of $S(^3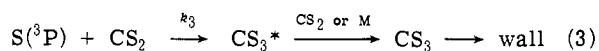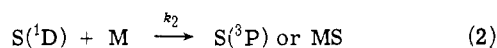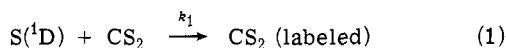P)$ with CS_2 in this system unless the sulfur has excess translational energy.[7,8] The existence of a reactive intermediate cannot be ruled out, but it seems unlikely that any chemically realistic intermediate, except CS_3^*, which yields labeled CS_2 would react competitively with H_2.[9] Excited CS_3^* if formed might undergo exchange reaction with CS_2 or be stabilized by collision with bath gas as discussed below.

To distinguish between these mechanistic routes to labeled CS_2, a large excess of Ar was added to a 2 to 1 mixture of CS_2 and H_2 as shown in Table I. Argon is reported to have a very small quenching rate constant for $S(^1D)$ compared with H_2 and hydrocarbons and, therefore, it should not markedly affect the distribution of $S(^1D)$ to $S(^3P)$ atoms even at relatively high dilution.[3] It is, however, known to be a reasonably good hot atom moderator and is also expected to be as good an energy transfer agent as H_2 in stabilizing any excited CS_3^* present. The small decrease in labeled CS_2 product observed at high dilution with Ar is not consistent either with a model based primarily upon a translationally hot process or one in which exchange reaction between CS_3^* and CS_2 is dominant. In fact the contribution from the latter process is estimated to be less than 5% on the basis of these data.

The most reasonable reaction mechanism which accounts for the major features of the data is based upon excited singlet sulfur atom exchange reactions with CS_2 in competition with quenching as indicated in the following scheme.

$$S(^1D) + CS_2 \xrightarrow{k_1} CS_2 \text{ (labeled)} \quad (1)$$

$$S(^1D) + M \xrightarrow{k_2} S(^3P) \text{ or } MS \quad (2)$$

$$S(^3P) + CS_2 \xrightarrow{k_3} CS_3^* \xrightarrow{CS_2 \text{ or } M} CS_3 \longrightarrow \text{wall} \quad (3)$$

Chemically activated CS_3^* postulated in reaction 3 is not expected to competitively decompose at pressures of 200 Torr and greater.[4] This set of reactions can be treated quantitatively in a manner similar to that reported by Donovan et al.[10] in quenching studies of $S(^1D)$. The fraction of $S(^1D)$ which gives labeled CS_2 in experiments containing CS_2 reactant and additive M is equal to $k_1[CS_2]/(k_1[CS_2] + k_2[M] + T)$ where T represents the rate of removal of $S(^1D)$ by all additional reaction channels. If T and $[CS_2]$ are constant, a plot of the reciprocal of the CS_2 activity as a function of additive $[M]$ should yield a straight line whose slope is proportional to $k_2/k_1[CS_2]$. The reciprocal of the CS_2 activity as a function of H_2 additive shown in Table I was fitted by a linear least-squares procedure giving a correlation coefficient of 0.995. The resulting linear behavior indicates that the data are consistent with the mechanism involving $S(^1D)$ exchange reaction with CS_2.

This evidence for the existence of singlet sulfur atom reactions in no way excludes the possibility of concurrent triplet sulfur atom reactions, and indeed triplet sulfur atoms are expected to be present both as hot and thermalized species. The fact that they presumably do not play a significant role in yielding labeled CS_2 despite reports that triplet sulfur reacts with carbon disulfide is consistent with the formation of the relatively stable intermediate CS_3 postulated by Breckenridge and Taube.[4] Since the probability of a collision between this intermediate and either another CS_3 species or sulfur on the walls is vanishingly small in this system, the postulated decomposition to give labeled CS_2 is not important and any labeled CS_3 formed is expected to be lost to the quartz surfaces of the reaction vessel as indicated by reaction 3. Other mechanisms for removal of $S(^3P)$ atoms are also possible, of course, but there is no evidence that

they contribute significantly to the carbon disulfide product observed.

