
	[c]H	−1.48		
	[a]H	−3.39	0.90	−4.29
	[b]H	−1.24	1.33	−2.57
	[c]H	−0.94	1.41	−2.35
	[d]H	−1.13	2.27	−3.80
	[e]H	−3.18		

[a] Spectral data for many of the complexes reported in the Experimental Section were obtained at temperatures greater than 22 °C, and small differences resulted. [b] Assignments for $1{\cdot}(CH_3)_2NCHO$ and $1{\cdot}(CH_3)_2NCOCH_3$ were made by analogy with those for the guests of $8{\cdot}(CH_3)_2NCHO$ and $8{\cdot}(CH_3)_2NCOCH_3$ (see ref 5d).

$1{\cdot}(CH_3)_2NCOCH_3$ also gave an 18% signal for the carceplex. Complex $1{\cdot}(CH_3)_2SO$ gave **1** as the parent ion but a very weak molecular ion for the complex. Free hemicarcerand **1** gave the molecular ion as the parent ion. Attempts to obtain a FAB MS of $2{\cdot}(CH_3)_2NCHO$ failed, probably because of its insolubility in the matrix. Complex $3{\cdot}(CH_3)_2SO$ gave a molecular ion of 70% intensity for **3** and one of 20% intensity for $3{\cdot}(CH_3)_2SO$, whereas $4{\cdot}(CH_3)_2SO$ provided a molecular ion for only free **4** (90%). The FTIR spectra in $CDCl_3$ solutions of $1{\cdot}(CH_3)_2NCHO$ and $1{\cdot}(CH_3)_2NCOCH_3$ gave carbonyl bands at 1681 and 1644 cm^{-1}, respectively. The doubling of the carbonyl signal observed for $8{\cdot}(CH_3)_2NCOCH_3$ (KBr)[5d] was not observed for $1{\cdot}(CH_3)_2NCOCH_3$. The carbonyl band for $2{\cdot}(CH_3)_2NCHO$ (KBr) was found at 1682 cm^{-1}.

As with the carceplexes, the ^1H NMR spectra of the hemicarceplexes provide conclusive evidence for the incarceration of guests within the shell. The guest signals were all shifted upfield by 2–4 ppm due to the proximity of their hydrogens to the shielding faces of the eight aryl groups that line most of the cavity. Table I lists these chemical shifts of the guest peaks of $1{\cdot}G$ along with those described in future sections. In each of the complexes made by shell closures ($1{\cdot}G$, $2{\cdot}G$, $3{\cdot}G$, and $4{\cdot}G$), proton integration confirmed the one-to-one stoichiometry for the host and guest. The chemical shifts of the guests were all within 0.2 ppm of those reported for the corresponding carceplexes ($8{\cdot}G$),[5d] indicating the geometry of the two families of complexes to be similar. Notice that most spectra exhibit at least one guest proton signal upfield of that of $(CH_3)_4Si$ at $\delta = 0.00$. In the spectra of $1{\cdot}(CH_3)_2NCHO$, $1{\cdot}(CH_3)_2NCOCH_3$, and $1{\cdot}(CH_3)_2SO$ in $CDCl_3$ at 22 °C, the host's signals due to the inward-facing, intrahemispheric bridging protons were broadened due to partial restriction of guest rotations. The same proton signals for empty **1** were sharp at 22 °C. In the spectrum of $1{\cdot}(CH_3)_2NCOCH_3$ at 60 °C, the number of signals of the host's shell protons are doubled. This phenomenon is

attributed to the inability of the $(CH_3)_2NCOCH_3$ molecule to rotate around the short axes of the host, which causes the northern and southern hemispheres to be slightly different. This same restricted movement was also observed for $8\cdot(CH_3)_2NCOCH_3$, even at temperatures as high as 175 °C.[5d]

When the solutions were cooled to −53 °C, all three of the ^1H NMR host spectra showed further loss of symmetry, presumably due to slowed motions of the guest relative to the host. The guest signal of $1\cdot(CH_3)_2SO$ was unaffected by cooling, unlike that of $8\cdot(CH_3)_2SO$.[5d] Cooling of the $CDCl_3$ solution of $1\cdot(CH_3)_2NCHO$, however, resulted in the splitting of each of the guest's three signals into two sets of unequal proportion (5:1 ratio at −53 °C). This is interpreted as being due to two different guest orientations of minimum energy that possess a 13 kcal mol^{-1} energy barrier at −13 °C for interconversion.[8] A similar duality of structure was observed for $1\cdot(CH_3)_2NCOCH_3$ at −53 °C, and ^1H NMR peak integrations at that temperature indicated the two species to be present in a 25/1 ratio. No such isomeric complexes were observed for either $8\cdot(CH_3)_2NCHO$ or $8\cdot(CH_3)_2NCOCH_3$.[5d] Molecular model examination of $1\cdot(CH_3)_2NCHO$ suggests that the least constrained structure is that observed in crystal structure **10**, and that the less stable isomer might be one in which the plane of the guest is roughly normal to the long north–south axis of the host, with the carbonyl oxygen being located just inside the portal. A similar structure for the less stable form of $1\cdot(CH_3)_2NCOCH_3$ although somewhat strained is still possible.

In the 500-MHz ^1H NMR spectrum in $CDCl_2CDCl_2$ at 22 °C of $2\cdot(CH_3)_2NCHO$, the proton signals of both methyl groups of the guest are located upfield of 0 ppm, and integrated for three protons each. All signals are sharp at ambient temperature, as in the case of $8\cdot(CH_3)_2NCHO$.[5d] In the spectrum in $CDCl_2CDCl_2$ at 22 °C of $3\cdot(CH_3)_2SO$, several of the host signals were quite broad, and the guest signals were slightly broadened. All of the signals are sharp at 80 °C. The methyl protons of the guest at −1.07 ppm integrated for six protons, and no decomplexation was observed at this temperature. The 500-MHz spectrum of $4\cdot(CH_3)_2SO$ in $CDCl_2CDCl_2$ at 52 °C contained a six-proton singlet at −1.26 ppm for its guest's methyl groups. The methoxyl peak was a singlet at 3.93 ppm, and integrated to six protons. Molecular model examinations of both $3\cdot(CH_3)_2SO$ and $4\cdot(CH_3)_2SO$ show them to be almost as rigid as $8\cdot(CH_3)_2SO$, with no portals available for escape of the guest without covalent bonds being broken. Thus, they are probably carceplexes, like $8\cdot(CH_3)_2SO$.

The R_f values on TLC plates of silica gel with 15% hexane/85% $CHCl_3$ as the mobile phase for the various complexes decreased in the following order: $1 > 1\cdot(CH_3)_2SO > 1\cdot(CH_3)_2NCOCH_3 > 1\cdot(CH_3)_2NCHO$.

Decomplexation Kinetics. The first-order rates for decomplexation of $1\cdot(CH_3)_2NCHO$, $1\cdot(CH_3)_2NCOCH_3$, and $1\cdot(CH_3)_2SO$ were each determined in 1,2,4-$Cl_3C_6H_3$. Solutions, 0.3 mM in each complex, were prepared and heated in a temperature-controlled oil bath. Aliquots were removed at timed intervals, and the products were precipitated by the addition of excess hexane. The ratio of free to complexed host in each aliquot was determined by ^1H NMR methods. Plots of $-\ln (A/A_0)$ vs time (5–7 points) gave good straight lines whose slopes provided first-order rate constants for decomplexation as follows: at 140 °C, $1\cdot(CH_3)_2NCHO$ gave $k_d = 8.5 \times 10^{-4}$ min^{-1} ($t_{1/2}$ = 14 h); $1\cdot(CH_3)_2NCOCH_3$ provided $k_d = 3.4 \times 10^{-4}$ min^{-1} ($t_{1/2}$ = 34 h); at 195 °C, $1\cdot(CH_3)_2SO$ gave $k_d = 4.8 \times 10^{-4}$ min^{-1} ($t_{1/2}$ = 24 h). At 140 °C, the decomplexation of $1\cdot(CH_3)_2SO$ was immeasurably slow. The higher energy barrier to decomplexation of $1\cdot(CH_3)_2NCOCH_3$ as compared to $1\cdot(CH_3)_2NCHO$ is attributed to the greater size imparted by the extra methyl in the former as compared to the latter guest. Both guests are essentially planar, and possess disk-shaped cross sections generally complementary to those of the stretched, slot-shaped portal of the host (in models). Molecular model examination of the two complexes suggests that

(8) Interconverting signals separated by 25 Hz had a coalescence temperature of −13 °C. Atta-ur-Raman. *Nuclear Magnetic Resonance*; Springer-Verlag: New York, 1986; pp 131–133.

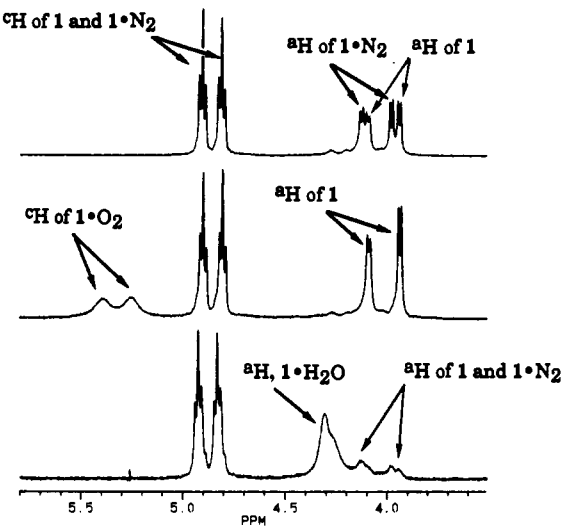


Figure 1. Partial 500-MHz ^1H NMR spectrum in $CDCl_3$ at 22 °C of mixtures of **1** and $1\cdot N_2$ (top), **1** and $1\cdot O_2$ (middle), and **1** and $1\cdot H_2O$ (bottom trace). Guests are exchanging slowly on ^1H NMR scale.

$1\cdot(CH_3)_2NCOCH_3$ itself is somewhat strained, whereas $1\cdot(CH_3)_2NCHO$ appears unstrained. This may explain why the difference in rate constants was not larger. The much higher barrier to decomplexation of $1\cdot(CH_3)_2SO$ is attributed to its tetrahedral shape, whose various cross sections are noncomplementary to the portal of **1**.

Free Hemicarcerand 1 and Its Complexation with N_2, O_2, H_2O, and CO_2. Molecular model examination indicates that chloroform is much too large to enter the cavity of **1** through its portal. Thus, dissolution of empty **1** in $CDCl_3$ amounts to the introduction of holes in solvent that might be filled by small molecules also dissolved in the solvent. The most ubiquitous of small molecules are N_2, O_2, H_2O, and CO_2. Solutions of **1** in untreated $CDCl_3$ gave a ^1H NMR spectrum that exhibits four separate sets of host signals. These arise from $1\cdot N_2$, $1\cdot O_2$, $1\cdot H_2O$, and free **1**, all of which exchange slowly on the ^1H NMR time scale at ambient temperature. The host's proton signals most sensitive to the presence of guests are those of the eight *inward-facing intrahemispheric* OCH_2O bridged protons which in free **1** occur at 3.93 and 4.09 ppm in $CDCl_3$ at 22 °C, and are labeled ^aH in the original structure of **1**. These protons face directly into the highly shielding cavity, and consequently are moved upfield by 2.2 ppm from their diastereotopically related counterparts (^bH), which face outward away from the cavity. In all of the complexes of **1** examined to date, the presence of a guest deshields the ^aH protons and moves them downfield relative to those of free **1**.

