

aqueous and the inner organic phases, respectively, after a capsule was crushed. This denies the possibility of the micellar formation or the emulsion-like environment in the interface of the capsule membrane. Kinetic results were properly consistent with the usual phase-transfer catalysis mechanism: the concentration of NaN_3 in the outer phase giving the saturated value is roughly consistent with the concentration of onium salts on a membrane surface, and

the reactivity reaches a plateau when the concentration of onium salts increases on a capsule surface. These results indicate that onium-polymers act as a true phase-transfer catalyst but not a micellar-like catalyst at the interface of the capsule membrane.

Summary

The PTC-grafted capsules showed the high reactivity in the reaction between substrates in the inner organic phase and aqueous nucleophilic anions in the outer phase. The reactivity was largely dependent on the hydrophobic property and the spacer chain length of onium salts, the ionic strength (concentration of NaN_3) of the outer aqueous phase, and the graft amount of polymers on the capsule. The capsule membrane supported PTC was the following features: (1) the high reactivity due to the onium salts attached as the long graft polymer chains; (2) no induction period for the reaction caused by swelling of supports, which has been frequently observed in the insoluble polymer-supported PTC; (3) easy separation of the catalyst and the inner organic phase from the outer aqueous phase by picking up the PTC capsule. PTC-grafted capsule membranes are the new type of phase-transfer catalysts and may be useful in many heterogeneous reactions.

Registry No. PhCH_2Br , 100-39-0; NaN_3 , 26628-22-8; poly(ethylene oxide), 25322-68-3.

Host-Guest Complexation. 41. Preorganization of a Host Enhances Its Binding of Aryldiazonium Salts¹

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Synthetic host 1, a spherand comprised of cyclic urea and aryl ether units, has been designed and examined. It displays markedly superior binding of aryldiazonium tetrafluoroborate salts over previously reported complexing agents. Qualitative experiments indicate a higher degree of stabilization of complexed diazonium salts toward thermal decomposition and azo dye formation than is given by 18-crown-6. Quantitative infrared studies yield an approximate binding free energy of $-5.9 \text{ kcal mol}^{-1}$ for the complexation of $p\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{N}_2\text{BF}_4$ by 1 in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at 25°C , appreciably higher than the $-3.6 \text{ kcal mol}^{-1}$ determined for 18-crown-6 under identical conditions. Addition of an aqueous solution of Na_2CO_3 to a colorless solution of CH_2Cl_2 containing $\text{C}_6\text{H}_5\text{N(CH}_3)_2$ and 1 complexed to $p\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{N}_2\text{BF}_4$ instantaneously released the aryldiazonium ion which coupled to form the azo dye. The alkali metal salts bind 1 much more strongly than does the aryldiazonium salt. Thus the Na^+ ion acts as a trigger for dye formation, the system as a whole acting as an indicator for the presence of alkali metal ions.

Following the first report^{3,4} in 1973 that corands (crown ether like hosts) lipophilize and stabilize aryldiazonium tetrafluoroborate salts, a variety of studies of coraplexes⁵ have been reported.⁶ The original evidence^{3,4} that com-

plexation occurred by insertion of the $-\text{N}_2^+$ group into the macroring was corroborated by the crystal structure determination of 18-crown-6- $\text{C}_6\text{H}_5\text{N}_2\text{PF}_6$.⁷ Figure 1 provides

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(5) Cram (Cram, D. J. *Angew. Chem.* 1986, in press) has suggested the general common names podaplex, coraplex, cryptaplex, spheraplex, etc. for denoting the complexes of podands, corands, cryptands, and spherands, respectively.

