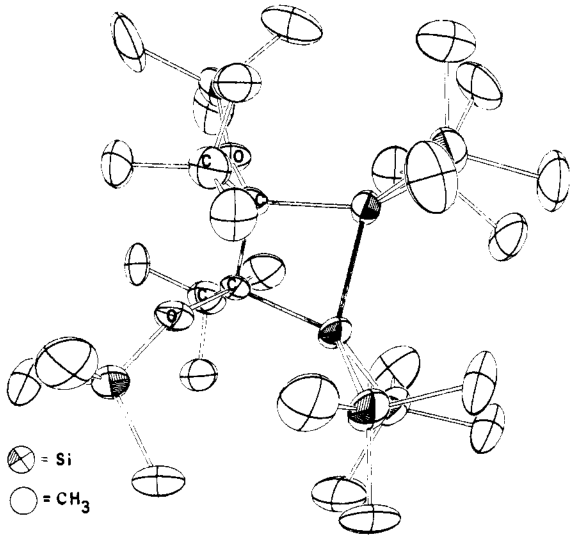

Figure 1. ORTEP plot of nonhydrogen atoms of silaethylene dimer III (R′ = *t*-Bu) showing 50% probability ellipsoids.

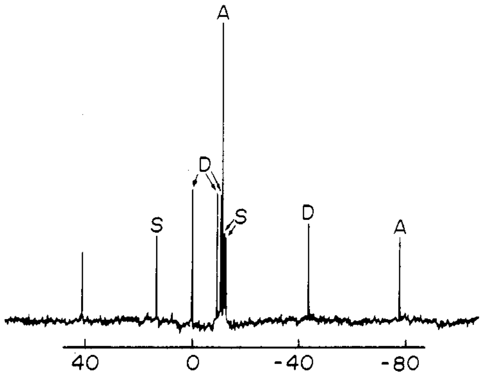

Figure 2. ^{29}Si spectrum of solution from photolysis of (Me$_3$Si)$_3$SiCOCMe$_3$ in C$_6$D$_6$ with signals attributable to acylsilane I (A), silaethylene II (S), and its dimer III (D) in parts per million relative to Me$_4$Si.

of the acylsilane I (R′ = *t*-Bu), a spectrum virtually identical (except for relative intensities) with that observed merely by dissolving the pure solid dimer III (R′ = *t*-Bu) in C$_6$D$_6$ at room temperature immediately prior to taking the NMR spectrum. The spectrum is characterized by three sets of signals, the bands at −11.49 and −77.90 being due to the acylsilane and those at −0.05, −9.50, −10.88, and −43.78 being due to dimer III. The remaining four bands of approximately equal intensity can be ascribed to the monomer II, the bands at −12.18 and −12.64 being due to Me$_3$Si groups, that at 13.34 to the trimethylsiloxy group, and the band at the very unusual low-field position at 41.44 ppm being consistent with an unusually hybridized silicon atom as would be found in a silaethylene.

This assignment, together with the previously observed ^{13}C signal at δ 112.7 ppm for the sp^2-hybridized carbon atom, fully characterizes the silicon-carbon double bond, a species that we regard as not significantly polarized (see reference 1), consistent with its unusual head-to-head dimerization, probably by radical coupling at silicon.

In contrast to the pivaloylsilane, where the photolysis system shows the presence of acylsilane, monomer and dimer, replacement of R′ in the acylsilane by the bulkier groups CEt$_3$ or adamantyl gives photolysis solutions which show evidence for acylsilane and silaethylene only, but no dimer. This result is in accord with our anticipation that increasing the bulk of the groups [illegible]ched to either the sp^2-hybridized carbon or silicon of the silaethylene would stabilize the monomer relative to the dimer because of increased steric strain in the latter. However, the increased bulk about carbon appears to also destabilize the silaethylene relative to the acylsilane. A photostationary state apparently develops between the species so that extended photolysis fails to reduce the amount of acylsilane, and, when the light is removed, the silaethylene returns to acylsilane more rapidly than was observed with the pivaloylsilane.

It is clear that these complex systems can be conveniently studied by ^{29}Si NMR, and the present data, taken with that reported earlier, establish unequivocally the presence of remarkably stable silaethylenes in these systems. Stabilization of the silaethylenes by increasing the bulk of the groups attached to carbon is not a straightforward matter. Further studies are in progress.