Figure 1 provides a partial trace of the 500-MHz ^1H NMR spectrum of a 5 mM solution of **1** in sieve-dried $CDCl_3$ that has been saturated with N_2 (5.6 mM).[9] The ^aH protons of the $1\cdot N_2$ formed are shifted downfield by 0.04 and 0.03 ppm due to the presence of the guest. The methine signals, ^cH, are remote from the cavity and are unaffected by this guest. The observation of separate signals for free and complexed **1** indicate that the barrier to decomplexation is >15 kcal mol^{-1}.[10] Proton-signal integration indicates that approximately 50% of the host contains N_2 under these conditions. The fact that only one set of signals due to complexed host are visible and that N_2 molecules do not possess cohesive interactions suggests the stoichiometry of binding is one-to-one. Subject to the validity of this assumption, we estimate an association constant (K_a) of ~180 M^{-1} ($\Delta G \sim -3$ kcal mol^{-1} at 22 °C) for **1** binding N_2.

(9) Battino, R., Ed. *IUPAC Solubility Data Series*, Pergamon Press: Oxford, 1982; Vol. 10, pp 232–233.

(10) Based on the observation that exchanging host signals separated by 15 Hz for the ^aH protons of $1\cdot N_2$ and by 220 Hz for the ^cH protons of $1\cdot O_2$ are below the coalescence temperature, and signals separated by 185 Hz for the ^aH protons of $1\cdot H_2O$ are close to the coalescence temperature (see literature cited in ref 8).

When the same solution of **1** in $CDCl_3$ was saturated with O_2 gas (11.5 mM),[11] the ^1H NMR spectrum exhibited two differences from that of **1** in degassed $CDCl_3$. First, the integrals of all the signals due to the "shell" protons were decreased by a factor of $^1/_3$ relative to those of the $C_6H_5CH_2CH_2$ groups. Second, two broad signals appeared at 5.24 and 5.38 ppm (see Figure 1). Bound paramagnetic O_2 appears to dramatically broaden and shift the host shell protons of **1**·O_2 due to both scalar coupling and dipole–dipole interactions between the proton nuclei and the unpaired electrons of triplet oxygen.[12] These effects are felt over a distance of several angstroms, and their magnitudes are highly dependent on the distance from the center of the cavity. With diamagnetic guests, the positions of the ^cH signals are relatively insensitive to the cavity occupant. In the spectrum of **1**·O_2, however, the broad signals are due to the ^cH protons, and have been shifted downfield from the positions in **1** (4.80 and 4.90 ppm) by 0.44 and 0.48 ppm, respectively. Their assignment was confirmed by saturation transfer experiments.[13] Irradiation of the signal at 5.24 ppm caused the triplet at 4.80 ppm (^cH of free **1**) to decrease in intensity by about 20%. Irradiation of the signal at 5.38 ppm had the same effect on the triplet at 4.90 ppm. Furthermore, the combined integrals of the methine signals due to **1**·O_2 and **1** are consistent with expectations for the integrals of the protons of the $C_6H_5CH_2CH_2$ groups, which are unaffected by the presence of oxygen. *All other host protons of* **1**·O_2 *are broadened and shifted so dramatically that they could not be located.*

Proton integration of the ^cH methine signals indicates that one-third of the host present contains oxygen. If we assume a one-to-one stoichiometry for the oxygen complex, $K_a = 44\ M^{-1}$ ($\Delta G° = -2.2$ kcal mol^{-1} at 22 °C). The separation of 220 Hz between the bound and free methine signals indicates that the barrier to decomplexation is greater than 14 kcal mol^{-1}.[10]

The addition of a saturating amount of water to the N_2-saturated sample of **1** in $CDCl_3$ produced the partial ^1H NMR spectrum shown in Figure 1. The broad signals centered at 4.3 ppm are assigned to the ^aH protons of **1**·H_2O, whose integration indicates 80% of the host molecules contain water. They were accompanied by a very broad peak at −1.87 ppm that is assigned to the protons of incarcerated water. The broadness of the peaks is attributed to a rate for decomplexation that approaches coalescence on the ^1H NMR time scale. Thus, the barrier to decomplexation is close to 14 kcal mol^{-1}.[10] When the solution was cooled to 0 °C, the signals sharpened. When D_2O was substituted for H_2O in identical experiments, the same effects on the host's signals were observed, but the guest signal at −1.87 ppm was absent. The integral for the bound H_2O at 0 °C when compared to that of the methine peaks of the host suggests the stoichiometry of the complex is essentially that of one host to one guest.

A solution of **1** in $CDCl_3$ was degassed by repeated freeze–evacuate–thaw cycles, and the ^1H NMR tube was sealed at 0.1 atm. The resulting spectrum contained only signals corresponding to **1** and a trace of **1**·H_2O. When **1** was dissolved in $(CD_2)_4O$, the solution's ^1H NMR pattern of signals corresponded to those for **1**, **1**·N_2, and **1**·O_2, but those for **1**·H_2O were negligible. A degassed sample of **1** in $(CD_2)_4O$ gave a ^1H NMR spectrum containing only the signals for free **1**. The good hydrogen-bonding ability of tetrahydrofuran relative to the host's interior explains the absence of **1**·H_2O in this solution.

The ^1H NMR spectrum of **1** in carbon dioxide saturated $CDCl_3$ contained one unique set of host signals. The ^aH protons were located at 4.03 and 4.17 ppm. This observation suggests that at least 95% of the host had gone to **1**·CO_2. This high degree of complexation is attributed at least in part to the high solubility of CO_2 in organic solvents.[14]

Empty host **1** is incapable of undergoing any conformational change to fill its own vacuum. The question arises as to what is the thermodynamic driving force for molecules such as N_2 entering empty **1** dissolved in a solvent such as $CDCl_3$, itself much too large to enter. Organic liquids are only ~30% empty space[15] which is broken into small volumes between molecules that inefficiently contact one another because of their shapes. The gathering together of many small volumes into a single large volume as in the hole of **1** is entropically disfavored. The filling of that space with a dissolved molecule of N_2 would be entropically favorable both because of the resultant entropy of dilution of the N_2, *but also because of the entropy of dilution that accompanies turning a large localized vacuum into many small vacuums scattered throughout the solvent.*

Hemicarceplexes Formed at Ambient Temperature. The diameter of a xenon atom present in a clathrate crystal is 4.4 Å (X-ray crystallography).[16] This is considerably greater than the interhemispheric distance in the portal of **1** in either CPK models or the crystal structure of **1**·$(CH_3)_2NCHO$. However, in the models, the portal can be forced open enough to accept a 4.4-Å diameter sphere without breaking bonds because of the large number of bonds among which the strain energy can be distributed. A solution of **1** (5.0 mM) in $CDCl_3$ saturated with Xe gas (0.14 M)[17] was quickly prepared. Its immediately taken ^1H NMR spectrum showed signals only for **1** and **1**·H_2O. As the solution stood at 22 °C, a new set of signals attributed to **1**·Xe grew into the spectrum which completely replaced the old set. The half-life for **1** + Xe → **1**·Xe was 90 min, from which the second-order rate constant for complexation was estimated to be 0.055 min^{-1} M^{-1}.

The chemical shift of ^{129}Xe (26% abundance) is very sensitive to its environment due to its large, polarizable electron cloud, and solvent-dependent shifts of as much as 200 ppm have been observed.[18] The ^{129}Xe NMR spectrum of **1**·Xe in $CDCl_3$ saturated with Xe shows a large signal set at 0 ppm for the uncomplexed Xe, and a prominent signal at −101 ppm for **1**·Xe. A control spectrum of **1**·$(CH_3)_2NCHO$ in xenon-saturated $CDCl_3$ gave no signal at −101 ppm, which indicates that Xe in **1**·Xe has entered the cavity. The ability of Xe to enter the cavity of **1** through the noncomplementary portal testifies to the "soft shapes" of both xenon and the portals.

The rapid addition of CH_3CN to a solution of **1**·Xe in ethanol-free $CHCl_3$ precipitated **1**·Xe, which gave excellent elemental analyses (C, H, O). The percentage weight of Xe was estimated by thermal gravimetric analysis.[19] A 5.1% decrease in weight (theory, 6.05%) was observed between 165 and 200 °C, and the host began to decompose and vaporize rapidly at 360 °C. The vapors produced by heating **1**·Xe to 230 °C when passed through a mass spectrometer gave the correct isotope pattern for Xe, whereas a ^1H NMR spectrum of the residue contained only the signals expected for **1** free of guest.

The rate decomplexation of **1**·Xe as a 0.70 mM solution in CD_2Cl_2 was measured in a ^1H NMR tube (sealed at atmospheric pressure). The solvent rapidly enters free **1**, so the transformation observed by the ^aH ^1H NMR changes at 25 °C was **1**·Xe + CD_2Cl_2 → **1**·CD_2Cl_2 + Xe. A six-point plot of $-\ln [\mathbf{1}\cdot Xe]/[\mathbf{1}\cdot Xe]_0$ vs time was linear, and the slope gave $k_d = 2.5 \times 10^{-4}$ min^{-1}. Thus,

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(13) Craik, D. J.; Higgins, K. A. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: San Diego, 1990; Vol. 22, pp 72–76.
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(15) We thank Dr. Raymond A. Firestone for the following references and for a discussion of this question: (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Verlag Chemie: New York, 1988; p 5. (b) Cameron, C.; Saluja, P. P. S.; Floriano, M. A.; Whalley, E. *J. Phys. Chem.* **1988**, *92*, 3417–3421. (c) Reichardt, C. *Ibid.* p 280. (d) Asano, T.; le Noble, W. *Rev. Phys. Chem. Jpn.* **1973**, *43*, 82–91. (e) Nishimura, N.; Tanuka, T.; Motoyama, J. T. *Can. J. Chem.* **1987**, *65*, 2248–2253. (f) Firestone, R. A.; Smith, G. *Chem. Ber.* **1989**, *122*, 1089–1094. (g) Markus, Y. *Introduction to Liquid State Chemistry*; Wiley: New York, 1977; p 58.
(16) Lee, F.; Gabe, E.; Tse, J. S.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6014–6019.
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(18) (a) Miller, K. W.; Reo, N. V.; Uiterkamp, A. J. M. S.; Stengle, D. P.; Stengle, T. R.; Williamson, K. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 4946–4949. (b) Stengle, T. R.; Reo, N. V.; Williamson, K. L. *J. Phys. Chem.* **1981**, *85*, 3772–3775.
(19) We warmly thank Phil Sawin for carrying out this analysis, and Mike Geckle for the ^{129}Xe NMR spectral determination.

the decomplexation was first order in 1·Xe, with a $t_{1/2}$ of 47 h. If we make the reasonable assumptions that the decomplexation rate of 1·Xe is approximately the same in $CDCl_3$ as in CD_2Cl_2, and that guest substitution of 1·Xe has free 1 as an intermediate, the rough estimate of $K_a \approx 200\ M^{-1}$ at 22–25 °C can be made. Similar studies with argon gas and 1 in $CDCl_3$ led to 1·Ar whose ^1H NMR spectrum was indistinguishable from that of 1·Xe.

As expected from molecular model examination, 1 was found to readily complex CH_3CN. A 0.7 mM solution of 1 in a 30:1 (v/v) $CHCl_3/CH_3CN$ solution was equilibrated for 48 h, and the 1·CH_3CN formed was precipitated by the rapid addition of excess pentane. The white solid produced gave the correct C, H, and N analysis for a one-to-one complex. The ^{a}H resonances of the complex in its ^1H NMR spectrum in $CDCl_3$ appear at 4.19 and 4.30 ppm, and the incarcerated CH_3CN protons at −2.42 ppm ($\Delta\delta$ = 4.42). This hemicarceplex was found to have a half-life of ~13 h in CD_2Cl_2 at 22 °C.