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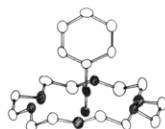
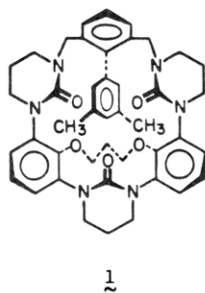


Figure 1. Simplified Ortep drawing of 18-crown-6- $C_6H_5N_2PF_6$ coraplex (PF_6 omitted).

a drawing of the complex.⁷ Of particular interest are those investigations that demonstrated that complexation resulted in stabilization and deactivation of the ArN_2^+ guest toward heat,⁸ light,⁹ and the azo coupling reaction.^{10,11} However, throughout these studies, the equilibrium constants for formation of the complexes were too low to block the reactions of the equilibrium concentrations of the free diazonium salt. Even a recently reported intramolecularly complexed aryldiazonium salt¹² reacted rapidly with $C_6H_5N(CH_3)_2$ to form an azo dye.

To date, only corands have been reported to complex aryldiazonium salts. Past work has shown that the more highly preorganized hemispherands containing cyclic urea units provide higher association constants for binding the larger alkali metal and ammonium ions than do the corands.¹³⁻¹⁵ This paper reports that a bicyclic spherand containing three cyclic urea units binds aryldiazonium ions well enough to effectively "turn off" their azo coupling reaction and that the reaction can be "turned on" by the addition of alkali metal ions that displace the aryldiazonium ion from the host.

Macrocyclic host **1** was selected as the prototype for a series of rigid analogues of the more flexible macrocycles previously examined by our group.^{14,15} The synthesis of **1** will be reported elsewhere.¹⁶ The key structural features



of **1** include a hydrophilic nest lined by three cyclic urea carbonyl groups and two aryl ether oxygens. The bottom of the nest is positively polarized, and the rim is negatively polarized. The system is organized and rigidified by the macrocycle, by the additional trimethylene bridge, and by the location of the dimethylphenyl group syn to the trimethylene bridge. The steric requirements of the dimethylphenyl group combined with its attachment to the *m*-xylyl bridging group locates the latter moiety syn to the

Table I. Effect of Host **1** on the Pseudo-First-Order Rate Constants for Azo Coupling of *p*-(CH_3)₃ $CC_6H_4N_2BF_4$ (**2**)^a with $C_6H_5N(CH_3)_2$ ^b To Give **3** at 25 °C in $ClCH_2CH_2Cl$

conc of 1 , M	equiv 1/2	$k_{obsd} \times 10^3$, s ⁻¹
0	0	1.79 ± 0.13
5.92×10^{-6}	0.0990	1.44 ± 0.01
2.96×10^{-5}	0.495	0.589 ± 0.028
5.92×10^{-5}	0.990	0.119 ± 0.004
2.96×10^{-4}	4.95	0 ^c

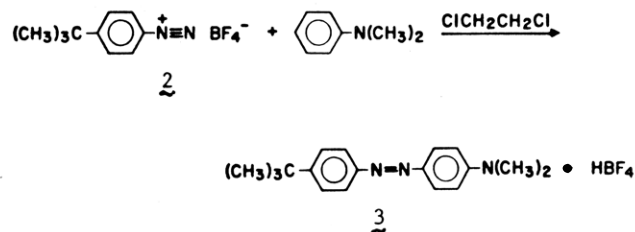
^a 5.984×10^{-5} M. ^b 1.709×10^{-3} M. ^c No dye formation observable after 1 h.

binding site but not blocking it. This geometry, anticipated by CPK model examination, was confirmed by crystal structure determination, which is reported elsewhere.¹⁷ The high preorganization of the compound for binding makes it one of the strongest general complexing agents of the alkali metal cations yet prepared. In $CDCl_3$ saturated with D_2O at 25 °C, the $-\Delta G^\circ$ of binding of the alkali picrate ions ranges from 13.6 to 16.7 kcal mol⁻¹.¹⁶

Results and Discussion

Solubilization Experiments. When a solution of spherand **1** in $CDCl_3$ was shaken with solid *p*- $CH_3OC_6H_4N_2BF_4$ (itself completely insoluble in $CDCl_3$), the ¹H NMR spectrum of the resulting solution compared to that of the original showed that exactly 1 mol of salt had been solubilized per mole of host. The spectrum of the complex was significantly different from that of free host **1** (see Experimental Section). Identical results were obtained with *p*- $CH_3C_6H_4N_2BF_4$, also insoluble in $CDCl_3$ in the absence of **1**. Under similar conditions, 18-crown-6 and binaphtho-20-crown-6 typically solubilized only 0.8–0.9 mol equiv of these salts.⁴

