taken in the single-pulse and cross-polarization (CP) modes, both with proton decoupling during data acquisition.[11,12] On the basis of model compound studies, we have assigned the highest shielding resonance (40 ppm) to physisorbed $(CH_3)_3PO$, the shoulder at 53 ppm (which is more visible in the CP spectrum) to Lewis-bound $(CH_3)_3PO$ and the lower shielding resonance at 65 ppm to $(CH_3)_3POH^+$ bound to surface Brøsted sites. The spinning side bands (marked by asterisks), which are more pronounced in the CP spectra, are due to excess crystalline $(CH_3)_3PO$, which has the same $^{31}P$ chemical shift as physisorbed material but can be differentiated by a 3-s $T_1$ value, which contrasts with the much shorter $T_1$ (0.15 s) for the surface-physisorbed species.

Figure 2 displays CP and single-pulse $^{31}P$ MAS spectra of a high-loading sample of $(C_2H_5)_3PO$ on silica–alumina. In contrast to trialkylphosphines, for which the greatest chemical difference between species occurs for the smallest phosphine, $(C_2H_5)_3PO$ shows better chemical shift differentiation among the various surface species than does $(CH_3)_3PO$. The highest shielding resonance at 49.5 ppm has been assigned to surface-physisorbed $(C_2H_5)_3PO$ species, the central resonace at 63 ppm to Lewis-bound species, and the lowest shielding resonance at 76 ppm to $(C_2H_5)_3POH^+$ bound to surface Brønsted sites. As can be clearly seen in Figure 2, the CP spectrum enhances the signals due to molecules bound to the Brønsted sites and Lewis sites, presumably because these molecules are more rigidly bound to the surface than are the physisorbed species. As in the case of Figure 1, the spinning side bands, due to crystalline phosphine oxide, are enhanced in the CP spectra.

The 13-ppm decrease in $^{31}P$ shielding upon complexation to Al is larger than that seen for the analogous system of trialkylphosphines on silica–alumina.[10] We have not been able to prepare a satisfactory model compound with $R_3P{:}OAl(\text{–O–})_3$ coordination, but 1:1 mixtures of $(CH_3)_3PO$ and $AlCl_3$ and of $(C_2H_5)_3PO$ and $AlCl_3$ in $CH_2Cl_2$ give $^{31}P$ shifts of 58 and 64 ppm at −60 °C, respectively, corroborating the above assignments and illustrating that Lewis complex formation can cause a substantial decrease of $^{31}P$ shielding in phosphine oxides. The chemical shifts assigned here for the Brønsted complex, Lewis complex, and physisorbed molecules agree with our interpretation of corresponding peaks in the $^{31}P$ NMR spectra (not shown here) of $(C_2H_5)_3PO$ adsorbed on $\gamma$-alumina and give the same order as observed previously for phosphines.[10]

It should be noted that, although hydrogen-bonding $^{31}P$ shifts of several ppm have been reported for phosphine oxides,[13] we have not distinguished hydrogen-bonded phosphine oxides in the present work. To the extent that hydrogen-bonded species are present in these systems, their resonances are presumably contained in the region we have identified with physisorption.

With the much larger dispersion found in the $^{31}P$ chemical shifts among the surface-bound species of trialkylphosphine oxides, it now appears practical to quantitate not only the number of Brønsted sites but also the number of Lewis sites on an amorphous surface. Also, by making use of the appearance of signals due to crystalline trialkylphosphine oxide, one can obtain an estimate of the total number of physisorption "sites" for a specific probe molecule on a surface. In addition, through a surface concentration study one can estimate the relevant surface binding constants and compare them to those of other probe molecules investigated. Detailed studies of this type are currently in progress.

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[11] The $^{31}P$ NMR spectra were obtained at 60.745 MHz on a modified NT-150 spectrometer, using MAS speeds of 3.0–3.5 KHz.

[12] The silica–alumina (from American Cyanamid) was formally 75% $SiO_2$/25% $Al_2O_3$ by weight, with a surface area of 485 $m^2/g$, as determined by the nitrogen BET method. The silica–alumina was dried for 12–16 h at $10^{-4}$ torr and 160–170 °C prior to treatment with the phosphine oxides (Strem), adsorbed onto the silica–alumina from $CH_2Cl_2$ solution.