When a 1 mM solution of 1 in a 5:2 $CHCl_3/CH_3CN$ (v/v) was allowed to evaporate over a 3-day period, thin, white needles were formed whose ^1H NMR spectrum in $CDCl_3$ indicates them to be a one-to-one mixture of 1·CH_3CN and 1·$2CH_3CN$. The ^{a}H protons of 1·$2CH_3CN$ gave signals at 4.71 and 4.75 ppm, whereas the methyl protons of the two incarcerated CH_3CN guests appeared as a singlet at −2.15 ppm (6 H). The positions of these signals suggest that the two acetonitriles are aligned with a common axis with their methyl groups facing one another, as in $N{\equiv}CCH_3{\cdots}CH_3C{\equiv}N$. This arrangement locates the CH_3 groups further from the shielding aryl groups of the host than alternate arrangements. The noticeable deshielding of the host's ^{a}H protons in 1·$2CH_3CN$ is attributed to their location in the deshielding zone of the C≡N groups. This arrangement of the two guests is also sterically compatible with the "chicken-egg shape" of the cavity.

In $CDCl_3$ solution at 22 °C, 1·$2CH_3CN$ converts to 1·CH_3CN + CH_3CN. This conversion was followed by integration of the ^1H NMR guest methyl peaks at different times to provide a half-life of 26 min. Only by having a very high concentration of CH_3CN in the solution can 1·$2CH_3CN$ be formed at all. We attribute the relatively high stability of 1·CH_3CN compared to 1·$2CH_3CN$ as reflecting the high entropic cost of collecting the three molecules that compose 1·$2CH_3CN$, coupled with the loss of much of the translational degrees of freedom of the guests in passing from 1·CH_3CN to 1·$2CH_3CN$. Even in the solid state, 1·$2CH_3CN$ slowly goes to 1·CH_3CN at ambient temperature. A ^1H NMR spectrum of a 1-month-old sample of 50% 1·$2CH_3CN$–50% 1·CH_3CN revealed its composition had changed to 15% 1·$2CH_3CN$–85% 1·CH_3CN.

Additional examples of hemicarceplexes that form at ambient temperature are 1·CH_2Cl_2, 1·CH_2Br_2, and 1·CS_2. The first two complexes were prepared by stirring 1 into solution in CH_2Cl_2 and CH_2Br_2, and precipitating the complexes with excess pentane. Complex 1·CS_2 was formed similarly by using a 6% solution of CS_2 in $CHCl_3$ (v/v) as the solvent, and precipitating the complex with pentane. Good elemental analyses were obtained for C, H, and Cl in 1·CH_2Cl_2, for C, H, and Br in 1·CH_2Br_2, and for C, H, and S in 1·CS_2. The fact that the host and guests contained different elements coupled with the analytical results indicated each complex was one-to-one.

Each complex displayed a unique set of ^{a}H host signals in its ^1H NMR spectrum in $CDCl_3$. The incarcerated CH_2Cl_2 proton signal occurred at 2.64 ppm ($\Delta\delta$ = 2.66), and overlapped with the $C_6H_5CH_2CH_2$ signals. The incarcerated CH_2Br_2 signal was hidden under the $C_6H_5CH_2CH_2$ signals at 2.4 ppm as shown by integration experiments. Both 1·CH_2Br_2 and 1·CS_2 had half-lives for decomplexation of greater than 400 h in CD_2Cl_2 at ambient temperature. This conclusion was based on the fact that when either complex was dissolved in CD_2Cl_2 at 25 °C and allowed to stand for 30 h, no signals for the formation of 1·CH_2Cl_2 could be detected in the solution's ^1H NMR spectra (5% could easily have been observed). Treatment of a 0.5 mM solution of 1·CH_2Br_2 in dry tetrahydrofuran with 300 equiv of *n*-butyllithium for 1 min at 25 °C had no effect on the complex. Thus, the reactive CH_2Br_2 guest was inaccessible to the highly reactive reagent because of the guest protection afforded by the host. This phenomenon is being studied for a variety of host-protecting guest situations.

Hemicarceplexes Formed Only at Elevated Temperatures. Larger guests entered hemicarcerand 1 only when heated in the presence of high concentrations of guest. All of the complexes formed in this way appeared to be stable indefinitely to decomplexation at ambient temperature. Solutions of 1 in benzene, pyridine, or tetrahydrofuran remained uncomplexed at room temperature. The pyridine complex (1·C_5H_5N) formed quantitatively after 6 h at reflux temperature (115 °C), and gave good elemental analyses for C, H, N, and O, which when added gave 100.00%. The tetrahydrofuran complex 1·$(CH_2)_4O$ was only 70% formed after 3 days, but was completely formed after 12 days of reflux (67 °C), and gave good analyses for C and H. The benzene hemicarceplex was only 85% formed after 12 days at reflux (80 °C), and was only characterized by ^1H NMR of the mixture of 1·C_6H_6 and free 1.

The ^1H NMR spectra of these complexes were consistent with their possessing a one-to-one composition. The guest proton signals were shifted upfield by 1.4–4.5 ppm compared to guest alone dissolved in $CDCl_3$ (see Table I). The proton on C-4 of the bound pyridine was shifted upfield by only 1.45 ppm, indicating its equilibrium position was equatorial. The signals due to the host's protons in 1·C_6H_6 and 1·C_5H_5N are quite similar, as expected. Several of them were broad at ambient temperature due to restricted motion of the host and (or) guest with respect to one another. At 60 °C, these signals sharpened considerably, but the ^{a}H protons were still somewhat broad. This is probably associated with the northern and southern hemispheres of the host rotating with respect to one another, and the larger guest inhibiting slightly the equilibration of the rotomers with respect to one another. In the complexes containing the aromatic guests, the signals due to the interhemispheric methylene bridges flanking the shell portal were shifted upfield by 0.3–0.4 ppm relative to their positions in free 1. Both this observation and model examination suggest that, on average, the long, polar axis of the host lies roughly in the planes of the aromatic guests.

An attempt was made to regenerate 1·$(CH_3)_2NCOCH_3$ from 1 and $(CH_3)_2NCOCH_3$ by heating the solution of 1 in the amide at 140 °C for 15 h. Although the $(CH_3)_2NCOCH_3$ was freshly distilled from BaO, the complexation product was a mixture of 35% of 1·$(CH_3)_2NCOCH_3$ and 65% of what was probably 1·$CH_3NHCOCH_3$ (^1H NMR). Further heating of this material did not change its composition. Thus, the host scavenged the smaller guest, which was an impurity in the solvent. Although present in only small amounts, the rate of entry of the smaller guest into the host was fast enough to exceed that of the bulk solvent. Alternatively, the mixture might have reached equilibrium, with the smaller but less plentiful guest having the much higher association constant. Structural recognition of host and guest appears to be high, with respect to both complexation and decomplexation.

The complexation of 1 with $CH_3CH_2NHCH_2CH_3$ and $CH_3CH_2CH_2CH_2NH_2$ was also examined. Chlorobenzene was used as a cosolvent to produce homogeneous solutions. Heating of 1 in a 5:1 C_6H_5Cl/Et_2NH (v/v) solution at 65 °C for 4 h produced host only 70% filled with Et_2NH, the remaining material being composed of a two-to-one ratio of 1·CH_3CN/1 (^1H NMR spectra). Examination of the Et_2NH used revealed the presence of less than 1% CH_3CN. An increase in the heating time did not change the composition. Substitution of the C_6H_5Cl by $CHCl_3$ did not materially affect the ratio of the products. Similarly, heating 1 in a 4:1 mixture (v/v) of $C_6H_5Cl/CH_3(CH_2)_3NH_2$ gave a mixture of 90% 1·$CH_3(CH_2)_3NH_2$ and 10% 1. These complexes were stable indefinitely in CH_2Cl_2 solution at room temperature. The incomplete formation of these complexes suggests their association constants are not high valued.

The ^1H NMR spectra in $CDCl_3$ of both amine complexes showed all guest signals to be shifted upfield to the negative side of δ = 0 for $(CH_3)_4Si$ (Table I). Proton decoupling experiments were used to assign the methylene signals of the amine in 1·$CH_3(CH_2)_3NH_2$. The amine protons were coupled to their ad-

jacent CH_2 protons, and their signals broadened slightly due to the quadrupole moment of the ^{14}N nucleus. As expected from a molecular model examination, the long axis of the two amine molecules in the complexes appears to be roughly coincident with the long, polar axis of the host. The $\Delta\delta$ values of the protons change in magnitude as their positions in the chain vary in a neatly graded manner. Those at the chain ends reside in the northern and southern polar caps (composed of four aryl groups each in the host), and their $\Delta\delta$ values are greater than −4.0 ppm. Protons of the penultimate methylenes range from −2.6 to −3.8, whereas the central methylene of **1**·$CH_3CH_2CH_2CH_2NH_2$ provides a $\Delta\delta$ value of −2.35 ppm. Thus, the equatorial region of the cavity, which is defined largely by OCH_2O groups, is much less shielding than the polar cap region, as expected.

All host resonances were sharp in both complexes with the exception of those of ^aH in **1**·$CH_3(CH_2)_3NH_2$, which were somewhat broad. This is undoubtedly due to the inability of the non-like-ended structure of $CH_3(CH_2)_3NH_2$ to rotate rapidly around equatorial axes in **1**·$CH_3(CH_2)_3NH_2$.

Molecules That Do Not Complex 1. Solvents such as $CHCl_3$, C_6H_5Cl, $C_6H_5CH_3$, 1,3,5-$(CH_3)_3C_6H_3$, and 1,2,4-$Cl_3C_6H_4$ do not form detectable complexes even upon extended heating of their solutions of **1**. Either the portal is too small to admit these molecules, or the cavity is too small to accommodate them. Molecular model examination suggests that, at much higher temperatures, $CHCl_3$ might enter to form a stable complex. The portal is slot-shaped, whereas $CHCl_3$ is more ball-shaped. The fact that $(CH_3)_2SO$ was expelled from **1**·$(CH_3)_2SO$ only slowly at 195 °C suggests that portal size can be limiting as to what complexes can be formed. Possibly stable complexes of $C_6H_5CH_3$ and C_6H_5Cl might be preparable at very high temperatures, but there is no possibility of forming complexes of 1,3,5-$(CH_3)_3C_6H_3$ or 1,2,4-$Cl_3C_6H_3$.

Protonation of Guest Amines. The protonations of **1**·C_5H_5N, **1**·Et_2NH, and **1**·$CH_3(CH_2)_3NH_2$ dissolved in $CDCl_3$ were surveyed. A brief report on the binding of ammonium cations by aryl-lined, neutral hosts dissolved in $CDCl_3$ has appeared in the literature.[20]

Addition of a large excess of CF_3CO_2D to a solution of **1**·C_5H_5N in $CDCl_3$ had no effect on the ^1H NMR spectrum of the complex. Free pyridine in $CDCl_3$ is quantitatively protonated under the same conditions, as evidenced by upfield shifts of its ^1H NMR protons, which are independent of acid concentration. Thus, as expected, incarcerated pyridine is much less basic than freely dissolved pyridine. This is probably due to the inability of the host to effectively solvate the pyridinium ions, the hindrance that the cavity provides to contact ion pair formation, and the increased size of pyridinium compared to pyridine. It is conceivable but highly unlikely that the unshared electron pair of incarcerated pyridine is so hindered as to be kinetically unavailable to the acid.