Inhibition of Diazo Coupling Reaction. Further evidence of the binding power of **1** is found in its ability to switch off the coupling of aryldiazonium salt **2** with $C_6H_5N(CH_3)_2$ to give orange azo dye **3**. When 1 equiv of



1 in $ClCH_2CH_2Cl$ at 25 °C was complexed with 1 equiv of *p*-(CH_3)₃ $CC_6H_4N_2BF_4$ (**2**), the reaction rate of the latter coupling with a large excess of $C_6H_5N(CH_3)_2$ was reduced to about 6.6% of its original value. A similar study by Bartsch and Juri demonstrated that 18-crown-6 as host slowed the rate to 9.4% of its value in the absence of host.¹⁰ In our study, addition of as little as 0.1 equiv of **1** had a noticeable effect on the coupling rate. Addition of 5 equiv of **1** per 1 equiv of **2** essentially blocked the formation of azo dye **3**. Table I reports the variation in the pseudo-first-order rate constants for the diazo coupling reaction as the ratio of the equivalents of **1** to **2** was varied from 0 to 4.95.

These results indicate that host **1** complexes guest **2** and that the resulting complex is unable to react directly with $C_6H_5N(CH_3)_2$. The qualitative comparison between **1** and 18-crown-6 indicates that the former is the stronger complexing agent.

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Table II. Effect of Host 1 on the First-Order Rate Constants for Thermal Decomposition of p -(CH₃)₃CC₆H₄N₂BF₄^a at 50 °C in ClCH₂CH₂Cl

conc of 1, M	equiv 1/2	$k_{\text{obsd}} \times 10^{-4}, \text{s}^{-1}$
0	0	1.41
1.166×10^{-5}	0.199	1.23
2.915×10^{-5}	0.498	0.876
5.831×10^{-5}	0.997	0.420
2.915×10^{-4}	4.98	0.0135

^a Concentration, 5.850×10^{-5} M.

When solid p -CH₃C₆H₄N₂BF₄ was suspended in a CH₂Cl₂ solution of C₆H₅N(CH₃)₂, a yellow color due to azo dye formation appeared immediately. In a second experiment, a colorless solution of 5 equiv of 1 and 1 equiv of the same diazonium salt in CH₂Cl₂ at 25 °C was mixed with 10 equiv of C₆H₅N(CH₃)₂. After 1 h of standing, the solution developed no observable color. Addition of an aliquot of this solution to a large excess of solid p -CH₃C₆H₄N₂BF₄ produced an immediate color. Addition of a second aliquot of this solution to an aqueous Na₂CO₃ solution produced an immediate color. Thus Na⁺ displaced p -CH₃C₆H₄N₂⁺ from its complex with 1, and the released diazonium salt coupled instantly with the C₆H₅-N(CH₃)₂ present, forming the azo dye.

Inhibition of Thermal Decomposition. We applied the method of Bartsch⁸ to study the effect of varying concentrations of 1 on the rate of thermal decomposition of solutions of p -(CH₃)₃CC₆H₄N₂BF₄ in ClCH₂CH₂Cl at 50 °C. We hoped to obtain an estimate of the equilibrium constant for 1 complexing this salt from the results. Five equivalents of 18-crown-6 had been reported to have slowed the first-order rate of decomposition to about 17% of the rate observed in the absence of host, while 100 equiv reduced it to about 1.4%.⁸ Under identical conditions, we found that 1 equiv of 1 reduced the rate to about 30% of that observed in the absence of host, while 5 equiv reduced the rate to about 0.96% of that value. Table II reports these results. Since thermal decomposition was essentially completely inhibited in the presence of greater than 5 equiv of 1, the rates were immeasurably slow in the concentration regime required for use of the Bartsch kinetic derivation in extracting the host-guest association constant from the kinetic data. Nevertheless, the semiquantitative comparison of the effects of 1 vs. 18-crown-6 on the rate of thermal decomposition of p -(CH₃)₃CC₆H₄N₂BF₄ again indicates that 1 complexes this salt much better than 18-crown-6.

