The preparation of hexasilsesquioxane (T$_6$) cages by "non aqueous" hydrolysis of trichlorosilanes

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Hexasilsesquioxane cages (T$_6$) have been prepared from a range of alkyl and aryl trichlorosilanes using a "non aqueous" hydrolysis with dimethyl sulfoxide.

T$_6$ silsesquioxane cages $(RSiO_{1.5})_6$ have received a great deal of attention as cores for building octopus molecules[1] and dendrimers[2] and as models of resins. Such cages have also been used for the preparation of partially opened cages that themselves act as models for silica surfaces and supports for transition metal catalysts.[3–6] However, only a limited range of spherical organosilsesquioxanes have been prepared even though a large variety of trichlorosilanes are available.[7] This is because conventional aqueous hydrolysis, including "scarce water hydrolysis" leads to mainly resin and a large variety of cage and open cage compounds. Only with specific alkyl groups is particular cage formation favoured to such an extent and/or solubility differences large enough to enable isolation of pure silsesquioxane cages. Nevertheless the yields obtained by these methods are very poor and the octasilsesquioxanes, $(RSiO_{1.5})_8$, T$_8$, seem to be the preferred outcome. An alternative route to such species is the formation of the spherical hydrogen silsesquioxane followed by hydrosilylation using alkene.[1] We have used this approach to build T$_8$ molecules with a range of functionalities such as dendrimers, liquid crystals and surfactants. We are interested in the preparation of functionalised hexasilsesquioxanes, T$_6$, and the mechanism of their conversion into T$_8$ and larger cage structures.[8] However, we have been unable to prepare hydrogen hexasilsesquioxane for use in our hydrosilylation methodology and therefore we examined alternative methods of T$_6$ formation.

Hexa(cyclohexylsilsesquioxane) has been prepared by Feher[3] using a modification of Brown's method[9], involving aqueous hydrolysis in a water/acetone mixture. Reasonable yields are obtained, but only after long periods. For example, after four months of hydrolysis, Molloy obtained sufficient crystals to carry out an X-ray crystal structure analysis.[10] We have obtained reasonable yields of this T$_6$ molecule in a shorter time using a similar aqueous/organic hydrolysis, however, this route is limited to a few compact substituents with secondary or tertiary groups adjacent to the silicon. Matsumoto has developed an alternative approach to T$_6$ based on the dicyclohexylcarbodiimide coupling of the silane triol or 1,1,3,3-tetrahydroxydisiloxane.[11] Unfortunately this route seems only possible with bulky substituents such as *tert*-butyl or 1,1,2-trimethylpropyl.

We thus looked for an alternative method of constructing the T$_6$ cage that was easy to carry out, used readily available starting materials and was applicable to a wide range of substituents on silicon. The "non-aqueous" hydrolysis of dichlorosilane using dimethyl sulfoxide was first reported in

1965[12] and has subsequently been revisited by Voronkov[13], Weber[14] and Brook.[15]

Brook's most recent study has shown that early in the reaction the six membered cyclotrisiloxane, D$_3$, is formed in good yields. If six membered rings are preferred with trichlorosilanes this should favour T$_6$ formation through the ring acting as a template or through the coupling of two such T$_3$ rings.

Table 1 gives the results of our study†. We found that trichlorosilanes could be reacted with dimethyl sulfoxide (2 equivalents) in chloroform at room temperature to give T$_6$

Table 1 Yields and properties of T$_6$ cages prepared by the "non aqueous" hydrolysis of trichlorosilanes using DMSO

Starting trichlorosilane	^{29}Si-NMR/ppm	Physical state of T$_6$ product	Yield/%
Octyltrichlorosilane	−54.2	Gel	25
Cyclohexyltrichlorosilane	−56.6	Solid	11
Cyclopentyltrichlorosilane	−54.4	Solid	9
2-Methylpropyltrichlorosilane	−55.4	Solid	11
Phenyltrichlorosilane	−66.9	Solid	7
3-(*p*-Methoxyphenyl)propyl trichlorosilane	−54.4	Solid	6