C_2H_6 and C_2H_4 additives were also used to distinguish between triplet and singlet reactions as shown in Table I.[11] In both cases the yield of labeled CS_2 was significantly depressed in a reaction system consisting of CS_2 and hydrocarbon in a ratio of 1:2. Reaction and quenching of singlet sulfur by both C_2H_6 and C_2H_4 are known to be efficient whereas reaction of triplet sulfur is known to occur readily only with ethylene.[3b,c]

It appears then that there is clear evidence for the presence and reaction of $S(^1D)$ atoms in this nuclear recoil reaction system incorporating the $^{34}S(n,\gamma)^{35}S$ process. It is also probable that $S(^1D)$ reactions have played an important role in earlier reports of recoil sulfur atom reactions and are responsible for the complexity observed due to the large number of reaction paths available.

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(5) Activities reported in this way are directly proportional to the product yield under constant irradiation conditions. In these experiments the error in assuming uniform exposure is estimated to be 5%.

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(11) Recently separate experiments in this laboratory have indicated the formation of a sizable amount of ethyl mercaptan in the reaction between ethane and nuclear recoil sulfur atoms produced by the (n,p) process under conditions of 55% moderation. This result also strongly indicates the presence and reaction of $S(^1D)$ atoms.

(12) Camille and Henry Dreyfus Teacher–Scholar, 1971–1976.

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Synthesis and Cryptate Complexes of a Spheroidal Macrotricyclic Ligand with Octahedrotetrahedral Coordination[1]
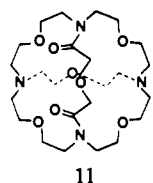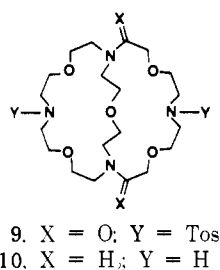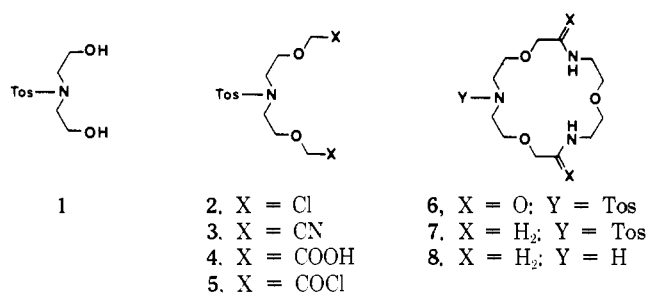
Sir:

The molecular recognition of the spherical alkali and alkaline earth cations by an organic ligand should be ideally achieved by a system containing a spherical intramolecular cavity into which the cation may be included. Macrocyclic systems define a circular cavity and macrobicyclic ligands an ellipsoidal one. In an analysis of the features of polycyclic ligands,[2] a spheroidal macrotricyclic system (see type I

in ref 2) was shown to display a particularly attractive topology.

We wish to report the synthesis of such a ligand bearing ten coordination sites. The molecular architecture is cemented together by four nitrogen cornerstones linked by bridges each containing an oxygen site. The synthetic plan is based on the stepwise construction of a macrocyclic, macrobicyclic, and macrotricyclic system. The intermediate products may also be expected to display interesting properties and may serve as building blocks for other ligand systems.

Chloromethylation at 0° in chloroform of the tosylate 1, prepared from tosyl chloride and diethanol amine,[3] gives the bischloromethyl ether 2 (mp ~30°; 98% yield). Treatment of 2 with sodium cyanide in dimethylformamide at 0° for 3 hr affords the biscyanide 3 (mp 48°; 50%) which, on hydrolysis with barium hydroxide followed by HCl decomposition of the precipitated organic barium salt, leads to the dicarboxylic acid 4 (mp 87-88°; 80%). Direct conversion of 1 into 4 without isolation of the intermediate substances gives recrystallized 4 in 40% yield. The acid chloride 5 is obtained by allowing 4 to react with oxalyl chloride in benzene[4] (mp 57-59°; 95%).