Association Constants and Free Energies of Binding. The values of K_a and $-\Delta G^\circ$ of 1 binding p -(CH₃)₃CC₆H₄N₂BF₄ (2) were determined at 25 °C in ClCH₂CH₂Cl and compared with those values for 18-crown-6 binding 2. The solution infrared spectra of free and complexed aryldiazonium salts generally are markedly different.^{6,18} In ClCH₂CH₂Cl solution, 2 displays an absorption band at 2268 cm⁻¹. For complex 1-2 in the same solvent this band shifts to 2302 cm⁻¹. Titration of a solution of 2 with increments of 1 clearly demonstrated that the presence of 1 equiv of 1 was sufficient to complex virtually all of the 2 present. Thus the ratio of intensities of peaks due to complexed vs. uncomplexed 2 was >12:1. Under analogous conditions, 1 equiv of 18-crown-6 afforded a ratio of intensities of complexed to free host of 1:1.4.¹⁸ The derived association constants¹⁹ for 1 binding 2 were

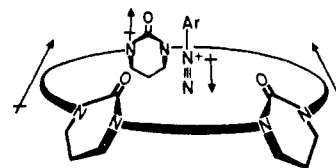


Figure 2. Partial drawing of the structure envisioned for spheraplex 1-2 which indicates the anticipated alignment of dipoles.

averaged (six determinations) to give $K_a = 2.10 \times 10^4$ ($\pm 0.45 \times 10^4$) M⁻¹, which provides $-\Delta G^\circ = 5.9$ kcal mol⁻¹. Application of the same technique to 18-crown-6 in our hands provided estimated values of $K_a = 6.9 \times 10^2$ M⁻¹ and $-\Delta G^\circ = 3.6$ kcal mol⁻¹. Thus host 1 forms a complex with 2 that is >2 kcal mol⁻¹ more stable than that of 18-crown-6. Bartsch⁸ reports $K_a = 1.71 \times 10^4$ M⁻¹ derived from kinetic data for 18-crown-6 complexing 2 at 50 °C in ClCH₂CH₂Cl, whereas Izatt et al.²⁰ report $K_a \sim 1.8 \times 10^2$ M⁻¹ in CH₃OH at 25 °C, using a calorimetric method.

The value of $-\Delta G^\circ \sim 6$ kcal mol⁻¹ for spherand 1 forming spheraplex 1-2 in ClCH₂CH₂Cl is much lower than the free energy of binding that 1 has for the alkali metal picrates (13.6–16.7 kcal mol⁻¹) in CDCl₃ saturated with D₂O at 25 °C. In view of this difference, it is hardly surprising that addition of Na⁺ to a solution of 1-2 essentially instantaneously liberates 2, which couples with any C₆H₅-N(CH₃)₂ present to give the azo dye. Such a system might be used as the basis for an indicator to detect the presence of alkali metal ions.

Structure of Spheraplex 1-2. The interesting question arises as to the structure of 1-2. We have been unable to obtain crystals of sufficient quality for crystal structure determination. However, CPK molecular model examination of 1-2, coupled with the crystal structure of 1 in Figure 1 and the relatively high $-\Delta G^\circ$ value for complexation, make it clear that the N≡N group of ArN≡N⁺ is inserted into the nest formed by the three carbonyl and two ether oxygens. Models of the complex also suggest that the para hydrogen of the biphenyl unit in 1 should lie well within the shielding region of the complexed aryldiazonium salt, and, indeed, the ¹H NMR signal for this proton (a triplet) in the complex is shifted roughly 1 ppm upfield (to ca. 6.3 ppm) from its position in the free host (ca. 7.2 ppm; see Experimental Section). The axis of the Ar-N bond should be normal to the plane of the three carbonyl oxygens, with the positive nitrogen being close to equidistant from the three partially negative oxygens. The favorable dipole-dipole interactions between host and guest, coupled with the high degree of preorganization of 1, appear responsible for the relatively high $-\Delta G^\circ$ value. Figure 2 contains a partial drawing of the structure envisioned for spheraplex 1-2.

