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Catalytic oxidation of diorganosilanes to 1,1,3,3tetraorganodisiloxanes with gold nanoparticle assembly at the water-chloroform interface⁺

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The formation of the spherical self-assembly of gold nanoparticles (AuNPs) of 200 ± 20 nm size at the water-chloroform interface is achieved by employing the cyclotetrasiloxane [RSCH₂CH₂SiMeO]₄ (R = CH₂CH₂OH) as the stabilizing ligand. The interfacially stabilized AuNPs act as a versatile catalyst for selective hydrolytic oxidation of only one of the Si-H bonds in secondary organosilanes, RR¹SiH₂ (R, R¹ = alkyl, aryl, and sila-alkyl), to afford the high yield synthesis of 1,1,3,3-tetraorganodisiloxanes, (HRR¹Si)₂O. The study unravels for the first time the role of the photothermal effect arising from the excitation of the surface plasmon resonance of the AuNPs under visible light irradiation in enhancing the catalytic activity at ambient temperature.

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Introduction

Discrete siloxane frameworks bearing Si-H bonds, also referred to as hydrosiloxanes, represent an important family of molecular synthons, and the practical applications of these compounds as substrates in hydrosilylation, dehydro/dealkylative coupling reactions and thiol-ene click chemistry have been widely recognized to accomplish new silicon-based materials.¹⁻³ The use of 1,1,3,3-tetramethyldisiloxane as a reducing agent is also well established to furnish products with a high degree of regioselectivity and/or stereoselectivity in organic synthesis.⁴ Conventionally, such siloxanes are synthesized by careful hydrolysis of the corresponding haloorganosilanes, HR_2SiX or H_2 RSiX (X = Cl, Br, and F; R = alkyl, aryl).⁵ The method, however, has limited applications in view of the sensitivity of Si-H/Si-O bonds under acidic conditions.⁶ Another impediment in this approach is the limited availability of appropriate organosilicon precursors. As a result, catalytic routes that enable a high degree of selectivity are being explored to expand the library of hydrosiloxanes.

The catalytic method for the oxidation of Si–H bonds in organosilanes using water as an oxidant is a useful approach to construct Si–O bonds. The reaction is of relevance in view of the ready availability of stable organosilane precursors. In addition, the formation of dihydrogen as the only byproduct during the reaction eliminates the need for a cumbersome work-up procedure. While transition metal-based catalysts have been widely investigated,⁷ recent efforts have been devoted to the use of supported AuNPs or unsupported nano-porous gold as reusable heterogeneous catalysts.⁸ However, the method often requires elevated temperatures for the activation of the substrates and leads to complete oxidation to either a mono-, di- or trisilanol depending on the number of Si–H bonds in the organosilane precursor. In a seminal report, Shimada *et al.* showed that the Au(1)PPh₃/PPh₃ system acts as an efficient catalyst for dehydrogenative coupling between an organosilanol and an organosilane to afford di-/trisiloxanes bearing SiH₂ or SiH groups.⁹

It is well established that the liquid–liquid interface offers a useful platform to stabilize the self-assembly of metal nanoparticles with interesting structural attributes and optical properties.¹⁰ Although there exist intriguing possibilities of such NPs to act as a catalyst for the hydrolytic oxidation of organosilanes, there has been no precedence to validate this concept until the publication of recent reports from our group.¹¹ AuNPs were synthesized by employing a triblock copolymer, PiBA₂₀-*b*-PDMS₇₅-*b*-PiBA₂₀ [PiBA = poly(isobornylacrylate), PDMS = poly(dimethylsiloxane)], as the stabilizing matrix. Nevertheless, NPs stabilized at the water–chloroform interface tend to agglomerate and are not robust enough to exhibit reusability in subsequent cycles during the hydrolytic oxidation of primary organosilanes to linear poly(hydrosiloxane)s, {R(H)SiO}_{*n*} (R = alkyl or aryl). There has been ample precedence in the literature



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highlighting the role of small molecules (ligands) such as amines, phosphines, thioethers, *etc.* to achieve a fine balance between stability and surface activity of the NPs during a catalytic event.¹² Taking precedence from our earlier work¹³ and that reported by others,¹⁴ herein, we present the self-assembly of AuNPs at the water-chloroform interface (hereafter referred as **PIC-1**) by employing $[\text{RSCH}_2\text{CH}_2\text{SiMeO}]_4$ (R = CH₂CH₂OH) as the stabilizing ligand.