Treatment of a 1 mM solution of **1**·Et_2NH (70% filled) with 100 equiv of CF_3CO_2D resulted in instantaneous decomplexation of the **1**·$Et_2ND_2^+$, leaving the **1**·CH_3CN (impurity) and empty host unaffected. Thus, **1**·$Et_2ND_2^+$ is both kinetically and thermodynamically unstable relative to **1** + $Et_2ND_2^+$ in $CDCl_3$. The location of the N: atom in **1**·Et_2NH in the equatorial region close to the portal undoubtedly facilitates the proton transfer, and in effect, the counterion can be envisioned as pulling the guest out of the host. The addition of 100 equiv of CD_3CO_2D to **1**·Et_2NH (70%, 0.1 mM in $CDCl_3$) had no effect on the spectrum except for the disappearance of the amine proton signal due to NH to ND exchange, and a slight change in the coupling pattern of the CH_2N protons. Thus, this incarcerated amine protonates and exchanges its hydrogen for deuterium much more rapidly than decomplexation occurs. Only an undetectably small amount of **1**·Et_2NHD^+ or **1**·$Et_2ND_2^+$ was formed at any one time when CD_3CO_2D served as the acid.

Figure 2 shows that part of the 500-MHz ^1H NMR spectra of **1**·$CH_3(CH_2)_3NH_2$, 90% complexed (1.5 mM in $CDCl_3$), due

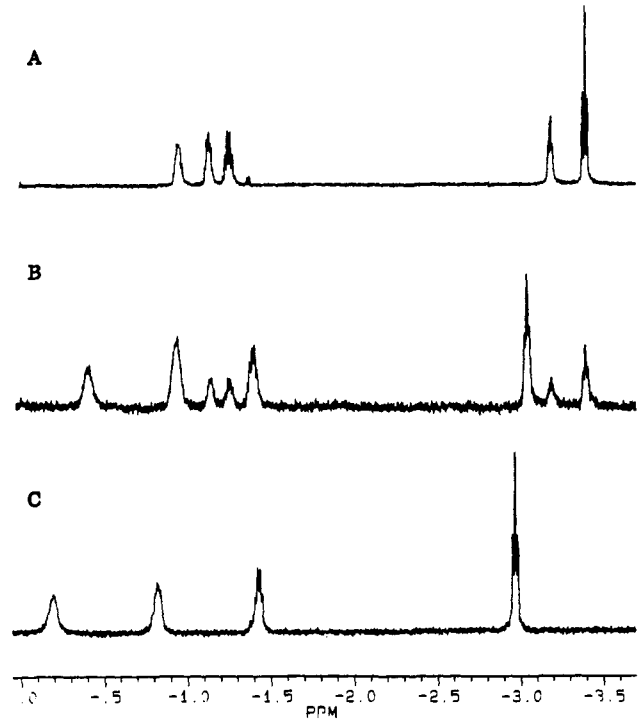


Figure 2. Partial 500-MHz ^1H NMR spectra at 22 °C of **1**·$CH_3(CH_2)_3NH_2$ (1.5 mM) in $CDCl_3$: curve A, no added acid; curve B, immediately taken after addition of 10 equiv of CF_3CO_2D; curve C, immediately taken after addition of 100 equiv of CF_3CO_2D.

to the complexed guest signals. Upon addition of 10 equiv of CF_3CO_2D, a spectrum taken immediately shows a new set of guest signals that accounts for two-thirds of the bound amine signals. The downfield shifts of these signals relative to those of **1**·$CH_3(CH_2)_3NH_2$ are consistent with their assignment as the protonated form of the amine. The remaining one-third of the amine signals appears as **1**·$CH_3(CH_2)_3NH_2$. The new set of *guest* signals is accompanied by a new set of *host* signals. The observation of both **1**·$CH_3(CH_2)_3NH_2$ and **1**·$CH_3(CH_2)_3ND_3^+$ signals simultaneously in comparable amounts indicates that the pK_a of bound butylammonium ion is not far from that of CF_3CO_2D in $CDCl_3$ (curve B of Figure 2). Furthermore, it shows that proton transfers between **1**·$CH_3(CH_2)_3ND_3^+$ and **1**·$CH_3(CH_2)_3NH_2$ are slow on the ^1H NMR time scale. When the last experiment was repeated with the addition of 100 equiv of CF_3CO_2D, complete protonation and maximum shifting were observed (spectrum C of Figure 2). Addition of more acid had no spectral effect. Molecular model examination suggests that hydrogen–deuterium exchange of RNH_2 to give RND_3+ occurs through the holes in the polar caps of the host.

Several of the *host* signals of the protonated complex were broadened by formation of the conjugate acid of **1**·$CH_3(CH_2)_3NH_2$, which accentuated the north–south hemispheric dissymetry of this complex. As with **1**·Et_2NH, acidification of **1**·$CH_3(CH_2)_3NH_2$ greatly accelerated decomplexation. The half-life of **1**·$CH_3(CH_2)_3ND_3^+$ formed in the presence of 100 equiv of CF_3CO_2D was only 10 min at 22 °C. The half-life of the partially acidified complex toward decomplexation was 33 min at 22 °C. The 2:1 ratio of acidified to nonacidified amine (spectrum B of Figure 2) remained constant with time, although the decomplexation proceeded to completion to provide free **1** and free $CH_3(CH_2)_3ND_3^+ \cdot {}^-O_2CCF_3$. By adjusting this half-life for the amount of protonated complex present at any one instant, a corrected decomplexation half-life for the conjugate acid of **1**·$CH_3(CH_2)_3NH_2$ was estimated to be 22 min. As expected from the results with **1**·Et_2NH, the addition of a large excess of CD_3CO_2D to a solution of **1**·$CH_3(CH_2)_3NH_2$ in $CDCl_3$ at 22 °C resulted only in the exchange of the amine protons for deuterons.

Summary. We have reported the syntheses and binding properties of three new hemicarceplexes whose shell-closing re-

(20) Stauffer, D. A.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 6039–6042.

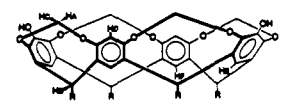
actions are templated by single aprotic, dipolar solvent molecules that become incarcerated as guest molecules. These guests can be expelled by heating the hemicarceplexes to high temperatures in high-boiling solvents (too large to enter the cavity) to give free hemicarcerand **1** and guest. When dissolved in $CDCl_3$, **1** readily and reversibly forms 1:1 complexes with small guest molecules such as N_2, O_2, H_2O, and CO_2 with binding free energies of −2 or −3 kcal mol^{-1} at ambient temperature. When dissolved in small guest solvents such as CS_2 in $CDCl_3$, CH_2Cl_2, CH_2Br_2, or Xe in $CDCl_3$, free **1** forms **1**·G, which is isolable and characterizable, and whose half-lives for decomplexation can be measured. When dissolved in $CDCl_3$ containing a high concentration of CH_3CN, a mixture of **1**·CH_3CN and **1**·$2CH_3CN$ is formed, which when isolated and dissolved in $CHCl_3$ goes to **1**·CH_3CN, which has a half-life of about 13 h at 22 °C in CD_2Cl_2. When heated in larger solvents, **1** incarcerates one solvent molecule to give hemicarceplexes such as **1**·C_5H_5N, **1**·C_6H_6, **1**·$(CH_2)_4O$, **1**·Et_2NH, or **1**·$CH_3(CH_2)_3NH_2$. The protonation, hydrogen–deuterium exchange, and acid-catalyzed decomplexation of the latter two incarcerated guests provide an unusual chemical picture for reactions that occur in the inner phase. The fact that **1**·CH_2Br_2 in $(CH_2)_4O$ does not react in a brief exposure to *n*-BuLi demonstrates that hemicarcerands are capable of acting as a removable protecting group in certain cases. We suggest the term "constrictive binding" for the decomplexation activation energy that must be overcome due to steric effects in decomplexation.

The inner phase of hemicarcerands as a seat for reactions puts geometric constraints on their course and time scale, as was observed in the protonation and hydrogen isotopic exchange reactions. Incarcerated guests are protected from many bimolecular reactions and solvent effects common in organic chemistry. The physical properties of both hosts and guests involving carcerands and hemicarcerands are greatly altered in their complexes. High structural recognition is observed for complexation based on the shape and size of the guest, the portal, and the host interior.

Experimental Section

General Procedure. All chemicals were reagent grade, and used as received unless otherwise specified. All reactions were conducted under an atmosphere of argon, unless otherwise specified. Tetrahydrofuran was freshly distilled from sodium benzophenone ketal prior to use. Dimethylacetamide, dimethylformamide, and dimethyl sulfoxide were dried by storage for at least 72 h over activated (24 h, 320 °C) 3-Å molecular sieves, and degassed under high vacuum immediately before use. In all procedures employing $CHCl_3$ with uncomplexed **1**, the solvent was passed through silica gel immediately prior to use to remove ethanol. Bruker AM-360- and AM-500-MHz spectrometers were used to record ^1H NMR spectra. Spectra taken in $CDCl_3$ were referenced to residual $CHCl_3$ at 7.26 ppm. Those spectra taken in $CDCl_2CDCl_2$ were referenced to residual $CHDCl_2CDCl_2$ at 5.99 ppm. NMR samples that were saturated with a gas were prepared by passing a stream of the desired gas through the sample for a minimum of 10 min. Degassed NMR samples were prepared by freezing the samples in liquid nitrogen, evacuating to 0.1 Torr, and thawing. This was repeated three times, and on the final cycle the NMR tubes were sealed prior to thawing. FAB mass spectra were determined on a ZAB SE instrument. NOBA as a matrix stands for 3-nitrobenzyl alcohol. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR instrument. All compounds decomposed without melting above 300 °C. Gravity chromatography was performed on E. Merck silica gel 60 (70–230 mesh). Silica thin-layer chromatography was done on E. Merck glass-backed plates (silica gel 60, F_{254}, 0.25 mm).

The following four structures label the protons to which ^1H NMR chemical shift assignments are made. Notice that, for all structures, R = $CH_2CH_2C_6H_5$.