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(4) Ishikawa, M.; Fuchikami, T.; Kumada, M.; Heguchi, T.; Miyamoto, S. *J. Am. Chem. Soc.* **1979,** *101,* 1348.
(5) The dimer III crystallizes in monoclinic system, space group $P2_1/c$, with a unit cell of dimensions a = 12.21 (6), b = 22.31 (4), c = 18.18 (7) Å; β = 120.3 (7)°; and Z = 4. The crystal structure is still being refined (R = 0.082), not all the hydrogen atoms having yet been found. No significant changes in interatomic distances are expected. Full details will be published elsewhere by S. C. Nyburg and J.-S. Lee.
(6) All spectral data are relative to Me$_4$Si. Spectra were measured at 15.9 MHz, using a pulse flip angle of 45°, a pulse repetition time of 25 s, and gated decoupling to suppress nuclear Overhauser effects. Even with these precautions, the relative proportions of different species present could not always be reliably determined from the relative intensities of the ^{29}Si signals since artificial mixtures of compounds showed proportions in error by factors ranging from 1.5 to >3.3, depending upon the silicon signals being compared. In particular the central ^{29}Si signal of acylsilane I is often of lower than expected intensity, suggesting an extremely long spin-lattice relaxation time for this silicon.
(7) Satisfactory elemental analysis and ^{1}H NMR, IR, and mass spectral data were obtained for all new compounds.

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Spherands—Ligands Whose Binding of Cations Relieves Enforced Electron-Electron Repulsions[1]

Sir:

The crowns,[2] cryptands,[3] and natural ionophores[4] owe their metal-ion binding properties to varying degrees of organization (prior to complexation) of functional groups containing oxygen and nitrogen. In these hosts, the unshared electron pairs of their heteroatoms become focussed on cations *during* complexation by conformational reorganizations of their supporting chains. The X-ray structures of these hosts do not show the presence of the holes, which in their complexes are filled with metal ions. Rather, potential cavities in hosts are filled by a folding inward of their parts which turn outward when "displaced" by guests.[5] Thus the guest conformationally organizes some of the binding

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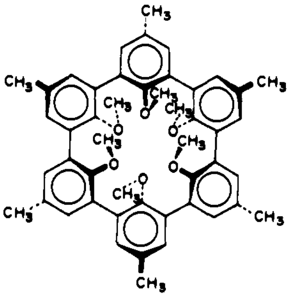
sites of the host during complexation, or displaces solvent which has helped organize the host.[6]

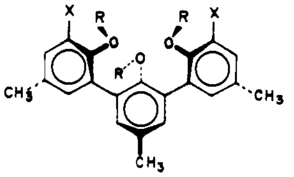
We have envisioned and designed with the help of CPK molecular models ligand systems which owe much of their cation-binding potential to relief of electron-electron repulsion upon complexation. This and other features differentiate our ligand systems from the crowns and cryptands. Ideal hosts of this new type describe an oxygen shell whose cavity can be occupied *only by spherical entities* such as single atoms or monatomic ions, and not by parts of the host or by solvent. The cavity is lined with unshared electrons of heteroatoms. We suggest the class name "spherands" for such ligand systems, and the class name "metallospherium" salts for their complexes with metal salts.[7]

In the spherand exemplified herein (**1**), a cyclohexametaphenylene[8] system provides a framework which holds the oxygens of six methoxyl groups in a perfect octahedral arrangement by their attachment to the six convergent positions of the aryl groups. In CPK models of **1**, only an alternating "up and down" arrangement of the six methoxyl groups accommodates their spacial requirements. The methyls of the methoxyls remain uncompressed only when turned away from the center of the system, three pointing in one direction and three in the opposite direction. Methoxyl groups cannot pass through the center of the macroring system.[9] Not unlike chair cyclohexane, a model of **1** has D_{3d} symmetry. In a sense, the six methoxyls of **1** occupy pseudoaxial positions and the *p*-methylphenyl groups, pseudoequatorial positions. The diameter of the central hole varies with the dihedral angle between the six aryl groups, restricted on the low side to ~1.3 Å by oxygen-oxygen contacts and on the high side to ~3.3 Å by the constraints of the arylene ring system whose bond angles must deform to exceed ~2.2 Å.[10] Most of the monatomic metal cations of the periodic table possess diameters within the 1.3-3.3-Å range.