1

2. X = Cl
3. X = CN
4. X = COOH
5. X = COCl

6, X = O; Y = Tos
7, X = H₂; Y = Tos
8, X = H₂; Y = H

9. X = O; Y = Tos
10. X = H₂; Y = H

11

High dilution condensation of 5 with H₂NCH₂CH₂OCH₂CH₂NH₂[4] as previously described[4,5] gives the macrocyclic triamide 6 (mp 117-118°; 63%) which on reduction with diborane in the usual fashion[4] gives 7 (mp 88-89°; 98%). Compound 7 contains two free secondary amino functions which will be used to construct the macrobicyclic system; the third amino function is kept in the protected tosylamide form until construction of the final macrotricyclic system.

Reduction of 6 by LiAlH₄ in tetrahydrofuran (THF) at reflux for 16 hr removes at once the carboxamide and tosylamide functions, giving the macrotricyclic triamine 8 (mp 135-136°; 78%). Compound 8 is an 18-membered ring with alternating O and N sites and should have interesting ligand properties.

Condensation of 7 with 5 in high dilution[4,5] affords the macrobicyclic molecule 9 (mp 110-111°; 75%). Reduction of 9 with LiAlH₄ in THF at reflux for 12 hr gives the tetramine 10 (mp 39-40°; 85%). This compound is in itself an interesting ligand which may be used for constructing various macropolycyclic systems. Reaction of the two secondary amino functions of 10 with ClCOCH₂OCH₂COCl[4] in high dilution affords the highly crystalline macrotricyclic diamine-diamide 11 (mp 220-224°; 52%). Finally, 11 is re-
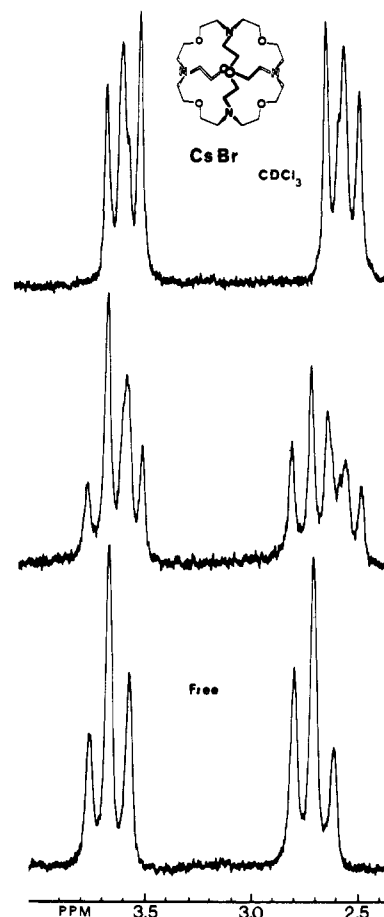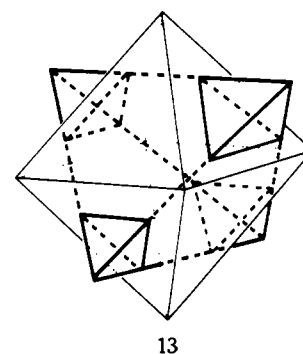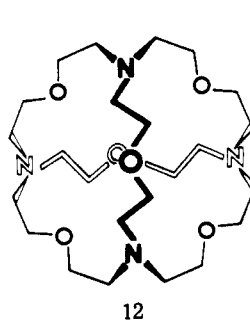

Figure 1. Proton NMR observation of CsBr complexation by ligand 12: free ligand (bottom), ligand + complex (middle), CsBr complex (top) (CDCl₃ solution, solid CsBr, 60 MHz).

