Ship-in-a-Bottle Synthesis of Otherwise Labile Cyclic Trimers of Siloxanes in a Self-Assembled Coordination Cage

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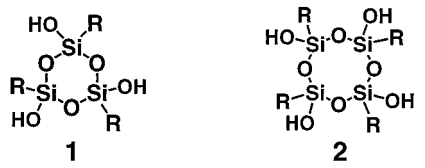
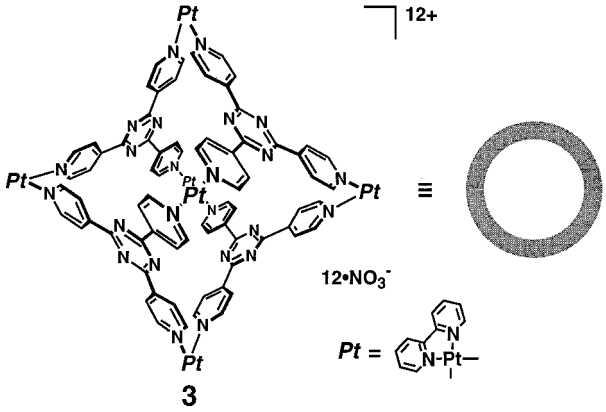
Molecular capsules provide isolated microspace within the molecules where otherwise labile species are protected and can be considerably stabilized.[1] The labile molecules are most effectively trapped in the capsules if they are prepared *in situ* from smaller components coming through small openings of the capsules.

Cyclic oligomers of trisilanols **1** and **2** are considered to be ephemeral intermediates in the polycondensation of trialkoxysilanes (so-called sol−gel condensation) that lead to the formation of siloxane networks or ladder polymers.[2] The preparation and isolation of these intermediates as stable forms are particularly important not only to understand the condensation process but also for modeling silica gel surface in a homogeneous system and for further conversion to silicon-based functional materials.[3] Whereas cyclic tetramer **2** has been prepared in low to moderate yields, cyclic trimer **1**, which is simpler but less stable, has never been isolated as a pure and stable form.[4,5] We report that cyclic trimer **1** can be prepared and observed as a stable form if the condensation reaction of trialkoxysilanes is carried out within the nanosized cavity of self-assembled coordination cage **3**, which shows remarkable binding ability for neutral molecules.[6−8]





The condensation of trialkoxysilanes within cage **3** described here is particularly featured by the following findings. First, the cyclic trimers are formed in a "ship-in-a-bottle" fashion:[9] while trialkoxysilanes can enter or exit through the portals of **3**, the trimers prepared in situ can no longer escape from the cage because their dimension becomes larger than the portal size. Second, the encapsulated cyclic trimers, being protected by the cage, are very stable and tolerant even in acidic aqueous solution and isolable as pure clathrate compounds. Third, stereochemistry of the condensation reaction is highly controlled within the cage giving only all-cis isomers.

A typical example is given by the selective condensation of phenyltrimethoxysilane (**4**) into cyclic siloxane trimer **1a** in the presence of nanocage **3**.[10] Thus, **4** (6.5×10^{-2} mmol) was hydrolyzed to **5** by suspending it in a D_2O (1.0 mL) solution of **3** (6.50×10^{-3} mmol) at 100 °C. After 5 min, ^{1}H NMR spectrum revealed the formation of the **3**•(**5**)$_n$ complex ($n = 3-4$) (Figure 1a). Within 1 h, the spectrum became simpler showing the formation of encapsulation complex **3**•**1a** (Figure 1b), whose structure was determined by NMR and ESI-MS as discussed later. An excess amount of **4** was condensed into oligomeric components and precipitated. After the precipitate was filtered, the clear filtrate was evaporated, and the residue was recrystallized from a small amount of water to give pure **3**•**1a** complex in 92% yield. Elemental analysis was consistent with the formula of **3**•**1a**•$(H_2O)_7$.[11]

The overall reaction is featured by the "ship-in-a-bottle" formation of **1a** within the cage. Obviously, **1a** was formed within cage **3** because the **3**•**1a** complex was not obtained when cage **3** was added *after* the treatment of **4** in water for 1 h at 100 °C. In addition, **1a**, once formed in cage **3**, was not extracted with $CHCl_3$ because of its steric demand.

Clear evidence for the structure of **3**•**1a** follows ESI-MS and NMR measurements. While empty **3** gave a prominent peak of $[\mathbf{3}\cdot(NO_3)_2]^{2-}$ at *m*/*z* 2112.7 (Figure 2a), the isolated clathrate complex showed a $[\mathbf{3}\cdot\mathbf{1a}\cdot(NO_3)_2]^{2-}$ peak at *m*/*z* 2319.8 (Figure

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(10) Complex **3** was prepared by a self-assembly of Pt(2,2′-bpy)$(NO_3)_2$ and tris(4-pyridyl)-1,3,5-triazine. This compound was shown to be stable under acidic and basic conditions. See Supporting Information.

(11) Physical properties of **3**•**1a**: See Supporting Information.

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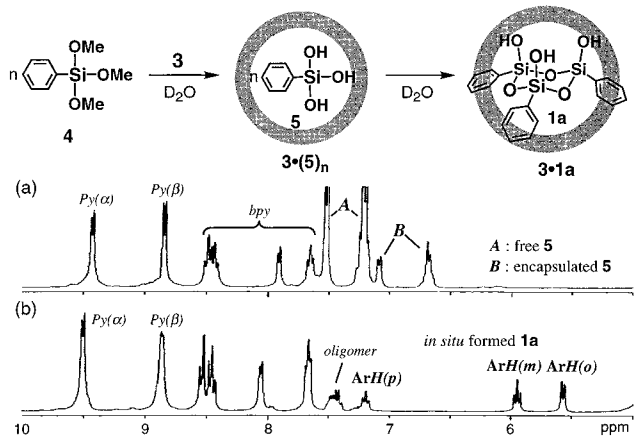

Figure 1. Monitoring of the condensation of **4** to **1a** in nanocage **3** by ^{1}H NMR (300 MHz, D_2O, 25 °C, TMS as an external standard): (a) after 5 min at 100 °C and (b) after 1 h at 100 °C.