Notably, the NPs thus formed act as a superior interfacial catalyst for the hydrolytic oxidation of phenylsilane to linear poly(hydrophenylsiloxane), H₂PhSiO[PhHSiO]_nSiPhH₂, in comparison to the polymer-stabilized AuNPs reported earlier^{11a} (for details, see the Experimental section). As part of our ongoing study, the efficacy of PIC-1 as a catalyst has been investigated for the oxidation of diorganosilanes. The method is a simple and viable approach for the high yield synthesis of 1,1,3,3-tetraorganodisiloxanes, $(HRR^{1}Si)_{2}O[R = Me, R^{1} = Ph(1),$ *n*-Hex (2), cyclo-Hex (3), *n*-Octyl (4), $Me_2PhSiCH_2CH_2$ (5), 2-ThMe₂SiCH₂CH₂ (6); $R = R^1 = Ph$ (7)]. A salient outcome emanating from this study is the revelation of the plasmoninduced photothermal effect arising from the excitation of the surface plasmon resonance of the AuNPs under visible light irradiation for the activation of Si-H bonds during the catalytic event. The results are described herein.

Results and discussion

Characterization of the catalyst

Following a modification of our earlier approach,¹¹ the interfacial catalyst **PIC-1** was synthesized by the reduction of $HAuCl_4 \cdot 3H_2O$ with six equivalents of triethylsilane in chloroform using $[RSCH_2CH_2SiMeO]_4$ (R = CH_2CH_2OH) as the molecular scaffold and subsequent addition of deionized water (chloroform : water = 4:1 v/v) into the reaction mixture (for details, see the Experimental section). The adsorption of AuNPs at the interface occurs readily and is accompanied by the formation of non-coalescent water droplets dispersed in chloroform and the visual disappearance of blue color in the organic layer (Fig. S1, ESI†). The NP assembly thus formed showed no signs of clouding and/or precipitation for several weeks under ambient conditions.

The assembly of AuNPs in **PIC-1** was characterized by XPS, HRTEM, FESEM and UV-Vis studies (Fig. S2–S4, ESI†). The results obtained from X-ray photoelectron spectroscopy (XPS) show a doublet for Au $4f_{7/2}$ (84.1 eV) and Au $4f_{5/2}$ (87.7 eV) corresponding to the valence state of Au(0) while the band due to Au(1) at 84.9 eV is absent.¹⁵ The FESEM and HRTEM micrographs reveal the formation of large aggregates of individual NPs featuring quasi-spherical ensembles of 200 ± 20 nm size with no signs of independent existence. We surmise that the self-assembly phenomenon likely arises due to the presence of intermolecular hydrogen bonding interactions between the appended hydroxyl groups¹⁶ as well as a contribution from multidentate thioether ligands¹⁷ on the cyclosiloxane scaffold that act as mediators for NP assembly. The UV-Vis spectrum of the AuNPs deposited on a glass surface shows distinct surface plasmon resonances in the visible (640 nm) and NIR (1120 nm) regions. It is well known that plasmonic coupling in self-assembled metal nanostructures leads to a red-shift in the visible and NIR regions, as observed herein.¹⁸

Synthesis of 1,1,3,3-tetraorganodisiloxanes

As a case study, methylphenylsilane was examined as a model substrate for hydrolytic oxidation of the Si-H bond using PIC-1 as the catalyst. Notably, the liquid-liquid interface stabilized by the AuNPs provides a platform for the catalytic reaction. The reaction was performed with 0.01 mol% Au (with respect to the silane) at 25 °C under ambient conditions and monitored by ¹H NMR spectroscopy. As the reaction progresses, the substrate concentration decreases steadily, as is evident from a decrease in the intensity of the signal at δ 4.34 due to the Si–H proton (Fig. 1). Concomitantly, a new signal at δ 5.1 grows with time, suggesting the formation of product(s) bearing Si-H bonded siloxy group(s). After complete consumption of the substrate, the product in the organic layer was identified by GC-MS analysis (Fig. S5, ESI†). The result reveals the formation of the disiloxane (HMePhSi)₂O, **1**, (retention time $(t_R) = 15.08$ min and m/z = 258) along with minor amounts (3-4%) of MePhSi- $(OSiMePhH)_2$ ($t_R = 26.9 \text{ min}, m/z = 394$). The ²⁹Si{¹H} NMR spectrum shows distinct signals at δ -11.5, -13.3 (major) and -30.2 (minor), which were assigned to HMePhSiO and MePhSiO₂ units, respectively. In the IR spectrum, characteristic absorptions for Si-O and Si-H groups appear at 1060 and 2131 cm⁻¹, respectively. Based on these results, it is inferred that the reaction proceeds selectively with the formation of [HMePhSiOH] as the intermediate, which subsequently undergoes condensation to yield (HMePhSi)₂O, 1. Further oxidation of the siloxy group containing the Si-H bond is extremely slow to yield the trisiloxane as the minor product. No perceptible change in the product composition was observed when the



