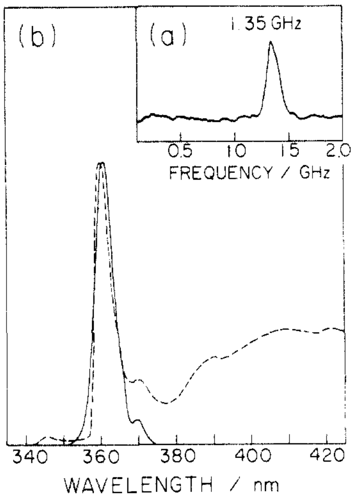

Figure 2. (a) ODMR spectrum of the phosphorescence of poly(methylpropylsilylene) (benzene solution) at 1.3 K. (b) The action spectrum of the ODMR signal (solid line) and the long-lived emission spectrum (broken line) shown in Figure 1b.

stants for T_1 and S_1 and k_{TT} is the rate constant for triplet–triplet annihilation. Further, *f* stands for the fraction of the annihilation rate constant yielding S_1. The decay curves of the 360- and 345-nm bands were successfully modeled by eqs 1 and 2, respectively, with the common k_P value of 200 s^{-1}. This kinetic analysis clearly shows that the 360- and 345-nm long-lived emissions are respectively the phosphorescence and delayed fluorescence.

In order to make the phosphorescence assignment more conclusive, we have made zero-field ODMR measurements at 1.3 K. As an example, the ODMR spectrum in the 0–2-GHz microwave range is shown in Figure 2a, which shows that the steady-state phosphorescence intensity increases by the application of 1.35-GHz microwave radiation. The ODMR action spectrum for the 1.35-GHz transition is shown in Figure 2b. The action spectrum well reproduces the phosphorescence spectrum without the perturbation of the impurity emission. Similarly, an ODMR transition is observed at 2.38 GHz, and its action spectrum again reproduces the phosphorescence spectrum. The other microwave transition is observed in the microwave induced delayed phosphorescence (MIDP) experiment (that is, the microwave is applied after the phosphorescence decays to a certain level) at 3.73 GHz, which agrees with the sum of the two transition frequencies. Thus, all three transitions among the three triplet sublevels are successfully observed. The finding that the ODMR action spectrum coincides with the phosphorescence very conclusively shows that the observed phosphorescence and ODMR spectra are genuine.

The observed zero-field splittings are relatively large as compared with those of carbon-based conjugated polymers such as polydiacetylene[12] (0.55, 1.11, and 1.66 GHz). The zero-field splittings of $(MePrSi)_n$ would be much smaller if they were governed solely by the spin–spin coupling. The relatively large zero-field splittings observed for the present polysilylene is most probably due to the large spin–orbit coupling.

The energy difference between the fluorescence and the newly observed phosphorescence is 1200 cm^{-1}. The smallness of the singlet–triplet splitting is in accord with the delocalized character of the excited states. Further, this singlet–triplet energy difference is almost in accord with the value 2000 cm^{-1} calculated recently by Takeda.[13]

Finally, the intensity of the phosphorescence strongly depends on temperature. The phosphorescence (except for the broad impurity band) is totally quenched at temperatures higher than 15 K. Unfortunately, the temperature dependence of the spectrum could not be measured between 4.2 and 15 K with our facilities at present. This thermal quenching, which, we surmise at this moment, is due to a mechanism proposed previously by one of the present authors,[14,15] is the main reason why the phosphorescence has not been detected so far.