Experimental Section

Compounds Used. Aryldiazonium salts were synthesized according to reported procedures,²¹ recrystallized from (CH₃)₂CO/Et₂O, and stored in a freezer at -20 °C. The synthesis of 1 will be reported elsewhere.¹⁶ Its characterization provided the following: mp >360 °C dec; IR (KBr) 1640 (vs) cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.2–1.3 (m, 1 H, OCH₂CH₂CH₂O), 1.1–2.1 (quintet, 4 H, NCH₂CH₂CH₂N), 2.2–2.4 (m, 3 H, XCH₂CH₂CH₂X), 2.36 (s, 3 H, ArCH₃), 2.50 (s, 3 H, ArCH₃), 2.7–3.0 (m, 4 H, NCH₂), 3.4–3.6 (m, 6 H, NCH₂), 3.7–3.9 (m, 6 H, NCH₂ + OCH₂), 4.3–4.5 (m, 2 H, OCH₂), 4.50 (d, 2 H, $J = 13.4$ Hz, half of AB, ArCH₂N),

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6.76 (s, 1 H, Ar H), 7.0–7.18 (m, 9 H, Ar H), 7.58 (d, 2 H, $J = 7.6$ Hz, o -HC₆H₂(CH₂N)₂Ar); mass spectrum (16 eV, 290 °C), m/z (relative intensity) 726 (M⁺, 100), 727 (51.1), 686 (19.2), 669 (13.7), 207 (19.7), 206 (12.7). Anal. Calcd for C₄₃H₄₆N₆O₅: C, 71.05; H, 6.38; N, 11.56. Found: C, 71.24; H, 6.49; N, 11.53.

Solid-Liquid Extraction Experiments. A 1-dram, plastic-capped vial was charged with 3–5 mg of 1, 0.5 mL of CDCl₃, and an excess of the solid diazonium salt. The vial was capped and shaken vigorously for 2.0 min. The contents were filtered through glass wool into an NMR tube, and the solution was examined by ¹H NMR spectroscopy on a 200-MHz Bruker Fourier transform spectrometer. In the absence of 1, no detectable amounts of diazonium salts (p -MeOC₆H₄N₂⁺BF₄⁻ or p -MeC₆H₄N₂⁺BF₄⁻) were extracted into the CDCl₃ phase. The ¹H NMR spectrum of uncomplexed 1 is recorded in the previous section. The ¹H NMR spectra of the two complexes formed by this solubilization technique are as follows: 1- p -MeOC₆H₄N₂⁺BF₄⁻ (CDCl₃) δ 1.2–1.3 (m, 1 H, OCH₂CH₂CH₂O), 1.7–2.8 (m, 11 H, XCH₂CH₂CH₂X + NCH₂), 2.38 (s, 3 H, ArCH₃), 2.60 (s, 3 H, ArCH₃), 3.0–3.2 (m, 2 H, NCH₂), 3.4–3.7 (m, 2 H, NCH₂), 3.57 (d, 2 H, $J = 13.7$ Hz, half of AB, ArCH₂N), 3.83 (s, 3 H, OCH₃), 3.9–4.0 (m, 2 H, NCH₂), 4.1–4.3 (m, 4 H, OCH₂), 4.39 (d, 2 H, $J = 13.7$ Hz, half of AB, ArCH₂N), 6.29 (t, 1 H, $J = 7.5$ Hz, m -H-C₆H₂(CH₂N)₂Ar), 6.6–6.8 (m, 3 H, Ar H), 7.0–7.5 (m, 12 H, Ar H); 1- p -MeC₆H₄N₂⁺BF₄⁻ (CDCl₃), identical with above complex, except aromatic triplet δ 6.23 (t, 1 H, $J = 7.6$ Hz) and CH₃C₆H₄N₂⁺BF₄⁻ δ 2.38 (s, 3 H). The integrals used to determine that the molar ratios of host to guest were unity, involved the following signals: for 1, δ 2.60 (3 H, ArCH₃); for p -MeOC₆H₄N₂⁺BF₄⁻ complexed, δ 3.83 (3 H, ArOCH₃); for p -MeC₆H₄N₂⁺BF₄⁻ complexed, δ 2.38 (3 H, ArCH₃).