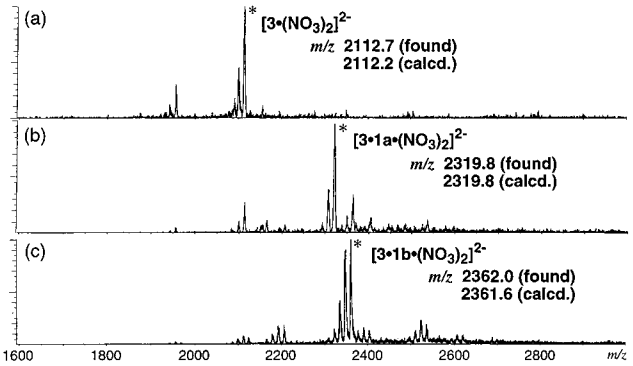

Figure 2. ESI-MS spectrum (negative mode) of an aqueous solution of (a) **3**, (b) **3·1a**, and (c) **3·1b**.

2b): the increase in the mass unit is calculated to be 414.2 corresponding to the molecular weight of **1a**. The signals of **1a** were highly upfield-shifted (Figure 1b) due to the efficient encapsulation in the cavity. The configuration of **3** is determined to be all-cis because phenyl groups, as well as Si atoms, are all equivalent in ^{1}H and ^{29}Si NMR, respectively.

The freedom of cyclic trimer **1** inside the cage was restricted when a bulky aromatic group was attached to the Si atom. Thus, the ^{1}H NMR of **3·1b**, which was derived from xylyltrimethoxysilane in 90% yield,[12] showed C_3 symmetry of the whole as depicted in Figure 3. Namely, the observed ^{1}H NMR spectrum includes one C_3-symmetrized ligand (**A**), three C_2-symmetrized ligands (**B**) and a C_3-symmetrized trimer **1b**. Ligand **A** showed

(12) Preparation of **3·1b**: Xylyltrimethoxysilane (9.75×10^{-2} mmol) was suspended in D_2O solution (1.5 mL) of **3** (9.75×10^{-3} mmol) and the mixture was stirred at 100 °C for 1 h. After the mixture was filtered the solution was purified by crystallization (H_2O) to give **3·1b** as a pale yellow powder in 90% yield. Physical properties of **3·1b**: See Supporting Information.

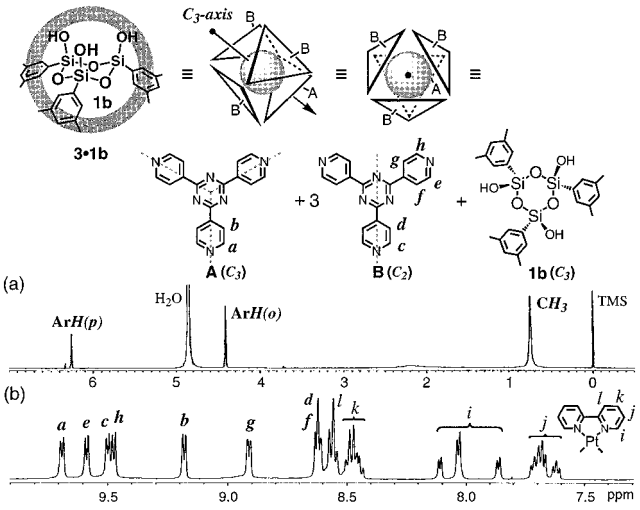

Figure 3. Schematic representation of the C_3-symmetric structure of **3·1b** and the ^{1}H NMR spectrum of **3·1b** (500 MHz, D_2O, 25 °C, TMS as an external standard): (a) guest signals and (b) host signals.

a pair of doublets (H_a and H_b, 6 H integral for each) while ligand **B** displayed three pairs of doublets (H_c and H_d, H_e and H_f, and H_g and H_h; 2 H integral for each). No peaks are coalesced even at 80 °C. The assignments for H_{a-h} were confirmed by COSY and NOESY.[13] The all-cis conformation of **1b** was again confirmed by ^{1}H and ^{29}Si NMR. Signals for CH_3, Ar*H*(*o*), and Ar*H*(*p*) of the xylyl group are highly upfield-shifted due to very tight fitting in the cage.[14]

Polycondensation of trisilanols is known to give cyclic trimer **1** as a kinetic, short-lived product that is rapidly converted to a thermodynamically favored cyclic tetramer and further condensed products.[2] In striking contrast, caged trimer **1** is remarkably stable. Under neutral conditions, complex **3·1b** remains intact even over a period of 1 month in water at room temperature. Surprisingly, the complex is also tolerant under acidic conditions (pH <1), which is essential in the isolation process of the encapsulation complexes.[15]

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Supporting Information Available: Preparation and physical properties of **3**, **3·1a**, **3·1b**, **3′·1a**, and **3′·1b** (**3′** is a Pd(II) analogue of **3**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The NOESY experiment supported the assignment of ligand **B**. Interestingly, H_d and H_f are strongly correlated with CH_3 of **1b**.

(14) We also prepared palladium(II)-linked analogues of **3·1a** and **3·1b**. An optimized structure of **3·1b** (Supporting Information) agrees very well with the proposed C_3-symmetric structure.

(15) The protection of **1b** might be afforded by the pyridine ligands which may trap any protons trying to pass through the portal.