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Host–Guest Complexation in the Gas Phase by Desorption Chemical Ionization Mass Spectrometry

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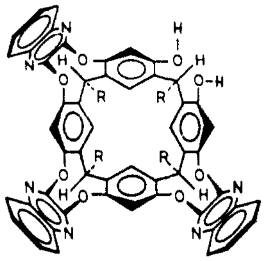
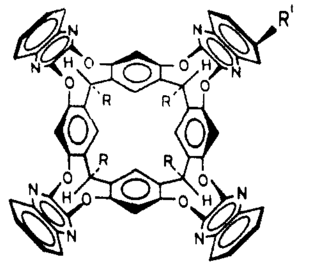
Cavitands are synthetic macrocycles capable of molecular recognition.[1] The structures and stabilities of supramolecular complexes formed by such hosts have been widely studied both in solution and in the solid state.[2] The few reports of gas-phase complexes in the literature refer to charged complexes formed in solution, which had been isolated and then evaporated.[3] We report the first study on the formation of caviplexes between gaseous reactants, wherein complexation occurs in the absence of solvation effects. Desorption chemical ionization[4] (DCI) mass spectrometry was used to evaporate the cavitand, provide an atmosphere of guest molecules, and ionize and analyze the reaction products.[5] Three differently shaped hosts of the same family were synthesized, namely, the cleft-shaped cavitand **1**,[7] the vessel-like cavitand **2**,[1c] and its derivative **3**,[7] in which a bulky menthoxy group perches on top of the cavity.[8]



1
R = C_6H_{13}



2 R' = H
3 R' = COO(-)Menthyl

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(5) DCI experiments were conducted on a Finnigan-MAT 8424 mass spectrometer (detailed experimental conditions are described in ref 6). Vapors of various guests were used as the CI reagent gas at uncorrected pressures of 0.3 mbar. The electron energy was set to 100 eV (positive ions) and 140 eV (negative ions). The magnet was scanned from 450 to 2100 Da in 1.3 s.

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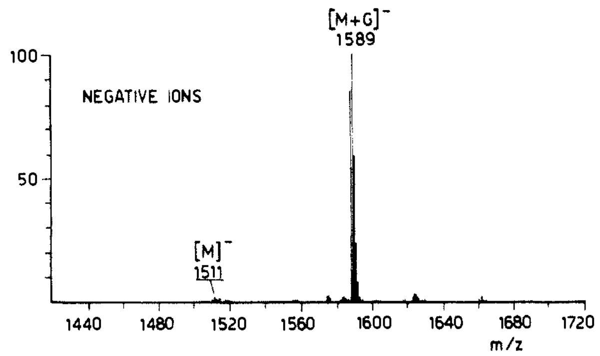

Figure 1. Desorption chemical ionization mass spectrum of cavitand **3** (M) using benzene (G) as reagent gas at a source temperature of 80 °C; negative ions.

Table I. Relative Abundance Percent of Molecular Ions and Host–Guest Adduct Ions for Various Cavitands and Guests under DCI Conditions[a]

run no.	components	negative ions [M], %	negative ions [M + G], %	positive ions [M], %	positive ions [M + G], %
1	**1** + benzene	50	100		
2	**2** + benzene	5	100	41	100
3	**3** + benzene	1	100	22	100
4	**1** + benzene (T = 100 °C)	100	9		
5	**2** + benzene (T = 100 °C)	56	100		
6	**3** + benzene (T = 100 °C)	34	100		
7	**3** + fluorobenzene	4	100	42	100
8	**3** + toluene	10	100	32	100
9	**3** + 2-fluorotoluene	3	100	16	100
10	**2** + 1,3-bis(trifluoromethyl)benzene	38	100		
11	**3** + 1,3-bis(trifluoromethyl)benzene	37	100		
12	**2** + isobutane	100	41	100[b]	3[c]
13	**3** + isobutane	65	100	100[b]	19[c]
14	**3** + ammonia	100	7	6[b]	100[d]

[a] The source temperature was set to 80 °C unless otherwise specified. [b] $[MH]^+$. [c] $[MH + G]^+$. [d] $[M + NH_4 + NH_3]^+$.