Thermal Decomposition of *p*-tert-Butylbenzenediazonium Tetrafluoroborate (2). A stock solution of 1.755 × 10⁻⁴ M 2 in 100 mL of ClCH₂CH₂Cl was prepared. To 0.50 mL of this solution was added 1.0 mL of a solution of 1 in ClCH₂CH₂Cl (4.378 × 10⁻⁴, 8.746 × 10⁻⁵, 4.373 × 10⁻⁵, and 1.749 × 10⁻⁵ M) or of pure ClCH₂CH₂Cl, giving [2] = 5.850 × 10⁻⁵ M and [1] = 2.915 × 10⁻⁴ (4.98 equiv), 5.831 × 10⁻⁵ (0.996 equiv), 2.915 × 10⁻⁵ (0.498 equiv), 1.166 × 10⁻⁵ (0.199 equiv), and 0 M, respectively. The resulting solution was placed in a 1.0-cm low-volume silica UV-vis cuvette. The cuvette was capped and placed in the cavity of a Cary 219 UV-vis spectrophotometer, thermostated to 50.0 ± 0.1 °C. The rate of decomposition was monitored by watching the disappearance of absorption due to 2 at 282 nm as a function of time. Plots of ln (A_t/A₀) vs. time (seconds) were linear for the lower concentrations of 1 (0, 0.2, and 0.5, equiv) but displayed some curvature when 1 was present in higher concentrations (1.0 and 5.0 equiv), apparently due to interference in the spectrophotometric analysis by an absorption band which appears at lower wavelength upon addition of these concentrations of 1. The slopes of these plots afforded the first-order rate constants for thermal decomposition, and these are reported in Table II.

Azo Coupling of *p*-tert-Butylbenzenediazonium Tetrafluoroborate (2) with *N,N*-Dimethylaniline. The following solutions were prepared: 1.795 × 10⁻⁴ M diazonium salt 2 in 100 mL of ClCH₂CH₂Cl; 5.128 × 10⁻³ M *N,N*-dimethylaniline in 100 mL of ClCH₂CH₂Cl; 8.883 × 10⁻⁴ M 1; 1.776 × 10⁻⁴ M 1; 8.883 × 10⁻⁵ M 1; 1.776 × 10⁻⁵ M 1. For each analysis, 0.5 mL of diazonium salt solution and 0.5 mL of host solution (or pure ClCH₂CH₂Cl) were mixed in a 1.0-cm low-volume silica cuvette, and then 0.5 mL of *N,N*-dimethylaniline solution was added by syringe. The mixture was mixed well, and the cell was capped and quickly placed in the cavity of a Cary 219 spectrophotometer, thermostated to 25.0 ± 0.1 °C. Initial concentrations thus obtained were [2] = 5.984 × 10⁻⁵ M, [1] = 0, 5.922 × 10⁻⁶ M (0.0990 equiv), 2.961 × 10⁻⁵ M (0.495 equiv), 5.922 × 10⁻⁵ M (0.990 equiv), and

2.961 × 10⁻⁴ M (4.95 equiv), and [*N,N*-dimethylaniline] = 1.709 × 10⁻³ M (pseudo-first-order conditions). The rate of appearance of azo dye (λ_{\max} 410 nm) was observed as a function of time. Plots of log (A_∞-A_t) vs. time (seconds) were essentially linear over several half-lives, and the slopes of these plots yielded the kinetic data reported in Table I ($k_{\text{obsd}} = -2.303 \times \text{slope}$). Duplicate analyses were performed, giving the sample standard deviations shown in Table I.

