Protonation of Fischer carbynes has been invoked as the initial step in numerous reactions where a trapping reagent then adds to maintain the metal electron count.[11,16] The product of simple protonation here resembles the high oxidation state agostic alkylidene complexes of groups V[17] and VI[18] where the hydrogen on the α-carbon is also bound simultaneously to the metal. Bridging μ_2-methyne units prepared by other methods have been well characterized in dinuclear iron,[19] ruthenium,[20] and rhenium[21] complexes. An agostic methyne entity was also produced by protonation of the four-iron butterfly cluster, $[Fe_4C(CO)_{14}]^{2-}$.[22]

Reaction of the dinuclear μ_2-carbide with carbon disulfide is promoted by light. The net result is insertion of CS_2 into the carbide–iron bond to form a dithio acid derivative which is chelated to iron in the $Tp'(CO)_2Mo{\equiv}CCS_2Fe(CO)Cp$ product. The lone iron carbonyl is assigned to the 1960-cm^{-1} absorption; the molybdenum dicarbonyl unit then accounts for infrared bands at 2003 and 1924 cm^{-1} in accord with insertion of the electrophilic CS_2 moiety into the C–Fe bond.

No thermal reaction was observed between **1** and either PMe_3 or Bu^tNC, but upon photolysis substitution of both iron carbonyl ligands occurred. Formation of $Tp'(CO)_2Mo{\equiv}CFeL_2Cp$ was evident from IR and NMR spectra for L = PMe_3 (**4**) and L = Bu^tNC (**5**). Particularly noteworthy are the low-frequency carbonyl absorptions (1910 and 1820 cm^{-1} for **4**; 1920 and 1830 cm^{-1} for **5**) and the very low field carbide ^{13}C chemical shifts (500 ppm for **4**; 452 ppm for **5**).

Access to the μ_2-carbide here is made possible by the unique ligating properties of Tp′, both electronic and steric.[23] In spite of the reactions reported here for this neutral carbide, we have been struck by the reluctance of this dinuclear carbide to undergo facile chemical transformations at the central carbon site. This reticence may reflect the dominant role of the Tp′ ligand in imparting kinetic, and perhaps thermodynamic, stability to $Tp'(CO)_2Mo{\equiv}CFe(CO)_2Cp$.

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Supplementary Material Available: Details of syntheses and full analytical and spectral data for **1–5** and tables of crystal data, positional and thermal parameters, bond lengths, bond angles, and torsion angles for **1** (12 pages); listing of calculated and observed structure factors for **1** (15 pages). Ordering information is given on any current masthead page.

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Inclusion Complexation by Bis(cyclodextrins) in the Presence of Phospholipid Vesicles

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Molecular recognition of organic ligands by synthetic receptors has been widely studied in both organic[1] and aqueous[2] solvents. In each circumstance the challenge is to design a recognition site that overcomes the tendency of the guest to partition into the bulk solvent. However, receptors in the biological setting must compete with both hydrophobic and aqueous microenvironments into which the ligand might partition. Synthetic receptors for organic ligands that model this complication have received less attention.[3,4] We have succeeded in constructing water-soluble receptors with sufficient specificity to overcome the tendency of organic ligands to partition into the hydrophobic interior of a phospholipid bilayer.

β-Cyclodextrin (β-CD), a macrocyclic oligomer of seven glucoses, has been widely studied as a water-soluble receptor that binds organic ligands by inclusion complexation.[5] The cooperative action of two covalently linked cyclodextrins (bis-CDs) has been shown by several groups[6–9] to provide powerful binding of ligands designed to exploit the extended recognition site, with equilibrium constants for binding (K_a) ranging from 10^5 to 10^9 M^{-1}. In contrast, β-CD binds organic guests with K_a values[5] of 10^2–10^4 M^{-1} (e.g., K_a = 1800 M^{-1} for 6-toluidino-2-naphthalenesulfonate (TNS)).[7,8,10] We have prepared bis-CDs **1**,[8a] **2**, and **3**[11] and