12

13

duced with diborane[4] in THF at 50° for 17 hr; the resulting crude product is hydrolyzed with 6 N HCl at reflux for 4 hr and evaporated to dryness and the residue is taken up in water. The macrotricyclic tetramine hexaether 12 is obtained by passing this solution over a quaternary ammonium anion exchange resin in its hydroxide form[4] and evaporating to dryness (recrystallization from hexane; mp 196-200°; 95%). Compound 12 is soluble in all solvents from petroleum ether to water. It forms nice cubic crystals. Because of its high symmetry, its proton and carbon-13 NMR spectra are very simple indeed, displaying two proton triplets (J = 5.5 Hz) for the CH₂-N and CH₂-O groups at 2.70 and 3.65 ppm, respectively (Figure 1), and two carbon resonances at 56.5 (CH₂-N) and 70.05 (CH₂-O) ppm from Me₄Si (in CDCl₃).

The macrotricyclic system 12 has four identical faces, each being an 18-membered ring of type 8, connected at the nitrogen sites and delineating an intramolecular cavity. Depending on the orientation of the nitrogen bridgeheads into

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(i or endo, n) or out (o or exo, x) of the cavity, **12** may exist in *five topological forms* in a way similar to the three forms of macrobicyclic compounds.[4,6] They may be described as i_4, i_3o, i_2o_2, io_3, o_4. The NMR spectrum corresponds either to one highly predominant symmetric form, i_4 or o_4, or to a mixture of all forms in rapid equilibrium since inversion of the nitrogen sites is expected to be very fast.

The i_4 form has a particularly attractive shape. The intramolecular cavity is *spherical* and lined with the ten binding sites in an octahedrotetrahedral arrangement **13**: the four nitrogens are located at the corners of a tetrahedron and the six oxygens are at the corners of an octahedron, the centers of the two polyhedra coincide and the ten corners lie on the same sphere. In addition to its chemical interest, such a ligand is not without aesthetic appeal![7]

Compound **12** should be able to form complexes with metal cations of appropriate size. Indeed, when solid CsBr is added to a CDCl₃ solution of **12**, the salt dissolves slowly and the initial NMR spectrum is progressively replaced by a new one (Figure 1) due to the formation of a complex of 1/1 stoichiometry. Complex formation is also observed by NMR in D_2O solution for instance with KBr, CsBr, and $BaBr_2$ as well as with NH_4I in CDCl₃.

Since in the slowly exchanging complex in CDCl₃ all bridges in the ligand are equivalent, the complex must have a center of symmetry; i.e., the cation is trapped inside the cavity of the ligand. The complexes formed by **12** are thus *macrotricyclic [3]cryptates*.[2] [Cs⁺ ⊂ **12**]Br⁻, analogous to the macrobicyclic [2]cryptates discovered earlier.[2,9] In the complex, the ligand certainly exists in form i_4 which allows optimal interaction of the cation with all four nitrogen sites as well as with the oxygens.

Compound **12** has a cavity radius of about 1.8 Å, larger than that of a given face of the polyhedron (about 1.5 Å) and its high connectivity ensures appreciable rigidity. These two features are expected to influence both stability constants and cation exchange rates of the complexes. Preliminary measurements show that the stability constants for the K⁺, Rb⁺, and Cs⁺ complexes are about 3.4, 4.2, and 3.4, respectively (log K_s in water at 25°). The Cs⁺ complex is probably the most stable known to date. The cation exchange rates (determined from ¹H NMR coalescence temperatures) are among the slowest observed,[2] with free energies of activation of 15.5 (at 28°), 16.7 (at 51°) and 16.1 (at 41°) kcal/mol for the K⁺, Rb⁺, and Cs⁺ complexes, respectively.

The properties of ligand **12** and of some derivatives will be described more extensively in future reports.

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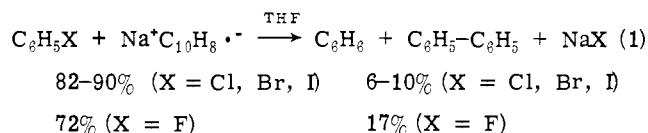(11) ERA No. 265 of the CNRS.