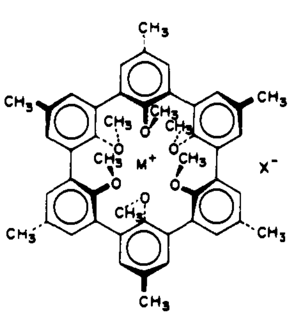


1

Spherand **1** was synthesized in six steps in 6.3% overall yield from *p*-cresol, which was oxidatively coupled ($FeCl_3$) to give oligomer **2** (20-40%).[11] Bromination of **2** gave **3**[11b] (98%), methylation of which with $(Me)_2SO_4$ gave **4**[12] (88%). Treatment of **4** with BuLi in THF at −80 °C gave material which, when added to 4 mol of $Fe(AcAc)_3$ in refluxing benzene (1 h), gave a solution that was washed with an aqueous solution of $HFeCl_4$ and evaporated. The residue was washed with ether and crystallized from CH_2Cl_2-AcOH to give **5**[12] (22%) as yellow needles, mp >400 °C. The yield of this new reaction increased with dilution, and the cyclization probably was templated by Li^+. A solution of **5** in CH_2Cl_2 was washed successively with aqueous solutions of EDTA and LiCl, and **6**[12] (95%) crystallized as white needles from toluene, mp >400 °C. When heated at 150 °C for 5 days in 1:4 (v/v) MeOH-H_2O, **6** gave **1**[12] (90%), white granules from C_6H_5Cl, mp 380-385 °C dec. The decomplexation appeared thermodynamically driven by the crystallization of **1**, which was very insoluble in the medium. The high temperature overcame the high activation energy required for decomplexation. Both **1** and its LiCl complex (**6**) gave three singlets in their ^1H NMR spectra, as required by their D_{3d} structures.

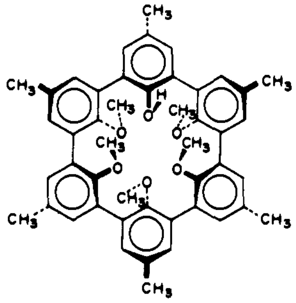


2, R = X = H
3, R = H, X = Br
4, R = CH_3, X = Br



5, M = Li, X = $FeCl_4$
6, M = Li, X = Cl
7, M = Li, X = ClO_4
8, M = Li, X = Br
9, M = Na, X = Cl
10, M = Na, X = Br
11, M = Na, X = ClO_4

The lithiospherium chloride (**6**) in $CHCl_3$ underwent ready anion exchange with $LiClO_4$ in water to give **7**[12] (mp >400 °C dec). The remarkable stability of the lithiospherium anion is indicated by its failure to decomplex or decompose in more than trace amounts when **7** was heated at 200 °C in 6:1 (v/v) water-pyridine for 1 h (80% recovery of **7**). When heated at 200 °C in 6:1 (v/v) pyridine-water for 2.5 h with the product being heated with boiling 6 N hydrochloric acid, **6** gave monophenol (70%) **12**[12] (mp ~370 °C dec). Sodiospherium chloride **8**[12] (mp ~370 °C dec) was produced (95%) when **9** was heated in THF with a large excess of NaOH and $(Me)_2SO_4$. A similar attempt to encapsulate K^+ with reagent grade KOH (99.95%) also led to **8** (40%), whose Na^+ at ≪1% levels was scavenged from bulk KOH. The three proton singlets in the 200-MHz spectra of **1**, **6**, and **8** in $CDCl_3$-$(CD_3)_2SO$ were easily distinguishable in the presence of one another at ~35 °C. No host-to-complex, complex-to-complex, or guest-to-complex cation exchange was visible in appropriate ^1H NMR experiments involving **1** and its spherium salts in $CDCl_3$ at 35 °C.