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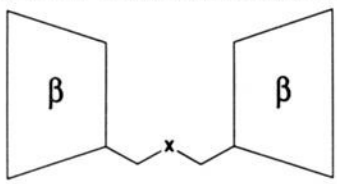
Table I. Aassociation Constants for Bis(cyclodextrins)[a]

receptor	ligand	[ligand], μM	lipid[b]	K_a,[c] M^{-1}
1	TNS	0.33	–	$2.8 \pm 0.11 \times 10^4$
1	BNS	3.33	–	$7.9 \pm 2.1 \times 10^4$
2	TNS	3.33	–	$7.4 \pm 0.79 \times 10^4$
2	BNS	0.33	–	$8.2 \pm 1.2 \times 10^6$
3	BNS	0.33	–	$2.6 \pm 0.15 \times 10^6$
1	TNS	3.33	eggPC	$1.8 \pm 0.17 \times 10^4$
1	TNS	3.33	DPPC	$1.8 \pm 0.33 \times 10^4$
2	TNS	3.33	eggPC	$5.5 \pm 1.2 \times 10^4$
2	BNS	0.33	eggPC	$1.4 \pm 0.19 \times 10^6$
3	BNS	0.33	eggPC	$6.9 \pm 0.88 \times 10^5$

[a] Titrations were performed at 23 °C in 10 mM phosphate buffer, pH 7.0. [b] DPPC = dipalmitoylphosphatidylcholine; eggPC = mixed phosphatidylcholines from egg yolk; [lipid] = 0.10 mM; see ref 14. [c] Titration data (ΔF at the λ_{max} for emission vs [receptor]) were analyzed by using HOSTEST II,[13] and K_a values are reported with intervals of 90% confidence.

assayed their binding behavior by titration against fluorophoric ligands TNS and BNS (6-(4-*tert*-butylanilino)-2-naphthalenesulfonate)[12] in aqueous buffer (10 mM phosphate, pH 7.0). Plotting change in fluorescence intensity (ΔF) at the λ_{max} for emission vs [bis-CD] affords hyperbolic graphs, which are analyzed by using HOSTEST II[13] to give values of K_a (see Table I). For



1 X = —S—S—
2 X = —SCH_2CH_2S—
3 X = —S-*o*-C_6H_4-S—

example, bis-CD **2** (0.033–6.67 μM) was titrated against BNS (0.33 μM) and monitored by fluorescence ($\lambda_{excitation}$ = 325 nm, emission λ_{max} = 440 nm) to give $K_a = 8.2 \pm 1.2 \times 10^6$ M^{-1}. We attribute the high affinity (relative to BNS and **1**, $K_a = 7.9 \pm 2.1 \times 10^4$ M^{-1}) to the longer tether connecting the two CD cavities, which apparently more than compensates for the increase in rotational degrees of freedom between the two cavities. Host **3** reduces by one the number of possible free rotations between the connected CDs, but actually lowers the K_a for BNS ($2.6 \pm 0.15 \times 10^6$ M^{-1}) relative to **2**, suggesting that the allowed geometries are not ideal for binding.

The spectroscopic features of TNS and, by analogy, BNS, in the presence of small unilamellar vesicles (SUVs),[14] indicate that they are adsorbed to the vesicle surface.[15-17] β-CD proved unable to extract TNS (3.33 μM) from the bilayer ([eggPC] = 0.10 mM) to form inclusion complexes, even at relatively high concentrations ([β-CD] = 1.0 mM).[4,10a] However, bis-CDs **1**, **2**, and **3** were all competent in this context: for example, titration of TNS or BNS (3.33 μM, 0.33 μM) in SUVs of eggPC (0.10 mM in pH 7.0 phosphate buffer) produced apparent equilibrium constants for inclusion of $5.5 \pm 1.2 \times 10^4$ and $1.4 \pm 0.19 \times 10^6$ M^{-1}, respectively

Table II. Fluorescence Decay Parameters for TNS in Various Microenvironments

system	τ_1, ps	τ_2, ps	τ_3, ps	A_1, %	A_2, %	A_3, %	χ^2
water	29	4604	11975	89	10	1	2.8
eggPC[a]	24	4595	11852	53	41	6	1.8
2[b]	415	2600	11300	27	22	50	1.3
2[c] + eggPC[a]	384	2800	11279	29	25	46	1.4

[a] [EggPC] = 0.10 mM in 10 mM phosphate buffer at pH 7.0. [b] [**2**] = 97 μM. [c] [**2**] = 93 μM.

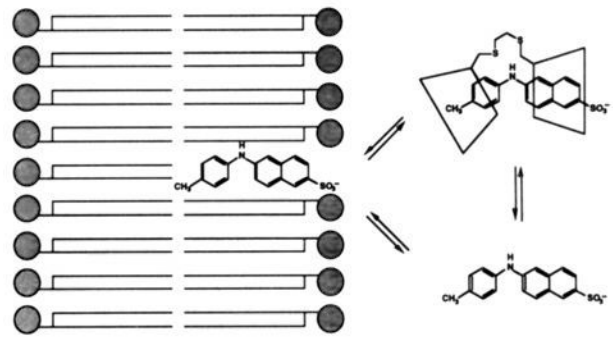


Figure 1. Proposed three-way equilibrium binding of TNS to bis-CD **2**, the vesicle bilayer, and bulk water.