Fig. 1 ¹H NMR monitoring of hydrolytic oxidation of methylphenylsilane.

reaction was performed at 80 $^\circ$ C. Compound **1** was obtained in pure form from the reaction mixture by fractional distillation.

The reaction can be represented as follows:



A plausible mechanistic pathway was assumed to be similar to that reported earlier for the hydrolytic oxidation of triorganosilanes to the corresponding silanols using heterogeneous Au catalysts. It has been suggested that the reaction proceeds with the activation of the Si-H bond on the NP surface to generate Au-Si and Au-H bonds.^{8b} The silvl metal hydride intermediate reacts with nucleophilic water to produce organosilanol and dihvdrogen. Since the existence of [HMePhSiOH] in the present case is not detected in the ¹H NMR and GC-MS spectra during the reaction, it is inferred that the formation of the silanol and its condensation product (1) occurs concomitantly on the surface of the nanoparticles. We surmise that the resulting product desorbs from the NP surface into the organic medium and further oxidation is not favoured, thus allowing selectivity to be achieved during the catalytic event. We attempted to isolate MePh₂SiOH in solution by the hydrolytic oxidation reaction of MePh₂SiH under similar conditions. However, monitoring the reaction using GC-MS did not reveal the identity of the silanol, and 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane (MePh₂Si)₂O (8) was isolated in quantitative vield.

The kinetic plots of $\ln[M_o]/[M]$, where [M] represents the concentration of the organosilane, at time (*t*) *vs.* time for the reaction of MePhSiH₂ at 25 and 80 °C are linear (Fig. S6, ESI†) and consistent with the first order rate law with respect to the concentration of the silane. The observed rate constants are $k_{25} = 1.8 (0.13) \times 10^{-2} (R^2 = 0.98)$ and $k_{80} = 4.8(0.43) \times 10^{-1} \text{ min}^{-1} (R^2 = 0.96)$, where values in parentheses represent standard deviation, suggesting a significant enhancement in the rate at elevated temperature.

The stability of the AuNP assembly in PIC-1 up to the fourth cycle of the reaction for methylphenylsilane at 80 °C was examined. Interestingly, the TOF values after the first and fourth cycle (43 680, 39 200 h^{-1}) of the reaction were comparable, suggesting no appreciable degradation of the catalytic activity. Moreover, the HRTEM micrograph of the catalyst after the fourth cycle (Fig. S7, ESI[†]) reveals large ensembles of the NPs similar to those observed in the primitive PIC-1, suggesting the interfacial stability of the NPs during the catalytic event. To validate the scope of PIC-1 as a "true" interfacial catalyst, a controlled experiment was performed wherein the organic layer was separated and used for the hydrolytic oxidation of methylphenylsilane in the presence of water as the oxidant. An examination of the reaction mixture by ¹H NMR spectroscopy revealed that the concentration of the substrate remains practically unchanged even after 24 h. The results are quite significant since the size of the catalytic metal NPs under homogeneous/heterogeneous conditions is prone to changing as a result of Ostwald ripening or digestive ripening processes, affecting the efficacy of the catalysts.¹⁹