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# Concave Functionality: Design of a Phenol Sticky Host

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There is considerable current interest in the design of host molecules possessing rigidly defined vacities capable of accommodating guests with a high degree of selectivity and binding.[1-4] We report here construction of a host molecule (**1**) possessing a phenol sticky[2b] cavity. Host **1** was designed to test the idea that an inwardly pointing (concave) functionality, e.g., a 4-(dimethylamino)pyridine, would exhibit guest stickiness in *nonaqueous media*.

Cyclization of **2**[5] afforded a 2:1 mixture of *dl*-**1** and its meso isomer. The structure of **1** was confirmed by a single-crystal X-ray structure of its ethylene dichloride (EDC) incavitated complex 1-EDC (Figure 1a). The EDC is in van der Waals contact with the sides and surfaces of the cyclophane box but not with the pyridine. The latter is rotated approximately 90° from the desired concave arrangement.[6]

Host *dl*-**1** binds certain phenols *very tightly*, thus confirming the above hypothesis. Titration of *dl*-**1** in $CHCl_3$[7] with *p*-nitrophenol (PN), with nonlinear least-squares treatment of $\delta_{obsd}$ vs. PN/**1** ratio, leads to chemical shifts of the **1**/PN complex and association constants for the 1:1 complex formed.[8] Both the PN protons and H1 or **1** show pronounced upfield shifts (ca. 1 ppm) in the complex. $K_{assoc}$ for **1**/PN is 3000 ± 300 $M^{-1}$; it is 1100 ± 300 $M^{-1}$ for **1**/*p*-cyanophenol, 500 $M^{-1}$ for (*p*-nitrophenyl)azophenol,[9] ~50 $M^{-1}$ for **1**/*p*-carboethoxyphenol, and ~20 $M^{-1}$ for phenol. A $\rho$ of ~6 may be calculated from these data. The **1**/PN complex was isolated. Its X-ray structure (Figure 1b) fully confirms the conclusions from the above NMR experiments. The pyridine now projects into the cavity, hydrogen bonding with the phenolic OH. The PN aromatic ring just fits the cavity, being in van der Waals contact with the surrounding carbon net.

We have been singularly unsuccessful in factoring out the forces involved in formation of these remarkably stable and guest-selective complexes. The following observations are salient with respect to this.

1. Prehost **2** exhibits *no* complexation behavior as described above for **1**. The three-dimensional cavity of **1** is thus required.

2. Non-phenolic isosteres, *p*-nitroanisole and *p*-nitrochlorobenzene, do *not* compete with PN for occupancy of the cavity. Acid–base interaction (hydrogen bonding) is thus required.

3. More acidic guests, benzoic acids and 2,4-dinitrophenol, do *not* form cavity complexes. Rather simple proton transfer occurs,

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[5] $Cu(OAc)_2$, pyridine, 40 °C: **2** was prepared from 3,7-bis(propargyloxy)-2-naphthoic acid[2c] and 4-(dimethylamino)-2,6-bis(hydroxymethyl)pyridine by standard procedures.

[6] MM2 calculations suggest that the desired concave arrangement of the pyridine is the minimum-energy conformation: the depth of this minimum appears not to be overwhelming.

[7] A "big" solvent, one incapable of fitting into the cavity.

[8] The nonlinear LS PC program SIMPLEX is available on request from the authors.

[9] The *p*-nitrophenyl group apparently protrudes from the cavity like a tongue, as only the phenol-ring protons move upfield.

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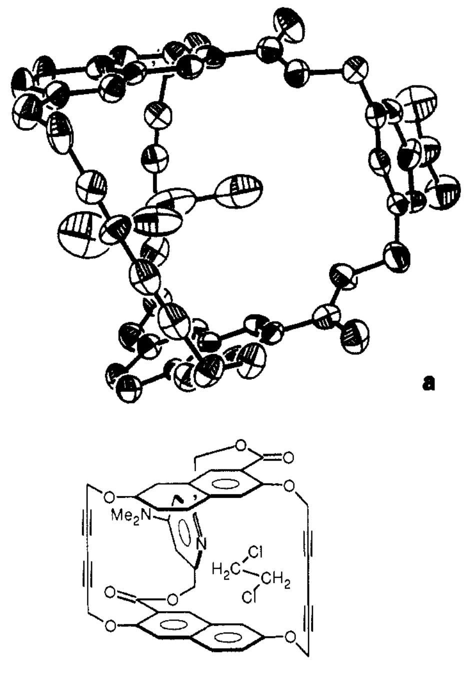
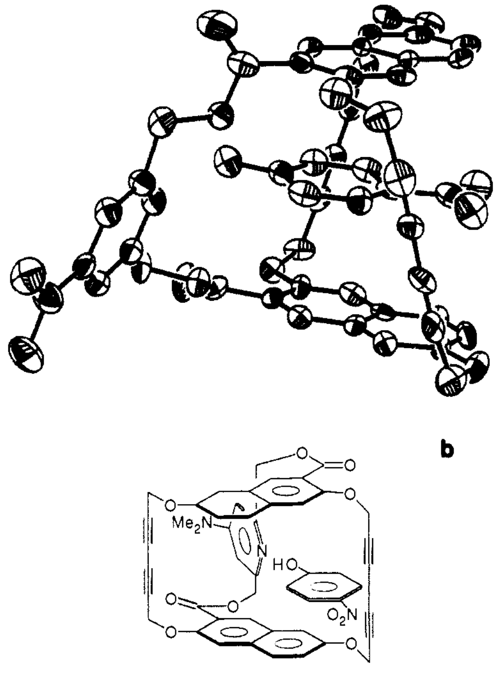


