

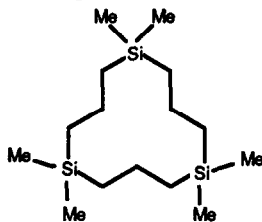
## Synthesis and Transport Properties of 12-Silacrown-3, a New Type of Anion Complexing Agent

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**Summary:** The synthesis of 1,1,5,5,9,9-hexamethyl-1,5,9-trisilacyclododecanone, **1**, a new anion complexing agent and its complexing ability for halide ions is described.

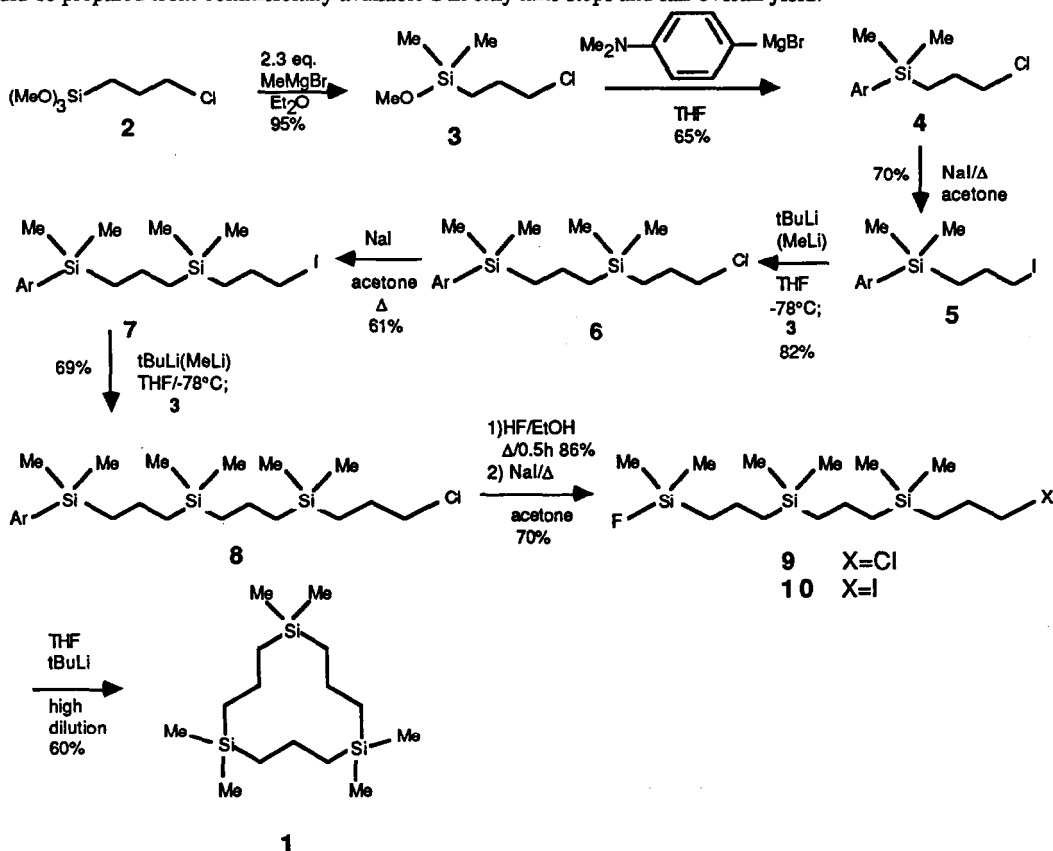
A very large amount of research has been carried out in the last twenty years aimed at the complexation of positively charged species (metal cations, ammonium salts, etc.). Due to the pioneering work of Pederson, Cram, Lehn and many others,<sup>2</sup> a large body of information is available for cation complexation using crown ethers, cryptands, cavitands, and spherands. This ability to complex cations has permitted the use of uncomplexed or "naked" anions with heightened reactivity in organic synthesis<sup>3</sup> as well as chiral hosts for the separation of enantiomeric ammonium species ( $\alpha$ -amino ester salts).<sup>4</sup> However, there is very little known about the complementary field of anion complexation and, in particular, anion complexation by organic-soluble agents. Lehn<sup>5a</sup> reported some years ago the complexation of chloride ion by a hexa-protonated cryptand, while Schmidtchen<sup>5b</sup> described the complexing ability of tricyclic tetra-quaternary ammonium salts. Recently Newcomb<sup>6</sup> has prepared some macrobicyclic alkanes with tin atoms at the bridgehead and has shown that they complex halide ions by <sup>119</sup>Sn NMR while Kuivila<sup>7</sup> and Gielen<sup>8</sup> have observed complexes between electron donors and acyclic bis(halostannyl)alkanes. We now wish to report the facile synthesis of a new type of anion complexing agents, namely the crown silane **1**, and our initial studies on its ability to transport halide ions. There is much evidence in the literature<sup>9</sup> for the ability of silicon to expand its valence shell and produce pentacovalent (monoanionic) or



even hexacovalent (dianionic) species. For example, Voronkov<sup>9a</sup> has pioneered the use of the pentacovalent silatranes **2** in medicinal chemistry while Kumada<sup>9b</sup> has utilized the hexacovalent alkylpentafluorosilane dianions in organic synthesis. We proposed that a cyclic polysilane of the right ring size and with the correct groups on silicon might be able to bind halide ions via partial bonding of the halide to each silicon atom, thereby effecting partial pentacovalency at each silicon. We decided to first test this overall concept with the symmetrical monocyclic trisilane **1**. Even though the methyl groups on silicon would not be as favorable for silicon anion stabilization (and pentacovalency) as several other groups (e.g.,

fluoride, substituted aryl, trifluoromethyl, etc.), the relatively inertness of the methyl groups would make the synthesis much easier. Therefore we set out to prepare **1** by a fast and efficient route.