Determinations of Association Constants by Infrared Spectral Method. A solution of 1.774 × 10⁻² M diazonium salt 2 in 100 mL of ClCH₂CH₂Cl was prepared. The same host solutions as used for the azo coupling study (above) were used in this experiment. Host solution (0.5 mL) and 0.5 mL of guest solution were mixed in a test tube and analyzed in a 0.5-mm solution infrared cell (against a ClCH₂CH₂Cl reference cell). Initial concentrations thus obtained were [2] = 8.870 × 10⁻³ M and [1] = 0, 8.880 × 10⁻⁵, 4.442 × 10⁻⁴, 8.880 × 10⁻⁴, and 2.220 × 10⁻³ M. To obtain a 1:1 stoichiometry, 0.5 mL of 5.85 × 10⁻⁵ M 1 and 0.5 mL of 5.85 × 10⁻⁵ M 2 were mixed; to obtain a 3.4-fold excess of 1, 0.5 mL of 1.774 × 10⁻² M 2, 0.5 mL of ClCH₂CH₂Cl, and 11.0 mg of 1 (1.513 × 10⁻⁵ mol) were mixed. Loss of absorption intensity at 2268 cm⁻¹ was monitored as a function of host concentration. Assuming a Beers law relationship is valid, the equilibrium constant for complexation was calculated from each of these experiments, by making use of eq 1–4, where *A* is the

$$K_{\text{eq}} = \frac{[\text{ArN}_2^+\text{host}]}{[\text{ArN}_2^+][\text{host}]} \quad (1)$$

$$[\text{ArN}_2^+] = \frac{A}{A_0} [\text{ArN}_2^+]_0 \quad (2)$$

$$[\text{ArN}_2^+\text{host}] = [\text{ArN}_2^+]_0 - [\text{ArN}_2^+] \quad (3)$$

$$[\text{host}] = [\text{host}]_0 - [\text{ArN}_2^+\text{host}] \quad (4)$$

absorption at 2268 cm⁻¹ in the presence of 1, A₀ is the absorption at 2268 cm⁻¹ in the absence of 1, []₀ represents initial concentrations, and [] represents equilibrium concentrations. The results of each run were calculated and averaged, and this average value is reported in the text.

The same technique was applied to 18-crown-6 as host. The diazonium salt solution was the same as that used above. Solutions of 18-crown-6 in ClCH₂CH₂Cl were made up of concentrations 1.797 × 10⁻³, 4.365 × 10⁻³, 1.797 × 10⁻², and 4.365 × 10⁻² M. Experiments were carried out as described above, giving initial concentrations [2] = 8.870 × 10⁻³ M and [18-crown-6] = 0, 8.984 × 10⁻⁴ (0.101 equiv), 2.182 × 10⁻³ (0.246 equiv), 8.984 × 10⁻³ (1.01 equiv), and 2.182 × 10⁻² M (2.46 equiv). Results from each run were calculated and averaged as described above, and this average value is reported in the text.

Liberation of 2 from Complex 1:2 with Sodium Ion To Produce Dye. A solution of 1 in CH₂Cl₂ (2 mL, 1.389 × 10⁻⁵ M, 5.06 equiv) was treated with 0.5 mL of a 2.747 × 10⁻⁶ M solution of 2 in CH₂Cl₂ (1.00 equiv) and then with 0.5 mL of a 2.761 × 10⁻⁵ M solution of *N,N*-dimethylaniline in CH₂Cl₂ (10.0 equiv). The solution remained clear and colorless even after prolonged standing (hours). Addition of 1.0 mL of 9.982 × 10⁻⁵ M aqueous Na₂CO₃ to a 1.0-mL aliquot of this solution produced the yellow color of the azo dye upon thorough mixing of the two layers. Addition of excess 2 to the solution of 1:2 and dimethylaniline immediately produced the color of the azo dye. If 1 was omitted from the above mixtures, the azo dye formed instantly on addition of dimethylaniline.

Registry No. 1, 105373-36-2; 1- p -CH₃OC₆H₄N₂BF₄, 105373-37-3; 1:2, 105373-38-4; 2, 52436-75-6.