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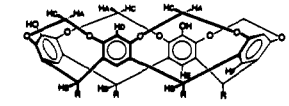

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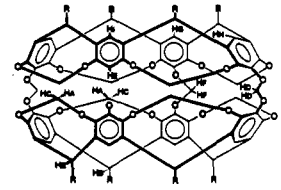

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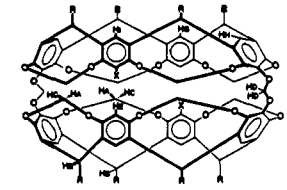


2, X = He, Hi = Hc

3, X = OH

4, X = OCH_3

1,21,23,25-Tetrakis(2-phenylethyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3]benzodioxocin-7,11-15-triol, Stereoisomer, 6. To 500 mL of 2-butanone were added 80 g (88 mmol) of octol **9** and 47 g (264 mmol) of recrystallized *N*-bromosuccinimide. The mixture, while stirred for 16 h at room temperature, formed a precipitate. The mixture was filtered to provide 24 g (20 mmol) of a light yellow solid that consisted mainly of the tetrabrominated octol. The filtrate was concentrated to 75 mL, and 500 mL of acetonitrile was added. A precipitate slowly formed upon cooling to ~5 °C for 12 h. This precipitate was collected by filtration, and provided 59 g (after drying under vacuum at room temperature) of a mixture of mono-, di-, and tribrominated octols. This mixture was dissolved in 1.1 L of DMA containing 81 g (0.59 mol) of K_2CO_3 and 16 mL (0.25 mol) of CH_2BrCl. This mixture was heated to 65 °C, and stirred for 12 h. An additional 5 mL (0.08 mol) of CH_2BrCl was added, and stirring was continued for 24 h more. The mixture was allowed to cool, and the solvent was removed in vacuo. The residue was extracted with $CHCl_3$ and water, and the organic layer was dried over $MgSO_4$. This produced a jet black oil. The oil was added to 240 mL of EtOAc and triturated at reflux for 20 min. The resulting solid was collected by filtration, and dried under high vacuum at 160 °C for 12 h. This produced 23.4 g of a mixture of mono-, di-, and tribrominated bridged cavitands. This material was divided in half for the lithiation step. In 1 L of dry THF was dissolved 11.7 g of the mixture. This solution was cooled to −78 °C, and 113 mmol of *n*-butyllithium (59 mL of a 1.9 M solution in hexanes) was added. The mixture was stirred for 1 min, and 24 mL (211 mmol) of trimethyl borate was added. This mixture was allowed to warm to ~0 °C, and then recooled to −78 °C. After the addition of 180 mL of a 15% aqueous H_2O_2/1.5 M NaOH solution, the mixture was allowed to warm to room temperature and was stirred for several hours. Gradual addition of 41 g of $Na_2S_2O_5$, followed by removal of the THF in vacuo, left a yellowish solid in the residual water that was filtered, and the solid was washed with water to provide 12.7 g of a mixture of phenols. This material was dissolved in $CHCl_3$, and preabsorbed onto 200 g of silica gel. Silica gel chromatography (two columns) was performed with a mobile phase gradient ranging from 1:1 to 7:3 EtOAc/$CHCl_3$. This provided 2.0 g (5%, based on 40 g of **9**) of **6** as an off-white solid. Also produced was 3.3 g (8%) of a 2:1 mixture of the bis-phenols **7** and **11**.

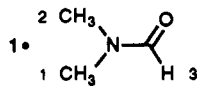
Triol **6** obtained in this fashion had the same ^1H NMR spectrum as, and behaved identically on thin-layer chromatography with an authentic sample of **6**.[5d]

1,21,23,25-Tetrakis(2-phenylethyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3]benzodioxocin-7,15-diol, Stereoisomer, 7. To 1.8 g (1.8 mmol) of the 2:1 mixture of **7**/**11** (see above) in 50 mL of dry THF were added 2.1 mL (18 mmol) of benzoyl chloride and 3.5 mL (25 mmol) of triethylamine. The mixture was refluxed for 15 min. The solvent was removed in vacuo, and the residue was passed through a short plug of silica gel with CH_2Cl_2 as the mobile phase. The CH_2Cl_2 was concentrated to 20 mL, and 100 mL of CH_3OH was added. The resulting precipitate was collected by filtration and provided 2.0 g of the bis-benzoylated compounds. Careful silica gel chromatography (35:65 hexanes/CH_2Cl_2) was used to separate the isomers. This provided 650 mg of the faster moving A–C substituted ester, 225 mg of the slower A–B substituted ester, and 915 mg of mixed fractions (the yields could be increased by rechromatographing the mixed fractions). The desired A–C substituted diester was dissolved in 75 mL of dry THF, and 200 mg of $LiAlH_4$ (5 mmol) was added. The mixture was stirred for 15 min, and 0.2 mL of H_2O was added, followed by 0.2 mL of 15% aqueous NaOH, and then 3 mL of H_2O. After an additional 1 h of stirring, the mixture was filtered. The filtrate was evaporated to dryness, and the residue was extracted with $CHCl_3$ and 0.5 M aqueous HCl. The organic layer was dried over $MgSO_4$ and evaporated. Drying the resulting solid at 80 °C under vacuum gave 480 mg (27%, based on the weight of the bis-phenol mixture) of **7**: mp >300 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 2.51 (m, 8 H, CH_2CH_2Ph), 2.68 (m, 8 H, CH_2CH_2Ph), 4.47 (d, 4 H, H_A, J = 7.0 Hz), 4.83 (t, 4 H, H_B, J = 8.0 Hz), 5.37 (s, 2 H, ArOH), 5.88 (d, 4 H, H_C, J = 7.0 Hz), 6.58 (s, 2 H, H_D or H_E), 6.70 (s, 2 H, H_D or H_E),

7.16 (m, 10 H, H_F and C_6H_5), 7.24 (m, 12 H, C_6H_5); MS (Xenon FAB, NOBA matrix) *m/e* 985 (M^+, 100%). Anal. Calcd for $C_{64}H_{56}O_{10}$: C, 78.03; H, 5.73. Found: C, 77.97; H, 5.87.

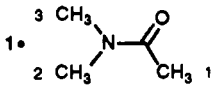
1,21,23,25-Tetrakis(2-phenylethyl)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3]dioxocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3]benzodioxocin-7,11-diol, Stereoisomer, 11. The A–B substituted bis-benzoyl ester obtained above (225 mg) was treated with $LiAlH_4$ in a manner identical with the A–C system. This produced 170 mg (9%, based on the weight of the bis-phenol mixture) of **11** as a white solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.50 (m, 8 H, CH_2CH_2Ph), 2.67 (m, 8 H, CH_2CH_2Ph), 4.46 (m, 4 H, H_A), 4.83 (m, 4 H, H_B), 5.38 (br 2 H, ArOH), 5.78 (d, 1 H, H_C, J = 7.1 Hz), 5.88 (d, 2 H, H_C, J = 6.9 Hz), 5.98 (d, 1 H, H_C, J = 6.8 Hz), 6.56 (s, 2 H, H_D), 6.70 (s, 2 H, H_E), 7.16 (m, 10 H, H_F and CH_2CH_2Ph), 7.22 (m, 12 H, CH_2CH_2Ph); MS (Xenon FAB, NOBA matrix) *m/e* 985 (M^+, 100%). Anal. Calcd for $C_{64}H_{56}O_{10}$: C, 78.03; H, 5.73. Found: C, 77.72; H, 5.64.

13,59-(Epoxymethanoxy)-23,27:51,55-dimethano-2,46:3,45:17,31:-18,30-tetrametheno-1*H*,19*H*,21*H*,29*H*,47*H*,49*H*-bis[1,3]benzodioxocino[9,8-*d*:9′,8′-*d*′][1,3,6,8,11,13,16,18]octaoxacycloeicosino[4,5-*j*:10,9-*j*′:14,15-*j*″:20,19-*j*‴]tetrakis[1,3]benzodioxocin, 1,19,21,29,47,49,57,62-Octakis(2-phenylethyl)-, Stereoisomer, 1·$(CH_3)_2$NCHO. A solution of 2.08 g (2.1 mmol) of triol **6** and 0.4 mL



(6.2 mmol) of CH_2BrCl in 50 mL of dry DMF was added over 16 h (via syringe pump) to a mixture of 7 g of Cs_2CO_3 (21 mmol) and 500 mL of dry DMF at 60 °C. The temperature was raised to 100 °C, and an additional 0.4 mL (6.2 mmol) of CH_2BrCl was added. After the mixture was stirred for 24 h, a final 0.4 mL (6.2 mmol) of CH_2BrCl was added. The mixture was stirred for 24 h more, and then allowed to cool. The solvent was removed in vacuo, and the residue was extracted with $CHCl_3$ and water. The organic layer was dried over $MgSO_4$, and evaporated to give 2.5 g of a brown solid. Silica gel chromatography ($CHCl_3$), followed by recrystallization from $CHCl_3/CH_3CN$, and drying at 90 °C under vacuum provided 465 mg (20%) of **1**·$(CH_3)_2$NCHO as white crystals: ^{1}H NMR ($CDCl_3$, 333 K, 500 MHz) δ −1.05 (s, 3 H, DMF H_1), 0.24 (s, 3 H, DMF H_2), 2.50 (m, 16 H, CH_2CH_2Ph), 2.68 (m, 16 H, CH_2CH_2Ph), 4.13 (s, 1 H, DMF H_3), 4.53 (d, 4 H, H_A, J = 7.2 Hz), 4.54 (br, 4 H, H_A), 4.88 (t, 4 H, H_B, J = 8.0 Hz), 4.92 (t, 4 H, H_B, J = 7.8 Hz), 5.81 (d, 4 H, H_C, J = 7.2 Hz), 6.19 (d, 4 H, H_C, J = 7.5 Hz), 6.26 (br, 2 H, H_D), 6.39 (d, 2 H, H_D, J = 5.9 Hz), 6.58 (s, 2 H, H_F), 6.78 (s, 2 H, H_E or H_G), 6.81 (s, 2 H, H_G or H_E), 6.87 (s, 4 H, H_H), 7.08 (s, 2 H, H_I), 7.19 (m, 16 H, CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph); MS (Xenon FAB, NOBA matrix) *m/e* 2039 (M^+ + 1 − DMF, 100%). FTIR ($CDCl_3$) 1681 cm^{-1} (CO stretch). Anal. Calcd for $C_{134}H_{119}NO_{23}$: C, 76.23; H, 5.68; N, 0.66; O, 17.43. Found: C, 76.29; H, 5.61; N, 0.59; O, 17.59. Summed analyses = 100.08%.

13,59-(Epoxymethanoxy)-23,27:51,55-dimethano-2,46:3,45:17,31:-18,30-tetrametheno-1*H*,19*H*,21*H*,29*H*,47*H*,49*H*-bis[1,3]benzodioxocino[9,8-*d*:9′,8′-*d*′][1,3,6,8,11,13,16,18]octaoxacycloeicosino[4,5-*j*:10,9-*j*′:14,15-*j*″:20,19-*j*‴]tetrakis[1,3]benzodioxocin, 1,19,21,29,47,49,57,62-Octakis(2-phenylethyl)-, Stereoisomer, 1·$(CH_3)_2$NCOCH$_3$. A solution of 480 mg (0.48 mmol) of triol **6** and 0.1



mL (1.5 mmol) of CH_2BrCl in 40 mL of dry DMA was added over 16 h (via syringe pump) to a mixture of 2.5 g of Cs_2CO_3 (7.7 mmol) and 220 mL of dry DMA at 60 °C. The temperature was raised to 100 °C, and an additional 0.1 mL (1.5 mmol) of CH_2BrCl was added. After stirring for 24 h, a final 0.2 mL (3 mmol) of CH_2BrCl was added. The mixture was stirred for 24 h more, and allowed to cool. The solvent was removed in vacuo, and the residue was extracted with $CHCl_3$ and water. The organic layer was dried over $MgSO_4$, and evaporated to give 600 mg of a brown solid. Silica gel chromatography ($CHCl_3$), followed by recrystallization from $CHCl_3/CH_3CN$, and drying at 90 °C under vacuum provided 215 mg (42%) of **1**·$(CH_3)_2$NCOCH$_3$ as a white powder: ^{1}H NMR ($CDCl_3$, 333 K, 500 MHz) δ −2.35 (s, 3 H, DMA H_1), −1.38 (s, 3 H, DMA H_2), 1.01 (s, 3 H, DMA H_3), 2.50 (m, 16 H, CH_2CH_2Ph), 2.69 (m, 16 H, CH_2CH_2Ph), 4.53 (d, 2 H, H_A, J = 7.4 Hz), 4.64 (d, 2 H, H_A, J = 7.2 Hz), 4.67 (d, 2 H, H_A, J = 7.7 Hz), 4.69 (d, 2 H, H_A, J = 7.1 Hz), 4.89 (t, 4 H, H_B, J = 8.2 Hz), 4.94 (t, 2 H, H_B, J = 8.2 Hz), 4.97 (t, 2 H, H_B, J = 8.2 Hz), 5.78 (d, 2 H, H_C, J = 7.0 Hz), 5.84 (d, 2 H, H_C, J = 7.2 Hz), 6.11 (d, 2 H, H_C, J = 7.6 Hz), 6.15 (d, 2 H, H_C, J = 7.4 Hz), 6.22 (d, 2 H, H_D, J = 5.6 Hz), 6.36 (d, 2 H, H_D, J = 5.6 Hz), 6.56 (s, 2 H, H_F), 6.67 (s, 1 H, H_E or H_G), 6.74 (s, 1 H, H_E or H_G), 6.78 (s, 1 H, H_E or H_G), 6.80 (s, 1 H, H_E or H_G), 6.83 (s, 2 H, H_H), 6.85 (s, 2 H, H_H), 7.03 (s, 1 H, H_I), 7.07 (s, 1 H, H_I), 7.15 (m, 16 H, CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph); MS (Xenon FAB, NOBA matrix) *m/e* 2039 (M^+ + 1 − DMA, 100%), 2126 (M^+ + 1, 18%); FTIR ($CDCl_3$) 1644 cm^{-1} (CO stretch). Anal. Calcd for $C_{135}H_{121}NO_{23}$: C, 76.29; H, 5.74; N, 0.66; O, 17.31. Found: C, 76.21; H, 5.70; N, 0.59; O, 17.45. Summed analyses = 99.95%.