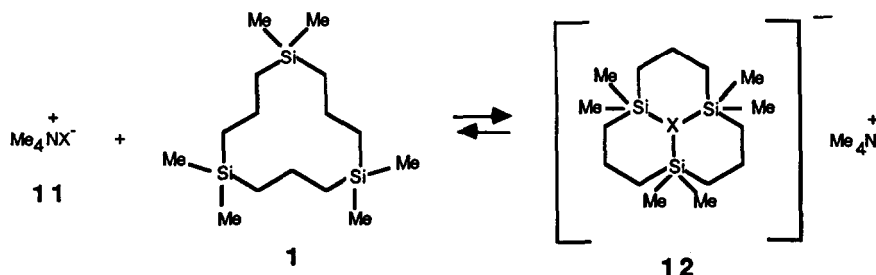
Treatment of commercially available (3-chloropropyl)trimethoxysilane **2** with 2.3 eq of methylmagnesium bromide in ether produced the dimethylmethoxysilane **3** in 95% yield. Addition of 4-(dimethylamino)phenylmagnesium bromide to **3** gave the aryl dimethylsilane **4** in 65% yield. Finkelstein reaction of **4** produced in 70% yield the iodide **5** which was coupled to the methoxysilane **3** by way of the lithium compound (prepared from **5** by treatment with *t*-butyllithium and a trace of methyl lithium at  $-78^{\circ}\text{C}$ ) to give the disilane **6** in 82% yield. Iteration of this sequence produce the trisilane **8** in two steps via the iodide **7**. Conversion of the chloride **8** to the iodopropyl fluorosilane **10** proceeded in two steps via the chloropropyl fluorosilane **9**. Finally intramolecular cyclization of the iodopropyl fluorosilane **10** was effected by addition of **10** to a solution of excess *t*-butyllithium in THF (high dilution conditions) to afford the cyclic trisilane **1** in 60% yield (after purification by distillation and flash chromatography). Thus the symmetrical cyclotrisilane **1** could be prepared from commercially available **2** in only nine steps and fair overall yield.



The structure of **1** was assigned by spectroscopic methods, especially mass spectroscopy and NMR. The mass spectrum (EI, 16ev) showed the molecular ion and a  $M^+ - 15$  peak corresponding to a loss of a methyl group. The <sup>1</sup>H NMR showed only three absorptions: a distorted multiplet at  $\delta$  1.47 corresponding to the three central methylene groups, a distorted triplet at  $\delta$  0.62 corresponding to the six methylene groups  $\alpha$  to silicon, and a singlet at  $\delta$  -0.06 corresponding

to the six methyl groups. The  $^{13}\text{C}$  NMR was also consistent with the structure of **1**, having only three absorptions at  $\delta$  19.46, 18.71, and -2.14, in a 2:1:2 ratio.

Having prepared **1** by a reasonably efficient route, we next decided to study its transport properties. We set up several U-tube experiments using a saturated aqueous solution of the tetramethylammonium halide in one arm, pure water in the other arm, and a methylene chloride solution of **1** in the center part of the U-tube which also had a magnetic stir-bar for mild mixing. After various periods of time, the arm originally containing pure water was checked for the presence of halide ion by treatment with silver nitrate to precipitate the silver halide. Blanks were run to determine that in the absence of **1** transport of halide was negligible over the time periods studied. The results are presented in the Table. As shown, no transport of fluoride or iodide ion was observed, while chloride and bromide were transported by **1** from one aqueous solution to the other. Of the two, bromide was transported to a greater extent over the same time period as indicated by the amount of precipitated silver bromide. Thus we assume that the halide salt **11** ( $\text{X}=\text{Cl}, \text{Br}$ ) reacts with **1** to produce

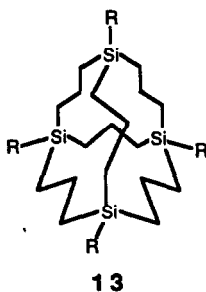


some type of host-guest complex, e.g., **12**, which is soluble in the organic solvent and thus allows for the slow transport of the ammonium halide from one aqueous solution to the other. The simple monosilane, tetramethylsilane, does not promote anion transport in analogous U-tube experiments nor does the simple large-ring hydrocarbon, cyclododecane.

#### Transport Studies of Tetramethylammonium Halides by **1**

Halide	Concentration of <b>1</b>	Time	Transport
F	0.023M	3h	-
		14.5h	-
Cl	0.084M	3h	-
		8h	-
		11h	+
		13h	++
Br	0.014M	1h	-
		5h	-
		12.5	+
		1h	-
		3h	+
	0.023M	5h	++
		1h	-
		2h	+
		4h	++
		0.092M	4h
I	0.078M	3h	-
		14.5h	-

We are currently attempting to quantify the complexation and to alter the cyclic polysilane so that better binding and selectivity might be achieved. For example changing the methyl groups on silicon to more electron-withdrawing groups (fluoro, trifluoromethyl, etc.) should produce much better Lewis acids and much stronger binding. Finally, we are attempting to modify the synthesis so that tricyclic tetrasilanes, (tetrahedral silacryptands) such as **13**, might be prepared.



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