Substrate scope

With the optimal conditions in hand, the scope of the PIC-1 catalyst towards the hydrolytic oxidation of other diorganosilanes was examined (Table 1). In each case, the corresponding 1,1,3,3-tetraorganodisiloxanes, (HRR¹Si)₂O, (2-7) were obtained in excellent yields irrespective of the nature of the alkyl/aryl substituents on the silicon atom. However, a marked variation in the TOF values for the substrates, $Me(R^1)SiH_2$, $(R^1 = n-Hex,$ n-Oct) with very similar alkyl chain lengths deserved a detailed inspection. Therefore, we performed parallel experiments on the hydrolytic oxidation of Me(n-Hex)SiH₂ under similar conditions using three PIC-1 catalysts that were prepared in separate batches. In each case, a complete conversion of the organosilane to 2 was observed in nearly 30 minutes and was comparable with the TOF value given in Table 1. The reaction when performed with the aged (7 days) sample of PIC-1 was completed in the same time scale. Based on these results, it is evident that subtle changes in size and consequently in the surface to volume ratio of the AuNPs obtained from different batches of PIC-1 do not influence the activity of the catalyst. While the plausible mechanism of the observed activity is not yet clearly understood, we surmise that the catalytic event is governed by other factors such as the number of exposed surface atoms on the NP ensembles, which function as the active sites, as well as the relative diffusion of the reactive species on the NP surface.²⁰

All the compounds obtained herein except 7 are distillable liquids and the relevant spectroscopic data along with the isolable yield of the products are summarized in the experimental section. A representative GC-MS profile of **2** is shown in Fig. S8 (ESI†). The molecular structure obtained at 298 K as well as selected bond lengths and bond angles of 7 [Si1A–O1 = 1.615(4), Si1B–O1 = 1.604(5) Å, Si1A–O1–Si1B = 162.2(4)°] (for details, see the ESI†) was found to be comparable with those reported earlier.²¹ Interestingly, compound 7 is known to exhibit static or dynamic disorder at the oxygen atom and undergoes a phase transition from monoclinic ($P2_1/n$) at 298 K to triclinic symmetry at 200 K.

 Table 1
 Synthesis of 1,1,3,3-tetraorganodisiloxanes, (HRR¹Si)₂O, (1–7)

Compound	(HRR ¹ Si) ₂ O			
	R	R ¹	Yield (%)	TOF (h^{-1})
1	Ме	Ph	96 (4)	43 680
2	Me	<i>n</i> -Hex	87 (13)	20410
3	Me	<i>cyclo</i> -Hex	88 (12)	10 690
4	Me	<i>n</i> -Octyl	96 (4)	9800
5	Me	Me ₂ PhSiCH ₂ CH ₂	>99	890
6	Me	2-ThMe ₂ SiCH ₂ CH ₂	>99	816
7	Ph	Ph	>99	4900

Conditions: 0.01 mol% Au; 80 $^{\circ}$ C; ambient light source. Yield based on GC-MS data. Values in parentheses represent the yield of RR¹Si(OSiRR¹H)₂.



Fig. 2 Substrate conversion (%) vs. time for the hydrolytic oxidation of $MePhSiH_2$ under different conditions.

Enhancement of the catalytic activity of PIC-1 by the photothermal effect

An underlying mechanism of plasmon-mediated catalysis involves the conversion of solar energy into heat energy (photothermal effect) through plasmon-phonon coupling and harnessing this energy to activate the substrate(s) during the catalytic event.²² The method offers a promising alternative to chemical transformations, which are conventionally performed by thermal heating. Herein, we performed preliminary studies to validate for the first time the role of the photothermal effect arising from plasmonic AuNPs in PIC-1 in the hydrolytic oxidation reaction of methylphenylsilane. In addition to the reaction conditions (25 and 80 °C, sunlight) described in the preceding section, separate experiments were performed to evaluate this phenomenon. Surprisingly, the reaction when performed in the dark at 25 °C did not proceed and the substrate was recovered unchanged after 24 h. The reaction, however, proceeds smoothly upon irradiation with an LED source (Thorlabs LED680L) with a maximum wavelength (λ_{max}) of 680 nm corresponding to the position of the plasmonic band of the AuNPs. A plot of percentage conversion of the substrate as a function of time (Fig. 2) reveals that the reaction profile closely resembles that observed for the analogous reaction performed by irradiation with sunlight and the turnover frequency values (TOFs) are on the order of 4266 and 3840 h^{-1} , respectively. We also performed a separate experiment at 80 $^\circ\mathrm{C}$ without exposing the reaction mixture to light irradiation. As is evident from Fig. 2, complete consumption of the substrate was observed in a time scale similar to that observed under illumination at 25 °C. These results provide a basis to infer that the plasmon-mediated photothermal effect likely contributes to activating the Si-H bond during the catalytic event. Further studies are in progress to understand this phenomenon in detail.