In Figure 1, the negative-ion DCI mass spectrum is shown for cavitand **3** in the presence of gaseous benzene. The cluster of peaks with the largest intensity is observed at m/z = 1589 Da (daltons) nominal mass.[9] This represents the supramolecular ion of the host–guest complex and is thought to originate from complexation of a neutral molecule of benzene by the gaseous neutral cavitand, followed by ionization of the reaction product. In this caviplex, the charge should be delocalized on the large and mostly aromatic structure of the host. Accordingly, the results for positive ions are similar to those shown in Figure 1 (Table I). An alternative mechanism, in which the ionization of the host precedes its complexation, is less reasonable, since the abundance of charged species in the chamber is much lower than that of the neutral guests. A mechanism in which the charged guest is trapped within the neutral host is also unlikely, since many charged ion–molecule reaction products are evident in the mass spectra taken in the absence of host (see supplementary material), but only one host–guest adduct is produced. A gas–solid complexation on the DCI wire followed by vaporization of the preformed complex can also be excluded, since, at the desorption temperature, all caviplexes are unstable and release their guests.[10] More likely, the host undergoes complexation after losing excess thermal energy upon collision with the reagent gas. The ionization process leading to both the charged adduct and a small amount of the cavitand molecular ion (m/z = 1511 Da) is electron capture (negative ions) or charge exchange with product ions of the reagent gas (positive ions).

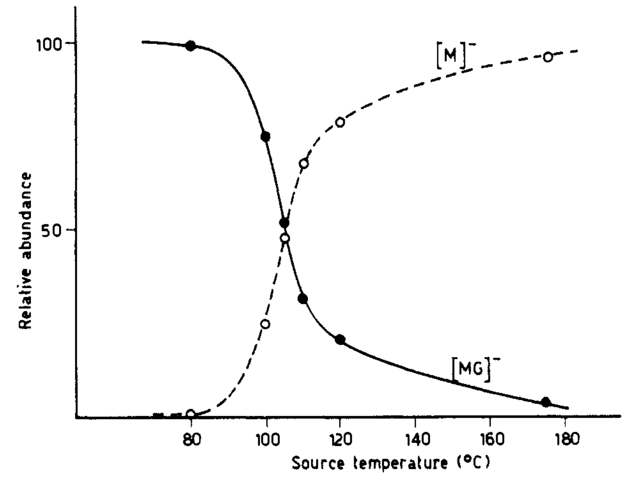

Figure 2. Plot of the relative abundance of the negatively charged $3\cap C_6H_6$ caviplex and free cavitand **3** vs temperature of the mass spectrometer ion source.

Among the candidate guests tested in our study, only xenon and methane do not form host–guest complexes. In contrast, isobutane, ammonia, and several aromatic compounds give rise to adduct ions by reaction with the various cavitands (Table I). Under constant experimental conditions, complexation is more extensive with aromatic reagent gases than it is with isobutane and ammonia. Moreover, the free cavitand is generally more abundant in the positive than it is in the negative mass spectrum. By comparing the results for various aromatic guests, similar caviplex/free host abundance ratios are uncovered; only when 1,3-bis(trifluoromethyl)benzene is used is the amount of cavitand free of guest higher, probably as a result of the steric hindrance to binding of the two CF_3 groups in the meta position.

The source temperature in the mass spectrometer plays a major role in influencing the equilibrium of the complexation process. In fact, a continuous increase in the fraction of free host is clearly visible as the source is heated (Figure 2). For example, 99% of **3** forms a complex with benzene at 80 °C, but most of it remains free of guest when the source temperature is set to 120 °C. The crosspoint of the two curves for **3** occurs at about 105 °C.