13,59-(Epoxymethanoxy)-23,27:51,55-dimethano-2,46:3,45:17,31:-18,30-tetrametheno-1*H*,19*H*,21*H*,29*H*,47*H*,49*H*-bis[1,3]benzodioxocino[9,8-*d*:9′,8′-*d*′][1,3,6,8,11,13,16,18]octaoxacycloeicosino[4,5-*j*:10,9-*j*′:14,15-*j*″:20,19-*j*‴]tetrakis[1,3]benzodioxocin, 1,19,21,29,47,49,57,62-Octakis(2-phenylethyl)-, Stereoisomer, 1·$(CH_3)_2$SO. A solution of 500 mg (0.50 mmol) of triol **6** and 0.1 mL (1.5 mmol) of CH_2BrCl in 40 mL of dry DMSO was added over 16 h (via syringe pump) to a mixture of 2.5 g of Cs_2CO_3 (7.7 mmol) and 220 mL of dry DMSO at 60 °C. The temperature was raised to 100 °C, and an additional 0.1 mL (1.5 mmol) of CH_2BrCl was added. After stirring for 24 h, a final 0.2 mL (3 mmol) of CH_2BrCl was added. The mixture was stirred for 24 h more, and then allowed to cool. The solvent was removed in vacuo, and the residue was extracted with $CHCl_3$ and water. The organic layer was dried over $MgSO_4$, concentrated to 30 mL, and passed through a bed of silica gel with $CHCl_3$ as the mobile phase. The resulting filtrate was concentrated to 50 mL, and 25 mL of CH_3CN was added. A white precipitate was formed. The mixture was allowed to stand for 24 h, and the solid was collected by filtration. Drying the solid at 90 °C under high vacuum provided 270 mg (51%) of **1**·$(CH_3)_2$SO as a white powder: ^{1}H NMR ($CDCl_3$, 333 K, 500 MHz), δ −1.14 (s, 6 H, DMSO CH_3), 2.49 (m, 16 H, CH_2CH_2Ph), 2.67 (m, 16 H, CH_2CH_2Ph), 4.34 (d, 4 H, H_A, J = 7.3 Hz), 4.71 (d, 4 H, H_A, J = 7.0 Hz), 4.87 (t, 4 H, H_B, J = 8.0 Hz), 4.93 (t, 4 H, H_B, J = 7.9 Hz), 5.92 (d, 4 H, H_C, J = 7.1 Hz), 6.21 (d, 4 H, H_C, J = 7.4 Hz), 6.49 (d, 2 H, H_D, J = 6.3 Hz), 6.53 (s, 2 H, H_E), 6.58 (s, 2 H, H_F), 6.69 (d, 2 H, H_D, J = 6.3 Hz), 6.80 (s, 2 H, H_G), 6.85 (s, 4 H, H_H), 7.12 (s, 2 H, H_I), 7.15 (m, 16 H, CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph); MS (Xenon FAB, NOBA matrix) *m/e* 2038 (M^+ − DMSO, 100%). Anal. Calcd for $C_{133}H_{118}O_{23}S$: C, 75.48; H, 5.62; O, 17.39; S, 1.51. Found: C, 75.40; H, 5.58; O, 17.15; S, 1.65. Summed analyses = 99.78%.

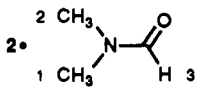
17,22:24,29:47,52:54,59-Tetramethano-2,44:3,43:13,33:14,32:21,25-:51,55-hexametheno-1*H*,15*H*,25*H*,31*H*,45*H*,55*H*-[1,3,6,8,11,13,19,-21,24,26,29,31]dodecaoxacyclohexatriacontino[4,5-*j*:10,9-*j*′:22,23-*j*″:28,27-*j*‴]tetrakis[1,3]benzodioxocin-62,66-diol, 1,15,31,45,61,63,68,70-Octakis(2-phenylethyl)-, Stereoisomer, 3·$(CH_3)_2$SO. The bis-phenolic hemicarceplex 3·$(CH_3)_2$SO was isolated from the reaction mixture obtained in the synthesis of **1**·$(CH_3)_2$SO using a slightly modified procedure. The reaction was run with 1.0 g (1.0 mmol) of triol **6** as described above. After extraction of the crude reaction mixture with $CHCl_3$, however, the organic layer was concentrated to 50 mL, and 25 mL of CH_3CN was added. The resulting precipitate contained **1**·$(CH_3)_2$SO and 3·$(CH_3)_2$SO. This was dissolved in 300 mL of $CHCl_3$ and preabsorbed onto 10 g of silica gel by evaporation of the $CHCl_3$ in vacuo. Silica gel chromatography ($CHCl_3$) provided 60 mg (6%) of the slower moving hemicarcerand 3·$(CH_3)_2$SO as a white powder: ^{1}H NMR ($CDCl_2CDCl_2$, 353 K, 500 MHz) δ −1.07 (s, 6 H, DMSO CH_3), 2.56 (m, 16 H, CH_2CH_2Ph), 2.71 (m, 16 H, CH_2CH_2Ph), 4.30 (d, 4 H, H_A, J = 7.1 Hz), 4.57 (d, 4 H, H_A, J = 7.1 Hz), 4.89 (m, 8 H, H_B), 5.75 (s, 2 H, ArOH), 6.05 (d, 4 H, H_C, J = 7.0 Hz), 6.06 (d, 4 H, H_C, J = 7.0 Hz), 6.53 (s, 2 H, H_E), 6.64 (ABq, 4 H, H_D, J = 6.5 Hz), 6.70 (s, 2 H, H_I), 6.93 (s, 4 H, H_H), 7.19 (m, 18 H, H_G and CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph); MS (Xenon FAB, NOBA matrix) isotope cluster centered at *m/e* 2026 (M^+ − DMSO, 70%), 2104 (M^+, 20%). Anal. Calcd for $C_{132}H_{118}O_{23}S$: C, 75.34; H, 5.65; S, 1.52. Found: C, 75.52; H, 5.76; S, 1.50.

17,22:24,29:47,52:54,59-Tetramethano-2,44:3,43:13,33:14,32:21,25-:51,55-hexametheno-1*H*,15*H*,25*H*,31*H*,45*H*,55*H*-[1,3,6,8,11,13,19,-21,24,26,29,31]dodecaoxacyclohexatriacontino[4,5-*j*:10,9-*j*′:22,23-*j*″:28,27-*j*‴]tetrakis-[1,3]benzodioxocin, 62,66-Dimethoxy-1,15,31,45,61,63,68,70-octakis(2-phenylethyl)-, Stereoisomer, 4·$(CH_3)_2$SO. To a solution of 4 mg (0.02 mmol) of 3·$(CH_3)_2$SO in 3 mL of dry THF were added 50 mg (2 mmol) of NaH (prepared oil free by rinsing with pentane) and 0.1 mL (1.6 mmol) of CH_3I. The mixture was refluxed for 2 h, and quenched by the addition of two drops of water. The solvent was removed in vacuo, and the residue was extracted with $CHCl_3$ and water. The organic layer was dried over $MgSO_4$ and evaporated. The resulting material (>80% yield) was essentially pure by ^{1}H NMR spectroscopy and TLC, and was not purified further. The compound was characterized by ^{1}H NMR and FAB mass spectroscopy only: ^{1}H NMR ($CDCl_3$, 325 K, 360 MHz) δ −1.13 (s, 6 H, DMSO, CH_3), 2.48 (m, 16 H, CH_2CH_2Ph), 2.64 (m, 16 H, CH_2CH_2Ph), 3.93 (s, 6 H, OCH_3), 4.03 (d, 4 H, H_A, J = 7.6 Hz), 4.68 (d, 4 H, H_A, J = 7.2 Hz), 4.85 (m, 8 H, H_B), 5.94 (d, 4 H, H_C, J = 7.2 Hz), 6.00 (d, 4 H, H_C, J

= 7.7 Hz), 6.52 (s, 2 H, H_E), 6.59 (d, 2 H, H_D, J = 6.5 Hz), 6.65 (d, 2 H, H_D, J = 6.4 Hz), 6.82 (s, 2 H, H_I), 6.86 (s, 4 H, H_H), 7.05 (s, 2 H, H_G), 7.14 (m, 16 H, CH_2CH_2Ph), 7.21 (m, 24 H, CH_2CH_2Ph); MS (Xenon FAB, NOBA matrix) isotope cluster centered at m/e 2054 (M^+ - DMSO, 90%).

13,59-(Epoxymethanoxy)-23,27:51,55-dimethano-2,46:3,45:17,31:-18,30-tetrametheno-1*H*,19*H*,21*H*,29*H*,47*H*,49*H*-bis[1,3]benzodioxocino[9,8-*d*:9',8'-*d*'][1,3,6,8,11,13,16,18]octaoxacycloeicosino[4,5-*j*:10,9-*j*':14,15-*j*'':20,19-*j*''']tetrakis[1,3]benzodioxocin, 1,19,21,29,47,49,57,62-Octakis(2-phenylethyl)-, Stereoisomer, 1. The following procedure describes the preparation of **1** from **1**·$(CH_3)_2NCOCH_3$. When **1**·$(CH_3)_2NCHO$ is used, the reflux time may be shortened to 24 h, and when **1**·$(CH_3)_2SO$ is used, the solvent was changed to 1,2,4-trichlorobenzene (bp 214 °C, vacuum distilled prior to use). A mixture of 650 mg (0.3 mmol) of **1**·$(CH_3)_2NCOCH_3$ and 250 mL of distilled mesitylene (bp 163 °C) was heated to reflux. The complex dissolved completely. After refluxing for 48 h, a small amount of precipitate was visible. The solution was allowed to cool, and was then concentrated to 50 mL under reduced pressure. To this mixture was added 100 mL of hexanes, and the resulting solid was collected by filtration. Drying this material at 70 °C (12 h, 10^{-5} Torr) provided 600 mg (96%) of **1** as a white powder: ^{1}H NMR (degassed $CDCl_3$, 500 MHz, spectrum will unavoidably contain signals due to **1**·H_2O) δ 2.48 (m, 16 H, CH_2CH_2Ph), 2.65 (m, 16 H, CH_2CH_2Ph), 3.93 (d, 4 H, H_A, J = 7.1 Hz), 4.09 (d, 4 H, H_A, J = 7.1 Hz), 4.80 (t, 4 H, H_B, J = 8.0 Hz), 4.90 (t, 4 H, H_B, J = 8.0 Hz), 6.07 (d, 4 H, H_C, J = 7.0 Hz), 6.29 (d, 4 H, H_C, J = 7.4 Hz), 6.45 (d, 2 H, H_D, J = 6.2 Hz), 6.48 (s, 2 H, H_E), 6.57 (s, 2 H, H_F), 6.67 (d, 2 H, H_D, J = 6.4 Hz), 6.75 (s, 2 H, H_G), 6.81 (s, 4 H, H_H), 7.15 (m, 18 H, H_I and CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph); MS (Xenon FAB, NOBA matrix) m/e 2038 (M^+, 100%). Anal. Calcd for $C_{133}H_{112}O_{22}$: C, 77.19; H, 5.54; O, 17.27. Found: C, 77.02; H, 5.40; O, 17.39. Summed analyses = 99.95%. Nitrogen analysis indicated that no nitrogen was present in the solid.