cages. All yields quoted are isolated yields after purification. The T$_6$ cage is formed together with resin by-products, which are sometimes difficult to separate. Silsesquioxane cages are often purified by column chromatography, however, because of the T$_3$ rings we found that the T$_6$ cages were particularly susceptible to decomposition in the presence of nucleophilic species. Thus the T$_6$ cages decomposed on the silica or alumina stationary phases used in column chromatography. However, we found that treating the silica gel with 5–10% (by mass) trimethylsilyl chloride before elution of the reaction mixture gave an ideal chromatography medium that was sufficiently active to maintain separation but not too active to cause degradation of the T$_6$. Although the yields are low in absolute terms, they are perfectly acceptable when compared to conventional cage syntheses. For example, scarce water hydrolysis of trichlorosilanes gives T$_8$ cages in about 15% yield. We have carried out the "non aqueous" hydrolysis of dichlorosilanes to give D$_3$, D$_4$, D$_5$ and D$_6$ rings using a range of other high oxidation state oxygen donors such as triphenylphosphine oxide, pyridine N-oxide, iodosobenzene and sulfur trioxide/pyridine. However, DMSO was the only reagent that gave specific cage compounds with organotrichlorosilanes.
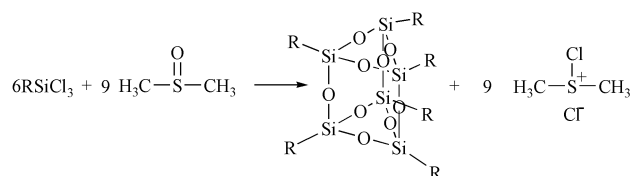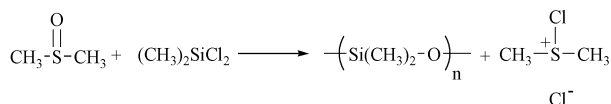
Table 1 shows that, as expected, compact substituents such as cyclopentyl, cyclohexyl and phenyl give T$_6$ cages in acceptable yields. Surprisingly, primary alkyltrichlorosilanes such as octyl, 2-methylpropyl and 3-(p-methoxyphenyl)propyl gave T$_6$ cages in comparatively good yields and this represents the first synthesis of this important class of compounds. In contrast to the Matsumoto route, we were unable to isolate T$_6$ cages when bulky substituents such as *tert*-butyl were employed. In this case a range of products were observed which were probably D polyol rings. Similarly cage structures were not produced with small substituents, for example, vinyltrichlorosilane gave no identifiable products. Chan has shown that HSiCl$_3$ reduces DMSO to dimethyl sulfide.[16] In contrast we have been able to form D$_3$ and D$_4$ rings from CH$_3$SiHCl$_2$ using DMSO, however, reaction of DMSO with trichlorosilane led to a complex mixture of products.

Our previous strategy for preparing organooctasilsesquioxanes relied on the synthesis of the alkene arm followed by attachment to hydrogen silsesquioxane by hydrosilylation.[1] We have been able to transfer this methodology to T$_6$ synthesis through hydrosilylation of the alkene with trichlorosilane followed by reaction with DMSO. For example, hydrosilylation of methyl 3,3-dimethylpent-4-enoate using chloroplatinic acid gives the corresponding trichlorosilane derivative, **1**, in 77% yield and thence the T$_6$ derivative in 6.3% yield.
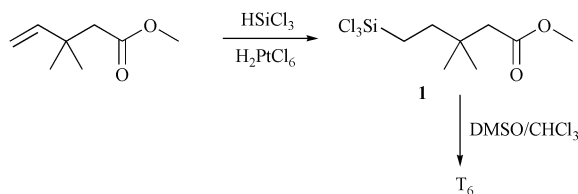
As with the T$_8$ cages we are interested in preparing polyfunctional cages and dendrimers. This requires the synthesis of cages with functionality on the arms. Reaction of the methyl dimethylpentanoate derivative with ethanediamine followed by methyl acrylate will give a dendrimer with twelve ester groups.[17]

The ^{29}Si NMR chemical shifts of the T$_6$ cage silicons are usually in the region −54 ppm to −57 ppm. This is in agreement with the chemical shifts of previously prepared T$_6$ cages.[4,11] The exception to this is phenyl hexasilsesquioxane which has a ^{29}Si NMR chemical shift of −66.89 ppm. This upfield shift is typical of a phenyl substituent, as observed in the D ring series. The corresponding range for T$_8$ cages is −65 ppm to −67 ppm. Marsmann and co-workers have developed a method to estimate the ^{29}Si NMR chemical shift of an unknown T$_{10}$ or T$_{12}$ cage based on the chemical shift of the corresponding T$_8$ cage.[18] For example, for T$_{10}$ cages the equation $\delta_{T10} = 1.028 \times \delta_{T8}$ holds.

A plot of the ^{29}Si NMR chemical shift of the T$_6$ cages in Table 1 *versus* the chemical shift of the corresponding T$_8$ cages has a slope of 0.82 ($R^2 = 0.94$ (forced to go through the origin)), suggesting the equation $\delta_{T6} = 0.82 \times \delta_{T8}$.

The chemical shifts estimated using this equation correlate well with the measured chemical shifts in Table 1, however, differ most significantly for the phenyl and benzyl substituents. The size of the constant in the equations above reflects the size of the rings associated with the silicon in question. A silicon in a T$_8$ is associated with three T$_4$ rings, whereas a silicon in a T$_{10}$ is associated with two T$_4$ rings and a T$_5$ ring, the relief of angle strain leading to a slightly higher factor. A silicon in a T$_6$ cage is associated with one T$_3$ ring and two T$_4$ rings, the increase in ring strain leading to lower factor and the decrease is relatively large. This matches the behaviour in D$_5$, D$_4$ and D$_3$ rings.

In conclusion we have developed a robust method for the synthesis of T$_6$ cages in reasonable yield with a wide range of substituents. This should lead to T$_6$ structures being used in exactly the same way that T$_8$ cages are employed for building octopus molecules and dendrimers, as models of resins and as starting materials for the preparation of partially opened cages.

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