1 : EDC complex



1 : PN complex

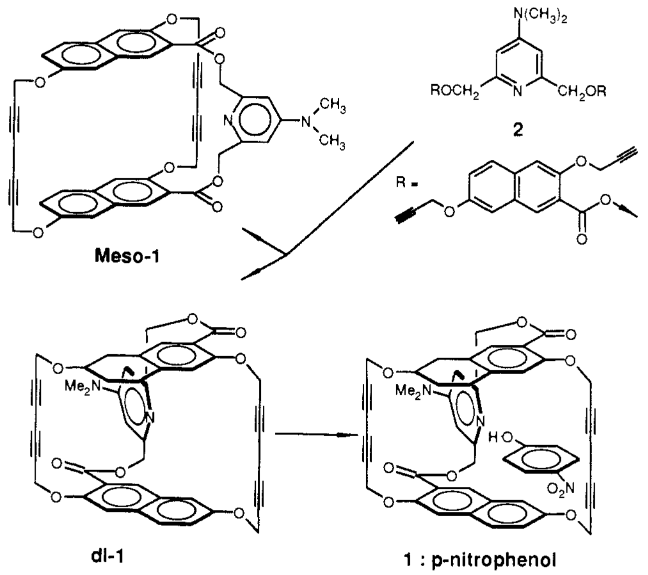
**Figure 1.** (a) X-ray structure of **1**/ethylene dichloride complex. (b) X-ray structure of **1**/*p*-nitrophenol complex.

with no apparent incavitation of the anion. This is consistent with requirement of an *optimum* $\Delta pK_A$ relating acid and base in this type of complex. Although of little precedent,[10] this idea seems reasonable when one considers those cases of "hydrogen bonding" when extremely large $\Delta pK_A$'s are involved.

A high degree of cooperativity between hydrogen bonding and intracavity interactions is indicated. We suggest that this is consistent with Menger's hypothesis[11] concerning temporal effects and intramolecular interactions.

**Conclusions.** One may construct host molecules possessing a rigidly defined cavity with concave functionality. These exhibit guest complexation characterized by large association constants in *nonaqueous* media and an exceptionally high but little-understood guest selectivity. The implications of this for the design of sequence-selective DNA intercalators and "artificial" enzymes is clear.[12]

**Scheme I**



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[12] Support of this work by the National Science Foundation is acknowledged.

## Synthesis of Tricyclo[3.3.1.0$^{3,7}$]non-3(7)-ene, a Highly Pyramidalized Olefin

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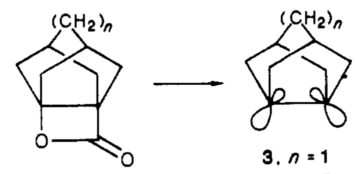
Alkenes in which the carbons forming the double bond are highly pyramidalized are a very interesting but not well-studied class of compounds.[1] We recently reported the generation of one member (**4**) of a homologous series of pyramidalized alkenes by pyrolysis of $\beta$-lactone **2**,[2] and, subsequently, the spectroscopic characterization of **4** in matrix isolation was described.[3] Herein



**1**, $n$ = 1
**2**, $n$ = 2

**3**, $n$ = 1
**4**, $n$ = 2

we communicate the results of our attempts to generate **3**, a more highly pyramidalized member of this series, by pyrolysis of $\beta$-lactone **1**, and we report the successful formation of this alkene at low temperatures in solution from a different precursor.

$\beta$-Lactone **1**[2] proved very resistant to pyrolytic loss of CO$_2$. Flash vacuum pyrolysis (FVP) of **1** at 550 °C led to only about

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