17,22:24,29:47,52:54,59-Tetramethano-2,44:3,43:13,33:14,32:21,25-:51,55-hexametheno-1*H*,15*H*,25*H*,31*H*,45*H*,55*H*-[1,3,6,8,11,13,19,-21,24,26,29,31]dodecaoxacyclohexatriacontino[4,5-*j*:10,9-*j*':22,23-*j*'':28,27-*j*''']tetrakis[1,3]benzodioxocin, 1,15,31,45,61,63,68,70-Octakis-(2-phenylethyl)-, Stereoisomer, 2·$(CH_3)_2NCHO$. A solution of 200 mg



(0.20 mmol) of diol **7** and 50 μL (0.77 mmol) of CH_2BrCl in 40 mL of dry DMF was added over 8 h (via syringe pump) to a mixture of 3 g of Cs_2CO_3 (9 mmol) and 200 μL of dry DMF at 65 °C. The temperature was raised to 100 °C, and an additional 100 mL (1.5 mmol) of CH_2BrCl was added. The mixture was stirred for 24 h more, and then allowed to cool. The solvent was removed in vacuo, and the residue was extracted with $CHCl_3$ and water. The organic layer was dried over $MgSO_4$, concentrated to 15 mL, and passed through a bed of silica gel with $CHCl_3$ as the mobile phase. The resulting filtrate was concentrated to 20 mL, and 3 mL of CH_3CN was added. A white precipitate formed. The mixture was allowed to stand uncovered for 24 h, and the solids were collected by filtration. Drying this material at 110 °C under high vacuum provided 45 mg (22%) of **2**·$(CH_3)_2NCHO$ as a white powder: ^{1}H NMR ($CDCl_2CDCl_2$, 500 MHz) δ -1.01 (s, 3 H, DMF H_1), 0.08 (s, 3 H, DMF H_2), 2.50 (m, 16 H, CH_2CH_2Ph), 2.65 (t, 16 H, CH_2CH_2Ph, J = 7.7 Hz), 4.03 (s, 1 H, DMF H_3), 4.39 (d, 8 H, H_A, J = 7.1 Hz), 4.84 (t, 8 H, H_B, J = 7.9 Hz), 5.94 (d, 8 H, H_C, J = 7.1 Hz), 6.44 (s, 4 H, H_E), 6.67 (s, 4 H, H_D), 6.88 (s, 4 H, H_H), 7.09 (s, 4 H, H_G), 7.14 (m, 16 H, CH_2CH_2Ph), 7.24 (m, 24 H, CH_2CH_2Ph); attempts to obtain FAB MS unsuccessful, probably due to the insolubility of the complex; FTIR (KBr pellet) 1682 cm^{-1} (CO stretch). Anal. Calcd for $C_{133}H_{119}NO_{21}$: C, 77.27; H, 5.80; N, 0.68. Found: C, 77.32; H, 5.86; N, 0.61.

1·Xenon. A vigorous stream of xenon gas was passed through a 0.7 mM solution of **1** in $CHCl_3$ for 10 min. The solution was allowed to stand under an atmosphere of xenon gas for 16 h at room temperature. The complex was precipitated by the addition of excess CH_3CN. The precipitate was dried at 90 °C under vacuum to produce **1**·xenon as a white solid: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.48 (m, 16 H, CH_2CH_2Ph), 2.65 (m, 16 H, CH_2CH_2Ph), 4.08 (d, 4 H, H_A, J = 7.1 Hz), 4.23 (d, 4 H, H_A, J = 7.5 Hz), 4.81 (t, 4 H, H_B, J = 8.0 Hz), 4.90 (t, 4 H, H_B, J = 7.9 Hz), 6.04 (d, 4 H, H_C, J = 7.1 Hz), 6.25 (d, 4 H, H_C, J = 7.4 Hz), 6.47 (d, 2 H, H_D, J = 6.3 Hz), 6.49 (s, 2 H, H_E), 6.58 (s, 2 H, H_F), 6.68 (d, 2 H, H_D, J = 6.3 Hz), 6.75 (s, 2 H, H_G), 6.82 (s, 4 H, H_H), 7.14 (m, 18 H, H_I and CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph); ^{129}Xe NMR (xenon saturated $CDCl_3$, 138 MHz) δ -101 (s, bound xenon), 0.0 (s, free xenon). Anal. Calcd for $C_{131}H_{112}O_{22}Xe$: C, 72.52; H, 5.20; O, 16.22; Xe, 6.05. Found: C, 72.29; H, 5.18; O, 16.55; Xe, 5.12. Xenon analysis was obtained by thermal gravimetric analysis. Summed analyses = 99.14%.

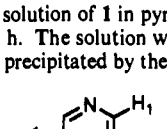
1·CH_3CN. A 0.7 mM solution of **1** in 30:1 $CHCl_3/CH_3CN$ (v/v) was allowed to equilibrate at room temperature for 48 h. The complex was precipitated by the addition of excess pentane. The precipitate was dried at 55 °C (2×10^{-5} Torr, 9 h). This produced **1**·CH_3CN as a white solid. Note that drying the complex at higher temperatures resulted in the loss of CH_3CN: ^{1}H NMR ($CDCl_3$, 360 MHz) δ -2.42 (s, 3 H, CH_3CN), 2.47 (m, 16 H, CH_2CH_2Ph), 2.65 (m, 16 H, CH_2CH_2Ph), 4.19 (d, 4 H, H_A, J = 7.0 Hz), 4.30 (d, 4 H, H_A, J = 7.1 Hz), 4.81 (t, 4 H, H_B, J = 7.9 Hz), 4.91 (t, 4 H, H_B, J = 7.8 Hz), 6.04 (d, 4 H, H_C, J = 7.0 Hz), 6.27 (d, 4 H, H_C, J = 7.3 Hz), 6.48 (d, 2 H, H_D, J = 6.3 Hz), 6.52 (s, 2 H, H_E), 6.59 (s, 2 H, H_F), 6.68 (d, 2 H, H_D, J = 6.3 Hz), 6.70 (s, 2 H, H_G), 6.77 (s, 4 H, H_H), 7.08 (s, 2 H, H_I), 7.15 (m, 16 H, CH_2CH_2Ph), 7.24 (m, 24 H, CH_2CH_2Ph). Anal. Calcd for $C_{133}H_{115}NO_{22}$: C, 76.82; H, 5.57; N, 0.67. Found: C, 76.78; H, 5.59; N, 0.75.

1·CH_2Cl_2. A 0.7 mM solution of **1** in CH_2Cl_2 was allowed to equilibrate for 10 min at room temperature. The complex was precipitated by the rapid addition of excess pentane. The precipitate was dried at 90 °C under vacuum to produce **1**·CH_2Cl_2 as a white solid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.47 (m, 16 H, CH_2CH_2Ph), 2.65 (m, 18 H, CH_2Cl_2 and CH_2CH_2Ph), 4.20 (d, 4 H, H_A, J = 6.6 Hz), 4.24 (d, 4 H, H_A, J = 7.1 Hz), 4.80 (t, 4 H, H_B, J = 8.0 Hz), 4.90 (t, 4 H, H_B, J = 7.9 Hz), 6.04 (d, 4 H, H_C, J = 7.0 Hz), 6.25 (d, 4 H, H_C, J = 7.3 Hz), 6.48 (br, 2 H, H_D), 6.52 (s, 2 H, H_E), 6.59 (s, 2 H, H_F), 6.71 (d, 2 H, H_D, J = 6.4 Hz), 6.73 (s, 2 H, H_G), 6.78 (s, 4 H, H_H), 7.08 (s, 2 H, H_I), 7.14 (m, 16 H, CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph). Anal. Calcd for $C_{132}H_{114}Cl_2O_{22}$: C, 74.67; H, 5.41; Cl, 3.34. Found: C, 74.62; H, 5.58; Cl, 3.24.

1·CH_2Br_2. A 1.3 mM solution of **1** in CH_2Br_2 was allowed to equilibrate for 68 h at room temperature. The complex was precipitated by the rapid addition of excess pentane. The precipitate was dried at 80 °C under vacuum to produce **1**·CH_2Br_2 as a white solid: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.45 (m, 18 H, CH_2Br_2 and CH_2CH_2Ph), 2.65 (m, 16 H, CH_2CH_2Ph), 4.30 (br dd, 8 H, H_A), 4.81 (t, 4 H, H_B, J = 7.9 Hz), 4.90 (t, 4 H, H_B, J = 7.7 Hz), 6.04 (d, 4 H, H_C, J = 7.0 Hz), 6.24 (d, 4 H, H_C, J = 7.4 Hz), 6.48 (br d, 2 H, H_D), 6.54 (s, 2 H, H_E), 6.60 (s, 2 H, H_F), 6.71 (s, 2 H, H_G), 6.72 (d, 2 H, H_D, J = 6.4 Hz), 6.76 (s, 4 H, H_H), 7.05 (s, 2 H, H_I), 7.14 (m, 16 H, CH_2CH_2Ph), 7.24 (m, 24 H, CH_2CH_2Ph). Anal. Calcd for $C_{132}H_{114}Br_2O_{22}$: C, 71.67; H, 5.57; Br, 7.22. Found: C, 71.44; H, 5.13; Br, 7.18.

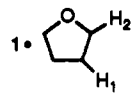
1·CS_2. A 0.8 mM solution of **1** in 15:1 $CHCl_3/CS_2$ was allowed to equilibrate for 68 h at room temperature. The complex was precipitated by the rapid addition of excess pentane. The precipitate was dried at 80 °C under vacuum to produce **1**·CS_2 as a white solid: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.45 (m, 16 H, CH_2CH_2Ph), 2.64 (m, 16 H, CH_2CH_2Ph), 4.23 (d, 4 H, H_A, J = 7.0 Hz), 4.36 (d, H_A, J = 7.3 Hz), 4.80 (t, 4 H, H_B, J = 7.9 Hz), 4.90 (t, 4 H, H_B, J = 7.8 Hz), 6.07 (d, 4 H, H_C, J = 7.0 Hz), 6.29 (d, 4 H, H_C, J = 7.4 Hz), 6.51 (d, 2 H, H_D, J = 6.5 Hz), 6.55 (s, 2 H, H_E), 6.61 (s, 2 H, H_F), 6.66 (s, 2 H, H_G), 6.72 (d overlapping s, 6 H, H_D and H_H), 7.04 (s, 2 H, H_I), 7.14 (m, 16 H, CH_2CH_2Ph), 7.22 (m, 24 H, CH_2CH_2Ph). Anal. Calcd for $C_{132}H_{112}O_{22}S_2$: C, 74.98; H, 5.34; S, 3.03. Found: C, 75.01; H, 5.40; S, 3.01.