Conclusions

In summary, we have developed a simple approach to construct a AuNP-based interfacial catalyst, **PIC-1**, in a water–chloroform biphasic medium. The catalyst exhibits high activity and selectivity for the hydrolytic oxidation of diorganosilanes to afford the formation of 1,1,3,3-tetraorganodisiloxanes, $(HRR^1Si)_2O$, in excellent yields. The present study also provides a manifestation of the photothermal effect arising from plasmonic AuNPs at the water-chloroform interface.

Experimental

Materials and methods

Solvents were freshly distilled over sodium wire/benzophenone (diethyl ether) and phosphorous pentoxide (acetonitrile) under an inert atmosphere. Chloroform (Fischer, HPLC grade) was used as received. Glassware was dried in an oven at 110-120 °C and further flame-dried under vacuum prior to use. 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, lithium aluminium hydride, diphenylsilane, methyldiphenylsilane, phenylsilane and azobisisobutyronitrile (AIBN) were purchased from Sigma Aldrich and used as procured. ¹H and ²⁹Si{¹H} NMR spectra were recorded in CDCl3 on a Bruker AVANCE II 400 MHz NMR spectrometer and the chemical shifts are quoted relative to Me₄Si. IR spectra were recorded on a Nicolet Protege 460 ESP spectrophotometer using KBr optics. Electrospray ionization (ESI) mass spectra were recorded on a micrOTOF-Q II 10262 mass spectrometer in positive ion mode using an internal standard. X-ray photoelectron spectroscopy (XPS) studies were carried out using a modified SPECS system equipped with a Mg Ka source (1253.6 eV, 100 W) and the pass energy of the analyzer was fixed to 40 eV. The samples were prepared by spin coating of the solution over a mica surface. The measured XPS spectra were fitted using Fityk. GC-MS was performed using an Agilent Technologies 240 Ion Trap GC/MS: VF-5MS Column in toluene. Temperature was programmed from 80 to 280 $^{\circ}$ C (with a flow rate of 8 $^{\circ}$ C min⁻¹ for the temperature range 80-220 °C and 15 °C min⁻¹ for the temperature range 220-280 °C). The UV-Vis spectra of the samples were obtained using a Perkin Elmer UV/Vis/NIR Lambda 1050 spectrophotometer. High resolution transmission electron microscopy (HRTEM) studies were carried out using a carbon coated copper grid on a Philips CM 20 electron microscope operating at 100 kV. Field emission scanning electron microscopy (FESEM) was performed using a glass slide on an FEI Quanta 200 FESEM. The molecular weight (M_w) and polydispersity index (PDI) of the polymer, H₂PhSiO[PhHSiO]_nSiPhH₂, were estimated using Waters gel permeation chromatography (GPC) equipped with an L-2414 refractive index detector and Waters styragel HR3 and HR4 columns in series using THF as an eluent (flow rate: 1 mL min $^{-1}$; polystyrene standards).

Crystallographic study

The intensity data of 7 were collected at 300 K using a Bruker APEX III CCD diffractometer, using graphite monochromated Mo-K α radiation (λ = 0.71069 Å). Cell parameter analysis and data reduction were performed using Bruker SAINT. Lorentz and polarization effects and empirical absorption corrections

were applied using SADABS from Bruker. The structure was solved by a direct method, using SIR-92 and refined by a full-matrix least square refinement method²³ based on F^2 , using SHELX-2014/7.

Synthetic methods

By following the procedure reported earlier,²⁴ the diorganosilanes $MeR^{1}SiH_{2}$ ($R^{1} = Ph$, *n*-Hex, *cyclo*-Hex *n*-Octyl, PhMe₂SiCH₂CH₂, 2-ThMe₂SiCH₂CH₂) were synthesized by the reduction of the corresponding dichlorodiorganosilanes with lithium aluminium hydride in diethyl ether.

Synthesis of [RSCH₂CH₂SiMeO]₄; R = CH₂CH₂OH

The reaction between 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane [CH=CH₂SiMeO]₄ (0.99 g, 1.0 mL, 2.8 mmol) and 2-mercaptoethanol (0.97 g, 0.88 mL, 12.5 mmol) was performed in acetonitrile using 2,2'-azobisisobutyronitrile (AIBN, 10 wt%) as a free radical catalyst. The mixture was heated at 70 °C for nearly 18 h. The oily liquid thus obtained was immiscible in acetonitrile. Repeated washing of the oil with the solvent yields the desired cyclosiloxane in pure form (yield: 85%).