Another factor influencing the extent of complexation is the shape of the cavitand, with more pronounced effects being revealed at source temperatures higher than 80 °C. At 100 °C (experiments 4–6), only a small amount of the $1\cap C_6H_6$ caviplex is formed and the fraction of free host is significantly higher for **2** than it is for **3**. Moreover, when isobutane is used as a guest, enhanced reactivity differences between **2** and **3** are observed (experiments 12 and 13). This behavior can be explained by considering that three types of host–guest interactions may play a role, namely, face-to-face (π–π) stacking,[11] edge-to-face interactions,[12] and shape complementarity.[13] The former takes place in caviplexes containing aromatic guests, but is weakened by the thermal energy transfer from the source walls. Thus, at higher temperatures, shape complementarity prevails and differences between **1**, **2**, and **3** are more easily detected. Likewise, isobutane cannot interact with the host by π–π stacking; therefore, it is more efficiently trapped by **3**, which contains a menthoxy group in-

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(8) The inner cavity of cavitand **2** is 7.2 Å wide and 8.3 Å deep, measured by X-ray analysis.[1c]

(9) A cluster of peaks is observed instead of a single peak because of the natural abundance of ^{13}C; the intensity distribution measured closely fits that calculated.

(10) The solid deposited on the DCI wire is a 1:1 $CHCl_3$ caviplex, which does not lose its guest under vacuum (1×10^{-5} mbar). Thermogravimetric analysis performed on the $2\cap CHCl_3$ caviplex showed that the guest is removed at 209 °C while the corresponding benzene caviplex releases its guest at 169 °C.

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termittently sealing the cavity entrance.

In conclusion, molecular recognition is demonstrated to occur in the gas phase, not only in solution and in solids. The dependence of complexation on various parameters can be studied easily. Since experiments are described in terms of bimolecular interactions, without involvement of solvating species, fundamentally important information on host-guest structures and thermochemistry is potentially accessible.

Supplementary Material Available: Chemical ionization mass spectra of reagent gases, recorded under the same experimental conditions adopted in the experiments reported in Table I and Figure 1 (1 page). Ordering information is given on any current masthead page.

A Rigorous Test for Orbital Symmetry Control in Cation Radical/Neutral Cycloadditions

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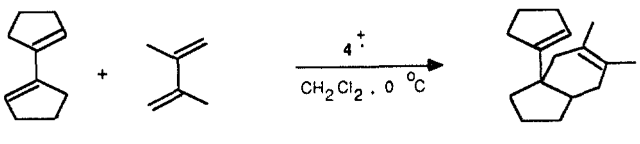
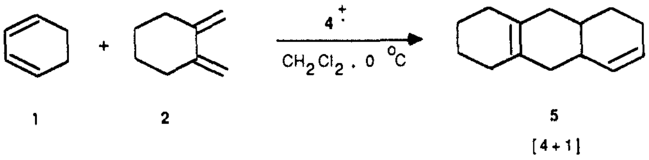
Two potentially distinct mechanistic role senses have been recognized for the cation radical Diels-Alder reaction.[1,2] The mechanism in which the cation radical component reacts as the dienophile is classified as a [4 + 1] cycloaddition and is formally symmetry allowed. The alternate reaction mode in which the cation radical component reacts in the s-cis diene role is classified as a [3 + 2] cycloaddition and is formally symmetry forbidden. In the preponderance of the cases thus far observed of cation radical Diels-Alder cross additions between two conjugated dienes, the more ionizable component is exclusively incorporated into the adduct as the dienophilic moiety (e.g., Scheme I), in apparent agreement with orbital symmetry considerations.[2-4] However, since cation radical cyclobutanation, another orbital symmetry forbidden cation radical cycloaddition, is extremely facile, it is probable that any symmetry-imposed barrier to [3 + 2] cycloaddition must be much more modest than analogous barriers to forbidden cycloadditions of neutrals. The feasibility of [3 + 2] cycloadditions, first as a minor reaction channel in competition with cyclobutanation in the reaction of relatively more ionizable dienes with electron-rich alkenes[5] and then as the major reaction channel where the less ionizable component, a styrene, is unable to function effectively in the dienic role,[6] has more recently been established. The fundamental question of whether orbital symmetry (or other) effects favor the [4 + 1] cycloaddition in systems in which both reaction components are comparably amenable to the dienic role remains to be rigorously addressed.