12

Solutions (500 μL) of **1** in $CDCl_3$ (0.0019 M) were mixed with 10 μL of $(CD_3)_2SO$ solutions that were ~0.04 M in $LiClO_4 \cdot 3H_2O$, or $NaClO_4 \cdot H_2O$, $KClO_4$, $RbClO_4$, $CsClO_4$, $Mg(ClO_4)_2$, or $CaBr_2$ to give homogeneous solutions of potential complexing partners in molar ratios that approximated 2.2:1 M ratios of host to guest. The 200-MHz ^1H NMR spectra were taken within 5 min to 3 h of mixing at ~35 °C. In the same solution, **1**, in the absence of salts, gave (200 MHz) singlets at δ 2.405 ($ArCH_3$, 18 H), 2.849 ($ArOCH_3$, 18 H), 7.167 (ArH, 12 H). All solutions gave identical signals for the free host. Only when Li^+ or Na^+ were present did additional signals appear at δ 2.508, 3.049, and 7.355 (Li^+ complex, **7**), and at 2.485, 2.974, and 7.320 (Na^+ complex, **11**). The peak intensities of complexed and uncomplexed **1** indicated that, within experimental error, all guest present was complexed.

When violently shaken (quartz tubes) with 1 mL of 0.0028 M solutions of **1** in $CDCl_3$ at 30 °C, a 6 M solution (1 mL) of LiBr converted **1** into **8** in ~8 h and a 6 M solution (1 mL) of NaBr converted **1** into **10** in <1 h (^1H NMR). A similar extraction with 1 mL of 0.0028 M solution of **1** in $CDCl_3$ of 1 mL of water that was 0.1 M in both NaCl and LiCl gave, after 284 h, 0% **1**, 89% **8**, and 11% **6** (^1H NMR). Thus **1** in $CDCl_3$ extracts NaCl from water ca. eight times as fast as LiCl. Extraction experiments with separate NaCl and LiCl solutions provided the same rate factor. Similar extractions with **1** in $CDCl_3$ of 1.5 mL of aqueous solutions of 4.5 M KBr, 2 mL of 3 M $MgBr_2$, 1 mL of 6 M $CaBr_2$, and 2 mL of 3 M $SrBr_2$ for from 24 to 180 h gave no evidence of any ions being complexed except for traces of Na^+ and sometimes Li^+. In all cases, the trace amounts were slowly scavenged from the bulk amounts of the other ions (^1H NMR and mass spectra).

These experiments provide the following conclusions. (1) A powerful ligand system of D_{3d} symmetry has been composed solely of *p*-methylanisole units, which when taken singly are poor ligands for metal ions.[15] (2) This spherand strongly complexes Li^+ and Na^+, since these ions can fill the enforced cavity and thus eliminate the electron-electron repulsions designed into the free ligand system. (3) Complexation rates of these ions in $CDCl_3$ at 30 °C are on the human time scale, but the decomplexation rate of Na^+ and Li^+ at 30 °C must be extremely slow. (4) Spherand **1** in $CDCl_3$ extracts NaBr from water eight times fater than LiBr, the scavenges from concentrated solutions of KBr, $MgBr_2$, $CaBr_2$, and $SrBr_2$ trace amounts of Na^+ and Li^+ without complexing the bulk ions. (5) Since Li^+ and Mg^{2+} on the one hand, and Na^+ and Ca^{2+} on the other, possess similar diameters, the high selectivity seems associated with both diameter and charge. Probably the selection of Li^+ and Na^+ over Mg^{2+} and Ca^{2+} is kinetic. The selection of Li^+ and Na^+ over that of the larger ions may either be kinetic or thermodynamic or both.

Molecular model examinations of **1** and of spheres of diameter 1.5-1.9 Å (e.g., Li^+ and Na^+) indicate that, to complex or decomplex, the cations must pass through a lipophilic sleeve composed of three CH_3-O groups. At the halfway point, the cations can have only one to two ligands external to the spherand and none in the spherand. This structural feature explains why complexation-decomplexation activation energies for these spherand-metallospherium salts are so high, particularly for the divalent ions.

We are designing, synthesizing, and studying the differential binding properties of spherands and hemispherands[16] composed of methoxycyclohexane, cyclic urea, pyridine oxide, cyclic ketone, and lactam units whose geometries resemble portions of **1**. Both atoms and ions as guests are being studied.

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(1) The authors thank the Division of Basic Energy Sciences of the Department of Energy for a contract, AT(04-3)34, P.A. 218, used in support of this research.