ESI-MS (+ve mode, *m*/*z*): 679.1227 (obs.)/679.1201 (calcd) [M + Na]⁺. ¹H NMR (CDCl₃): δ 3.63 (m, 2H, CH₂OH), 2.65–2.55 (t, 2H, SCH₂CH₂OH), 2.5–2.4 (m, 2H, SCH₂), 0.85 (t, 2H SiCH₂), 0.05 (m, 3H, SiCH₃). ¹³C {¹H} NMR (CDCl₃): δ 60.9 (CH₂OH), 35.3, 26.7 (SCH₂), 18.3 (SiCH₂), 0.00, -0.08 (SiCH₃). ²⁹Si {¹H} NMR (CDCl₃): δ -21.8 (SiO). IR (KBr, cm⁻¹): 3338 (ν OH), 1070 (ν SiO), 1261 (ν SiMe).

Synthesis of interfacial catalyst (PIC-1)

Triethylsilane (10 μ L, 0.06 mmol) was added to a sonicated solution of HAuCl₄·3H₂O (4.0 mg, 0.01 mmol) and [RSCH₂CH₂SiMeO]₄; R = CH₂CH₂OH (6.8 mg, 0.01 mmol) in chloroform (HPLC, 25 mL). A gradual colour change of the solution from yellow to blue within 4–6 h ensures the formation of AuNPs. The solution was left for equilibration for 24 h at room temperature and ultracentrifuged. The precipitated NPs were dissolved in chloroform and used for analysis. The solution of NPs (4.0 mL) was taken separately and mixed with 1.0 mL of deionized water with constant stirring. The confinement of the AuNPs at the water-chloroform interface was observed by the formation of non-coalescent water droplets in chloroform. The self-assembly was denoted as **PIC-1** and used for subsequent studies.

Synthesis of poly(phenylhydrosiloxane), H₂PhSiO[PhHSiO]_nSiPhH₂

In a typical procedure, the hydrolytic oxidation of primary organosilane, $PhSiH_3$ (2.0 mL, 0.02 mmol), was performed in the presence of Au-stabilized **PIC-1** under aerobic conditions at 80 °C. After complete consumption of the monomer, the organic layer was separated and dried over sodium sulphate. The solvent was evaporated under vacuum and poly(phenylhydrosiloxane) was isolated as a viscous oil.

¹H NMR (CDCl₃): δ 7.24 (br, 5H, SiPh), 5.14 (br, 1H, SiH). ²⁹Si{¹H} NMR (CDCl₃): δ 27.0 [H₂PhSiO], δ 44 to 47 (HPhSiO). IR (KBr, cm⁻¹): 3070, 3052 (ν CH, aromatic), 2173 (ν SiH), 1429 (δ CH), 1085 (ν SiO). $M_{\rm w}$ = 2.2 × 10³, PDI = 1.3.

Synthesis of 1,1,3,3-tetraorganodisiloxanes 1-7

In a typical procedure, hydrolytic oxidation of methylphenylsilane (2.0 mL, 16.39 mmol) was performed in the presence of the **PIC-1** catalyst under aerobic conditions. After complete consumption of the substrate, the organic layer was separated and dried over sodium sulphate. The solvent was stripped off to obtain the desired product, **1**. A similar procedure was followed for the synthesis of related **1**,**1**,**3**,**3**-tetraorganodisiloxanes, (HRR¹Si)₂O, **2–7** by using an appropriate diorganosilane precursor.

(HMePhSi)₂O, 1. B.p. 148 °C/2 mmHg, yield = 95%. ¹H NMR (CDCl₃): δ 7.56, 7.35 (m, 5H, *Ph*), 5.13 (s, 1H, Si*H*), 0.39 (s, 3H, *Me*). ²⁹Si{¹H} NMR (CDCl₃): δ -11.5, -13.3 (*Si*O). IR (KBr, cm⁻¹): 3069 (ν CH, aromatic), 2960, 2902 (ν CH, aliphatic), 2131 (ν SiH), 1255 (ν SiMe), 1061 (ν SiO). GC-MS: *m*/*z* = 258, retention time ($t_{\rm R}$) = 15.0 min.