In Diels-Alder cycloadditions to neutral dienes, dienic aptitude is, of course, strongly correlated with the s-cis conformational population of the diene. The same should be true of the [4 + 1] reaction. The [3 + 2] reaction, however, is even more acutely affected by diene conformation since the barrier to conformational equilibration in a diene cation radical is prohibitively high. Therefore, to the extent that dienes exist in the s-trans conformation and are ionized to the s-trans cation radical, [3 + 2] cycloaddition is precluded and either [4 + 1] or [2 + 1] cycloaddition must result (as in Scheme I). It was therefore critical to this study to involve only rigidly s-cis dienes. Further, to render mechanistic role assignments unequivocal, diene pairs were selected for which the oxidation potential differences are sufficiently large that the more ionizable diene can be reliably assumed to be the hole-carrying species. This assumption is scrutinized in a subsequent paragraph. The reactant pair selected for initial study was 1,3-cyclohexadiene (**1**; E_{ox} = 1.53 V) and 1,2-dimethylenecyclohexane (**2**; E_{ox} = 1.85 V).[7] The tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{4}^{\bullet+}$) initiated cycloaddition of **1** and **2** in dichloromethane at 0 °C yielded, as a cross adduct, essentially only **5** (Scheme II; 45% yield). The mechanistic classification of the reaction leading to **5** is [4 + 1] (i.e., $\mathbf{1}^{\bullet+}/\mathbf{2}$), based in part upon the previously stated assumption. The 1,4-dicyanobenzene photosensitized reaction of **1** and **2** in acetonitrile also yields **5** as the sole cross adduct.

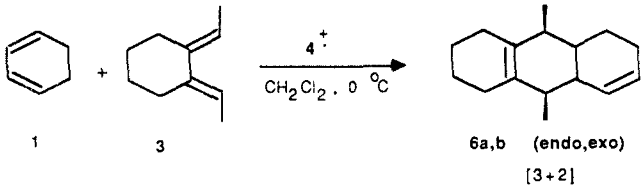
Scheme I



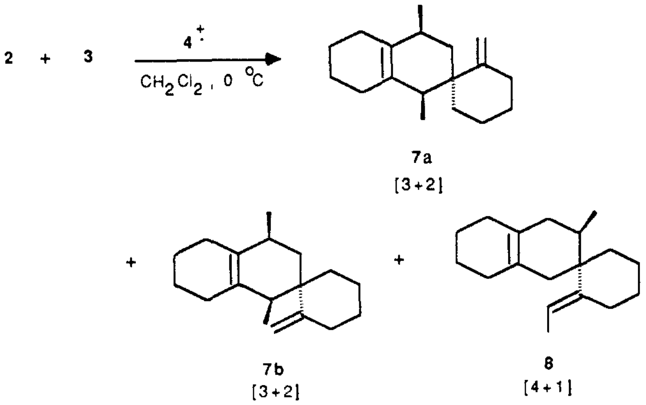
Scheme II



Scheme III



Scheme IV



The closely analogous reaction of **1** and **3** (E_{ox} = 1.36 V)[8] was then studied. In this case, **1** is the less ionizable component. The observed adducts (**6a,b**; Scheme III) now reflect a selective [3 + 2] cycloaddition ($\mathbf{3}^{\bullet+}/\mathbf{1}$). In agreement with this assignment, the dimer of **3** is a major coproduct of the reaction but that of **1** is produced in only minor amounts when **1** and **3** are used in a 1:1 ratio. Once more, the 1,4-dicyanobenzene photosensitized reaction gives the same cross adducts (**6a,b**) as in the aminium salt reaction and no others.

Finally, the reaction of **2** and **3** was studied in order to examine a case in which the [3 + 2] and [4 + 1] adduct structures are

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