(see Table I). The diminished values of K_a reflect the competition between the bis-CD and the bilayer surface.

Competitive inclusion complexation of the fluorophore as the explanation for the observed titration curves is supported by several lines of evidence: (i) The location of the fluorophore in the receptor/SUV/buffer system was determined by using time-resolved fluorescence.[18] The time constants that characterize the fluorescence decay were evaluated independently in each microenvironment (see Table II). Comparison of these decay parameters with that found in the combined system ([TNS] = 3.33 μM, [eggPC] = 0.10 mM, [**2**] = 93 μM) can be used to identify the dominant microenvironment. The decay parameters in Table II clearly show that the time evolution of the fluorescence in the combined system is indistinguishable from that of the receptor/buffer system, indicating that the bis-CD recognition site is the predominant microenvironment for TNS in the combined system. By fixing the time constants in the combined system to those found for the individual microenvironments, it is possible to fit the overall decay and estimate the relative amounts of TNS in the different environments. Such an analysis indicates that less than 7% of the fluorophore is in the lipid. (ii) Light scattering experiments (546 nm at a 90° fixed angle) exhibited negligible changes in optical density upon addition of β-CD or **1**. This is in sharp contrast to the addition of CDs (especially α-CD) to micellar structures, in which the CD disrupts the aggregate by sequestering the surfactants;[19] in this sense the phospholipid bilayer is more robust. (iii) Both receptor **1** and β-CD are known[8,10] to bind ANS (8-anilino-1-naphthalenesulfonate) poorly; this is attributed to the geometry of ANS, which, unlike TNS, is ill-suited to the cylindrical receptor cavities. Receptor **1** fails to extract ANS from eggPC vesicles, indicating that the competitive titration requires geometric complementarity between fluorophore and bis-CD cavity.

The binding of TNS to vesicles ($K_a = 3.38 \times 10^4$ M^{-1})[15] is difficult to overcome because the number of possible recognition sites presented by the vesicle surface is comparatively large (see Figure 1). Thus, if a receptor (at reasonably low concentrations) is to compete successfully with a vesicle surface, it must have a

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high specificity for the ligand. Receptor **2**, with $K_a = 8 \times 10^6$ M^{-1} for TNS, efficiently moves a small organic ligand (TNS or BNS) from the vesicle surface to the interior of the extended cavity provided by the bis-CD. The location of the resulting complex is still unclear, though it seems likely that the complex adsorbs to the vesicle surface in view of the relatively hydrophobic nature of portions of the exterior surface of β-CD. If so, then **1**, **2**, and **3** constitute the first synthetic membrane-bound receptors for organic ligands.

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"Molecular Hysteresis"

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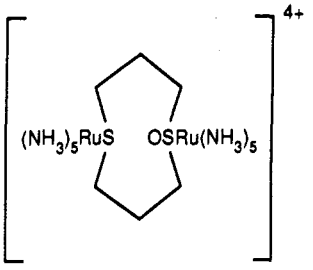
An early example of linkage isomerization coupled to electron transfer[1] is the redox behavior of the $[(NH_3)_5Ru(\text{dimethyl sulfoxide})]^{3+/2+}$ couple. When the S-bound isomer, $[(NH_3)_5Ru(SO(CH_3)_2)]^{2+}$, is oxidized by cyclic voltammetry, this change occurs at ca. 1.0 V vs NHE. The Ru–S linkage is retained in the immediate product of the reaction, but this then rearranges to the more stable O-bound form (specific rate at room temperature, 7.0×10^{-2} s^{-1}). To reduce the rearranged product, a potential more negative by almost 1 V than that required for oxidation of the S-bound form of Ru(II) must be applied, and the immediate product of the reduction is $[(NH_3)_5Ru(OS(CH_3)_2)]^{2+}$, which then rearranges to the more stable original state ($k = 30 \pm 7$ s^{-1}).

In the molecule we have synthesized, a reversible couple is combined with that just described so that there is the possibility of communication between the metal centers in the binuclear species. The reversible couple was chosen to have a potential bracketed by the irreversible potentials of the sulfoxide couple. We prepared (1,5-dithiacyclooctane 1-oxide)bis(pentaammineruthenium(II)) by the reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with the bridging ligand[2] in acetone.