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(6) For example, Goldberg, I. *Acta Crystallogr., Sect. B* **1975,** *31,* 754.

(7) This family name is composed from the word "sphere" (derived from the Greek sphaira and Latin sphaera) and from the suffix "and" taken from the word "ligand". The suffix "ium" for the complexes is appropriate since cation names have this ending, just as anion names have endings such as "ide" or "ate". The inserting of the letters "spher" into the names of the metal salts parallels the chemical operation of inserting a spherical ligand shell of oxygens between the cation and the anion. Thus complexed lithium chloride becomes a lithiospherium chloride (e.g., **6**) and a complexed sodium perchlorate becomes a sodiospherium perchlorate (e.g., **11**).

(8) Staab, H. A.; Binnig, F. *Chem. Ber.* **1967,** *100,* 293.

(9) If the dihedral angles between the benzene rings in CPK models of **1** are opened to ~70–80° and the Ar–Ar bond angles all deform by 10–20 Å, the two methyl groups (one on each side) can be turned inward to give a highly compressed conformation without a central cavity. We believe such conformations to be highly unlikely. The barrier to rotation around the Ar–OCH_3 bond appears in models to be high. Both X-ray crystallography and the temperature-dependent ^1H NMR spectrum of **1** and its complexes are being examined to check these predictions.

(10) Estimates of hole diameters are made by inserting graded spheres (ball bearings) into CPK models of **1**.

(11) (a) Bowden, K.; Reece, C. H. *J. Chem. Soc.* **1950,** 2249. (b) Bacon, R. G. R.; Grine, R. G.; Munro, D. J. *Ibid.* **1974,** 2275.

(12) Carbon and hydrogen analyses were within 0.30% of theory, and ^1H NMR and mass spectra were consistent with the structural assignments.

(13) Many other oxidants were tried but most of them failed. The reaction has been applied to making aryl-aryl bonds in a variety of systems.

(14) The mass spectra of the metallospherium salts gave base peak *m/e* values corresponding to the metal salts of the corresponding phenols, in which one methyl has been lost with complexes of Li^+ and Na^+.

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(16) The cyclic host composed of three bonded *p*-methylanisole units bridged by a $CH_2(OCH_2CH_2)_2OCH_2$ chain (compound **37** of ref 15) might be called a hemispherand, since half of the molecule has an enforced arrangement of the electrons of the three anisole oxygens and consequently exceeds the crowns in binding power of Na^+, K^+, Rb^+, and Cs^+ ions in $CDCl_3$. The X-ray structure of this free host shows the three methoxyl groups oriented as in structure **1**, but the crown part contains one to two inward-turning CH_2 groups (one disordered) which tend to fill the potential cavity. The OCH_2CH_2O oxygens are distant, and the OArArO oxygens are close to one another (private communication from I. Goldberg). This structure illustrates in the same molecule how three crown or cryptand units organize to fill potential holes, whereas three spherand units are unable to do so.

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An Unusually Long Cobalt–Carbon Bond. Molecular Structure of *trans*-Bis(dimethylglyoximato)(isopropyl)(pyridine)cobalt(III). Implications with Regard to the Conformational Trigger Mechanism of Cobalt–Carbon Bond Cleavage in Coenzyme B_{12}

Sir:

Homolytic cleavage of the Co–C bond is generally accepted as a key step in the mechanism of action of many enzymes which require a B_{12} coenzyme.[1-3] The factors which promote this cleavage are not yet understood.[1,3] Recent work with dioldehydrase by Abeles and his co-workers[1] has demonstrated that modification of the side chains on the periphery of the corrin ring leads to considerable variation in coenzyme activity. Since the changes in the side chains were not such as to alter significantly the electronic properties of the corrin ring system, it is unlikely that the variation in activity resulted from inductive effects. Variations in the ease of formation of cob(II)alamin correlated, to some degree, with alterations in activity.[1] A reasonable hypothesis advanced to explain these and other results is that specific tight interactions between the enzyme and coenzyme bring about distortion of the corrin ring system, thus facilitating cleavage of the Co–C bond. Comparisons between the stability of model organocobalt compounds and organocobalamins has led Halpern[3] to suggest that steric effects of the corrin ring may be important in promoting dealkylation.[16]

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