1·Pyridine. A 0.7 mM solution of **1** in pyridine (freshly distilled from CaH_2) was refluxed for 6 h. The solution was concentrated by a factor of 3, and the complex was precipitated by the addition of excess CH_3CN.



The precipitate was dried at 100 °C under vacuum to produce **1**·pyridine as a white solid: ^{1}H NMR ($CDCl_3$, 333 K, 500 MHz) δ 2.56 (m, 16 H, CH_2CH_2Ph), 2.70 (m, 16 H, CH_2CH_2Ph), 2.89 (m, 2 H, pyridine H_2), 4.16 (d, 2 H, pyridine H_1, J = 4.3 Hz), 4.18 (br, 4 H, H_A), 4.34 (br, 4 H, H_A), 4.89 (t, 4 H, H_B, J = 7.9 Hz), 4.96 (t, 4 H, H_B, J = 7.9 Hz), 5.80 (d, 4 H, H_C, J = 7.2 Hz), 6.07 (d, 4 H, H_C, J = 7.3 Hz), 6.18 (d, 2 H, H_D, J = 6.3 Hz), 6.26 (t, 1 H, pyridine H_3, J = 7.4 Hz), 6.37 (d, 2 H, H_D, J = 6.3 Hz), 6.73 (s, 2 H, H_E or H_F), 6.77 (s, 2 H, H_E or H_F), 6.92 (s, 4 H, H_H), 6.99 (s, 2 H, H_G), 7.17 (m, 16 H, CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph), 7.32 (s, 2 H, H_I). Anal. Calcd for $C_{136}H_{117}NO_{22}$: C, 77.15; H, 5.57; N, 0.66; O, 16.62. Found: C, 76.78; H, 5.65; N, 0.67; O, 16.90. Summed analyses = 100.00%.

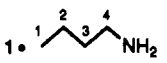
1·$(CH_2)_4O$. A 0.4 mM solution of **1** in THF was refluxed for 12 days. The solution was concentrated by a factor of 3, and the complex was precipitated by the addition of excess hexanes. The precipitate was dried at 110 °C under vacuum to produce **1**·$(CH_2)_4O$ as a white solid: ^{1}H



NMR ($CDCl_3$, 500 MHz) δ −1.22 (br, 4 H, THF H_1), −0.23 (br, 4 H, THF H_2), 2.48 (m, 16 H, CH_2CH_2Ph), 2.65 (m, 16 H, CH_2CH_2Ph), 4.38 (d, 8 H, H_A), 4.83 (t, 4 H, H_B, J = 8.1 Hz), 4.90 (t, 4 H, H_B, J = 7.9 Hz), 5.96 (br, 4 H, H_C), 6.19 (d, 4 H, H_C, J = 7.6 Hz), 6.47 (d, 2 H, H_D, J = 6.5 Hz), 6.54 (s, 2 H, H_E), 6.59 (s, 2 H, H_F), 6.66 (d, 2 H, H_D, J = 6.5 Hz), 6.75 (s, 2 H, H_G), 6.81 (s, 4 H, H_H), 7.14 (m, 18 H, H_I and CH_2CH_2Ph), 7.24 (m, 24 H, CH_2CH_2Ph). Anal. Calcd for $C_{135}H_{120}O_{23}$: C, 76.83; H, 5.73. Found: C, 76.65; H, 5.63.

1·C_6H_6. A 0.3 mM solution of **1** in benzene was refluxed for 12 days. The complex was precipitated by the addition of excess hexanes. Its ^1H NMR spectrum indicated that only 85% of the host contained benzene. No further purification was performed, and the hemicarceplex was characterized by ^1H NMR only: ^1H NMR ($CDCl_3$, 333 K, 500 MHz) δ 2.4–2.6 (m, 16 H, CH_2CH_2Ph), 2.70 (m, 16 H, CH_2CH_2Ph), 3.92 (s, 6 H, benzene), 4.27 (br, 8 H, H_A), 4.87 (t, 4 H, H_B, J = 7.8 Hz), 4.96 (t, 4 H, H_B, J = 7.8 Hz), 5.78 (d, 4 H, H_C, J = 6.9 Hz), 6.08 (d, 4 H, H_C, J = 7.4 Hz), 6.17 (d, 2 H, H_D, J = 6.3 Hz), 6.23 (d, 2 H, H_D, J = 6.3 Hz), 6.77 (s, 2 H, H_E or H_F), 6.84 (s, 2 H, H_E or H_F), 6.90 (s, 4 H, H_H), 6.99 (s, 2 H, H_G), 7.17 (m, 16 H, CH_2CH_2Ph), 7.23 (m, 24 H, CH_2CH_2Ph), 7.33 (s, 2 H, H_I).

1·$CH_3(CH_2)_3NH_2$. A solution of 50 mg of **1** in 20 mL of distilled C_6H_5Cl was prepared (heating was required). To this was added 5 mL of freshly distilled *n*-butylamine. The mixture was refluxed in a 105 °C oil bath for 24 h, during which time a small amount of precipitate formed. The complex was precipitated by the addition of excess hexanes.



The ^1H NMR indicated that only 90% of the host contained butylamine. No further purification was performed, and the hemicarceplex was characterized by ^1H NMR only: ^1H NMR ($CDCl_3$, 333 K, 500 MHz), δ −3.31 (t, 3 H, butylamine H_1, J = 7.5 Hz), −3.13 (br t, 2 H, butylamine NH_2, J = 5.9 Hz), −1.24 (m, 2 H, butylamine H_2), −1.04 (m, 2 H, butylamine H_4), −0.89 (m, 2 H, butylamine H_3), 2.49 (m, 16 H, CH_2CH_2Ph), 2.69 (m, 16 H, CH_2CH_2Ph), 4.37 (d, 4 H, H_A, J = 6.9 Hz), 4.44 (d, 4 H, H_A, J = 7.3 Hz), 4.87 (t, 4 H, H_B, J = 8.0 Hz), 4.96 (t, 4 H, H_B, J = 7.9 Hz), 5.93 (d, 4 H, H_C, J = 6.9 Hz), 6.17 (d, 4 H, H_C, J = 7.3 Hz), 6.47 (ABq, 4 H, H_D, J = 5.9 Hz), 6.50 (s, 2 H, H_F or H_E), 6.55 (s, 2 H, H_E or H_F), 6.74 (s, 2 H, H_G), 6.83 (s, 4 H, H_H), 7.11 (s, 2 H, H_I), 7.16 (m, 16 H, CH_2CH_2Ph), 7.24 (m, 24 H, CH_2CH_2Ph).

1·$(CH_3CH_2)_2NH$. A solution of 25 mg of **1** in 10 mL of distilled C_6H_5Cl was prepared (heating was required). To this was added 2 mL of freshly distilled diethylamine. The mixture was refluxed in a 65 °C oil bath for 4 h, during which time a small amount of precipitate formed. The complex was precipitated by the addition of excess hexane. The ^1H NMR indicated that only 70% of the host contained butylamine. The remainder was partitioned (2:1) between **1**·CH_3CN and **1**. The CH_3CN appeared as a very minor (<1%) impurity in the diethylamine (^1H NMR spectrum). No further purification was performed on the hemicarceplex, which was characterized by ^1H NMR only: ^1H NMR ($CDCl_3$, 295 K, 500 MHz) δ −2.95 (t, 6 H, diethylamine CH_3, J = 7.2 Hz), −1.48 (br t, 1 H, diethylamine NH, J = 6.0 Hz), −0.48 (m, 4 H, diethylamine CH_2), 2.48 (m, 16 H, CH_2CH_2Ph), 2.66 (m, 16 H, CH_2CH_2Ph), 4.42 (d, 4 H, H_A, J = 7.0 Hz), 4.47 (d, 4 H, H_A, J = 7.3 Hz), 4.83 (t, 4 H, H_B, J = 7.8 Hz), 4.93 (t, 4 H, H_B, J = 7.9 Hz), 5.93 (d, 4 H, H_C, J = 6.9 Hz), 6.17 (d, 4 H, H_C, J = 7.3 Hz), 6.48 (s, 4 H, H_D), 6.51 (s, 2 H, H_F or H_E), 6.55 (s, 2 H, H_E or H_F), 6.71 (s, 2 H, H_G), 6.83 (s, 4 H, H_H), 7.09 (s, 2 H, H_I), 7.15 (m, 16 H, CH_2CH_2Ph), 7.24 (m, 24 H, CH_2CH_2Ph).

Kinetics. The values of k_d for **1**·$(CH_3)_2NCHO$, **1**·$(CH_3)_2NCOCH_3$, and **1**·$(CH_3)_2SO$ in 1,2,4-trichlorobenzene were obtained as follows. Solutions 0.3 mM in each of the complexes were prepared in 100-mL culture tubes, and heated in a temperature-controlled (±1 °C), insulated oil bath. Aliquots were removed at timed intervals and added to excess hexanes. The resulting precipitate was collected by filtration and analyzed by ^1H NMR spectroscopy ($CDCl_3$, 333 K). The NMR samples were saturated with N_2 immediately prior to collecting the spectra. Proton integration was used to determine the ratio of free to complexed host as a function of time. A minimum of five data points over 2 half-lives were collected for each determination.

The value of k_d for **1**·xenon was determined by preparing a 0.7 mM solution in CD_2Cl_2. This was sealed in an NMR tube (1 atm) and placed in a 298 K constant-temperature bath (±1 °C). The conversion to **1**·CD_2Cl_2 was followed by ^1H NMR spectroscopy. Proton integration of the H_A signals of the respective complexes was used to determine their ratio. Six data points were taken over a period of 2 half-lives. The estimate of the half-life of **1**·CH_3CN was measured in the same fashion (two data points, capped tube).

Estimation of K_a Values for O_2 and N_2 Complexation. Solutions 5 mM in **1** were prepared in $CDCl_3$ (dried over activated 3-Å molecular sieves). These were placed in NMR tubes, and a small amount of $CDCl_3$ was added to compensate for any losses due to evaporation during the gas displacement procedure. A vigorous stream of the desired gas was passed through the samples for 15 min, and the ^1H NMR spectra were immediately recorded. The fraction of host containing nitrogen (50%) was determined from integration of the respective H_A proton signals of the host. The fraction of the host containing oxygen (33%) was determined from integration of the respective H_B (methine) proton signals. The concentrations of free O_2 and N_2 were taken as those at saturation (11.5 mM[11] and 5.6 mM[9], respectively).

Crystal Structure of 1·$(CH_3)_2NCHO$·2CH_3CN·2$CHCl_3$. Compound 1·$(CH_3)_2NCHO$·2CH_3CN·2$CHCl_3$ crystallizes from $CHCl_3/CH_3CN$ as colorless needles in the orthorhombic system *Pbna* (standard setting *Pbcn*). Unit cell dimensions are as follows: a = 20.455 (5), b = 20.773 (5), c = 30.307 (8) Å, V = 12878 Å^3, Z = 4 (the molecule has C_2 symmetry, and the guest is disordered about a 2-fold axis passing through O and N). The chloroform is disordered about a center of symmetry. The crystal was examined on a modified Syntex PĪ diffractometer, Cu Kα radiation, at 298 K. The structure was determined by direct methods. Refinement of 310 parameters (2449 reflections with $I > 3\sigma(I)$) has an agreement value, R, currently at 0.168. Details will be published elsewhere.