The behavior of this redox system in cyclic voltammetry[4] is shown in Figure 1. On scanning to an oxidation potential short of that required to oxidize the Ru(II)–sulfoxide center, a reversible couple ($E_{1/2} = 0.57$ V) appears (Figure 1a), which is close to that observed for other [pentaammineruthenium]$^{3+/2+}$ couples in which the heteroligand is a thioether.[5] Figure 1b shows the electrochemical behavior when the oxidation scan (100 mV s^{-1}) is continued to potentials high enough to involve also the sulfoxide center. As new features, we now observe an oxidation wave at 1.13 V, without a corresponding reduction wave, and reduction at −0.06 V, without a corresponding oxidation wave, these features being very much like those that would be expected for the mononuclear sulfoxide complex at sufficiently slow scan rates. The electrochemical behavior of the binuclear system can be represented by the scheme shown in Figure 2, but where the kinetic parameters are yet to be entered. It is to be noted that two states of the mixed-valence species are produced. One of the states is accessible only by reduction of the stable form $[S^{3+}/(OS)^{3+}]$, and the other, only by oxidation of the stable form $[S^{2+}/(SO)^{2+}]$. Starting with either of the stable extreme states, the loop made by following in the direction of the solid arrows has important features in common with the familiar hysteresis loop exhibited by certain ferromagnetic materials.

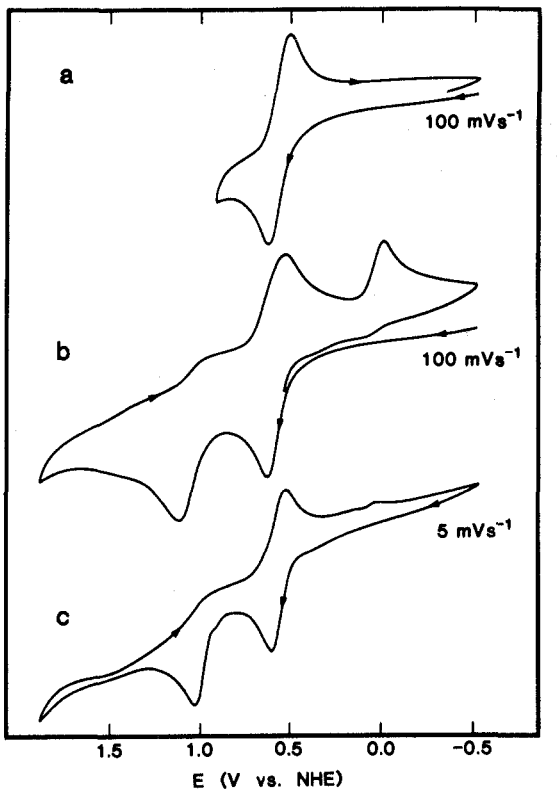


Figure 1. Cyclic voltammograms of the binuclear species as a function of scan rate.

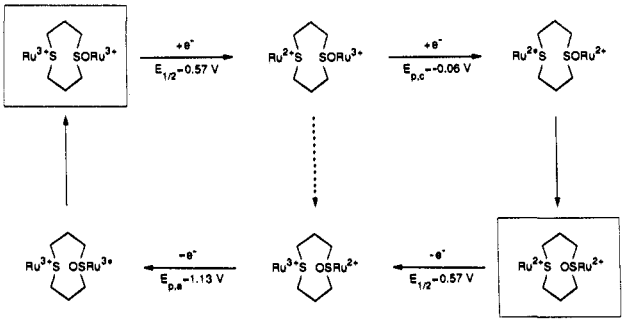


Figure 2. Hysteresis loop in the electrochemistry of the binuclear species. The specific rates for the linkage isomerization reactions reading from left to right (s^{-1}): $(5 \pm 0.5) \times 10$, $<4 \times 10^{-2}$, $(2.0 \pm 0.2) \times 10$, respectively.

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(3) All manipulations were done under dry argon in a Vacuum Atmospheres Co. glovebox. ^1H NMR (acetone-d_6, PF_6 salt): δ 2.0–2.1 (m, 4 H), 2.7–2.9 (m, 4 H), 3.8–3.9 (m, 4 H), 2.47 (s, 12 H), 2.55 (s, 12 H), 3.33 (s, 3 H), 3.81 (s, 3 H). The compound was isolated as a PF_6 salt with one acetone. Anal. Calcd for $C_9H_{48}N_{10}O_2S_2P_4F_{24}Ru_2$: C, 9.20; H, 4.11; N, 11.92. Found: C, 8.96; H, 4.08; N, 11.24.

(4) All voltammograms were measured in a standard three-electrode cell and are reported vs the normal hydrogen electrode. The reference electrode was calibrated with the ferrocene/ferrocenium couple (E = 0.55 V (NHE)) as measured in situ.

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