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Received February 13, 1975

The Mechanism of Dimer Formation in the Electroreduction of p-Fluorobenzonitrile

Sir:

The sodium naphthalenide reduction of several halobenzenes has been shown to result in dehalogenation and to give benzene and biphenyl as the two principal products.[1] The distribution of the principal products for both 1:1 and 2:1 molar ratios of sodium naphthalenide to halobenzene is summarized in eq 1.
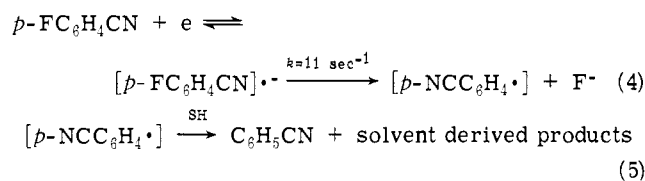
$$C_6H_5X + Na^+C_{10}H_8\cdot^- \xrightarrow{\text{THF}} C_6H_6 + C_6H_5-C_6H_5 + NaX \quad (1)$$

82–90% (X = Cl, Br, I)   6–10% (X = Cl, Br, I)

72% (X = F)   17% (X = F)

Although Cheng et al.[1] favored reaction pathways involving phenyl radicals, Sargent[2] disputed this suggestion and proposed instead phenyl anion as the reactive intermediate. The formation of benzene was suggested by Sargent[2] to occur by the abstraction of a proton from the solvent system by the phenyl anion (eq 2), while aromatic nucleophilic substitution was proposed for the formation of biphenyl (eq 3).

$$C_6H_5^- + THF \longrightarrow C_6H_6 + CH_2=CHCH_2CHO^- \quad (2)$$
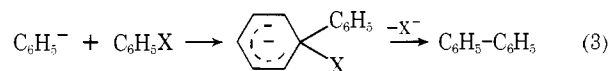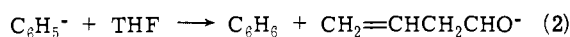
We have now obtained evidence that dimer formation in the reductive defluorination of p-fluorobenzonitrile occurs by neither of these pathways, but occurs, rather, via the apparent dimerization of the halogenated radical anion. The evidence is based upon kinetic studies and substitution experiments.

The electrochemical reduction of p-fluorobenzonitrile has been demonstrated in our laboratory to give both monomeric and dimeric products.[3] Although unimolecular decomposition of the intermediate p-fluorobenzonitrile radical anion and the formation of benzonitrile was shown to predominate in dilute solution ($<2.5 \times 10^{-4}$ F) (eq 4 and 5),

$$p\text{-}FC_6H_4CN + e \rightleftharpoons$$

$$[p\text{-}FC_6H_4CN]\cdot^- \xrightarrow{k=11 \text{ sec}^{-1}} [p\text{-}NCC_6H_4\cdot] + F^- \quad (4)$$

$$[p\text{-}NCC_6H_4\cdot] \xrightarrow{SH} C_6H_5CN + \text{solvent derived products}$$
$$(5)$$

a significant yield of the dimer, 4,4′-dicyanobiphenyl, was obtained via an undetermined pathway when the concentration of p-fluorobenzonitrile radical anion exceeded 10^{-3} F. Improved instrumentation has now allowed us to examine the kinetics of dimer formation under conditions which minimize the unimolecular decomposition pathway (eq 4 and 5).

The kinetics of the decomposition of the p-fluorobenzonitrile radical anion were studied by the single-potential-step chronoamperometric method.[4-6] In this technique the potential of the planar platinum electrode in a solution containing p-fluorobenzonitrile is changed abruptly from a value where no redox process occurs ($E = -2.00$ V vs. SCE) to a value sufficiently negative ($E = -2.70$ V) so as to cause the concurrent reduction of p-fluorobenzonitrile ($E_{1/2} = -2.33$ V) and the product of its radical anion decomposition, 4,4′-dicyanobiphenyl.[7] Theory[6] predicts for this sequence of electrochemical and chemical reactions (eq 6–8) that the apparent value of $n(n_{app})$ should vary from a lower limit of 1.0, when the only reaction which occurs is the one-electron reduction of p-fluorobenzonitrile to its rad-