{**HMe**(*n*-Hex)Si}₂O, 2. B.p. 121 °C/2 mmHg, yield = 85%. ¹H NMR (CDCl₃): δ 4.44 (br, 1H, Si*H*), 1.17 (br, 8H, *Hex*), 0.73 (m, 3H, C-*Me*), 0.47 (br, 2H, SiC*H*₂), 0.07 (br, 3H, Si*Me*). ²⁹Si{¹H} NMR (CDCl₃): δ -3.0, -5.3 (*Si*O). IR (KBr, cm⁻¹): 2959, 2923 (ν CH, aliphatic), 2119 (ν SiH), 1257 (ν SiMe), 1056 (ν SiO). GC-MS: *m*/*z* = 274, retention time (t_R) = 12.1 min.

{**HMe**(*cyclo*-**Hex**)**Si**}₂**O**, **3**. B.p. 142 °C/2 mmHg, yield = 86%. ¹H NMR (CDCl₃): δ 4.35 (br, 1H, SiH), 1.6–1.14 (br, 10H, *cyclo-Hex*), 0.61 (br, ¹H, C–C*H*), 0.06 (br, 3H, Si*Me*). ²⁹Si{¹H} NMR (CDCl₃): δ –1.7, –3.1 (*Si*O). IR (KBr, cm⁻¹): 2917, 2846 (ν CH, aliphatic), 2109 (ν SiH), 1250 (ν SiMe), 1058 (ν SiO). GC-MS: m/z = 270, retention time (t_R) = 15.3 min.

{**HMe**(*n*-**Octyl**)**Si**}₂**O**, **4**. B.p. 138 °C/2 mmHg, yield = 95%. ¹H NMR (CDCl₃): δ 4.44 (br, 1H, Si*H*), 1.11 (br, 12H, *n*-Oct), 0.74 (br, 3H, C-CH₃), 0.47 (br, 2H, SiCH₂), 0.04 (br, 3H, Si*Me*). ²⁹Si{¹H} NMR (CDCl₃): δ -3.0, -5.3 (SiO). IR (KBr, cm⁻¹): 2957, 2921 (ν CH, aliphatic), 2117 (ν SiH), 1252 (ν SiMe), 1056 (ν SiO). GC-MS: *m*/*z* = 330, retention time (t_R) = 20.39 min.

{**HMe(Me₂PhSiCH₂CH₂)Si**}₂**O**, 5. B.p. 210 °C/2 mmHg, yield = 96%. ¹H NMR (CDCl₃): δ 7.52, 7.37 (s, 5H, *Ph*), 4.64, 4.55 (br, 1H, Si*H*), 0.67, 0.57 (br, 4H, CH₂), 0.28 (s, 6H, *Me*₂PhSi), 0.15 (s, 3H, Si*Me*). ²⁹Si{¹H} NMR (CDCl₃): δ -1.7 (Me₂PhSi), -3.9 (*Si*O). IR (KBr, cm⁻¹): 3061, 3012 (ν CH, aromatic), 2956, 2905 (ν CH, aliphatic), 2115 (ν SiH), 1051 (ν SiO). GC-MS: *m*/*z* = 430, retention time (t_R) = 30.3 min.

{**HMe(2-ThMe₂SiCH₂CH₂)Si}₂O, 6.** B.p. 198 °C/2 mmHg, yield = 95%. ¹H NMR (CDCl₃): δ 7.46 (d, 1H, Th *H*-3), 7.11 (d, 1H, Th *H*-5), 7.06 (dd, 1H, Th *H*-4), 4.41 (br, 1H, Si*H*), 0.44, 0.58 (br, 4H, C*H*₂), 0.21 (s, 6H, 2-Th*Me*₂Si), 0.08 (s, 3H, Si*Me*). ²⁹Si{¹H} NMR (CDCl₃): δ -1.7 (2-ThMe₂Si), -3.5 (SiO). IR (KBr, cm⁻¹): 3074, 3017 (ν CH, aromatic), 2956, 2879 (ν CH, aliphatic), 2114 (ν SiH), 1250 (ν SiMe), 1049 (ν SiO). GC-MS: m/z = 442, retention time (t_R) = 30.1 min.

(HPh₂Si)₂O, 7. M.p. 48–49 °C, yield = 98%. ¹H NMR (CDCl₃): δ 7.63, 7.31, (m, 10H, *Ph*), 5.53 (s, 1H, Si*H*). ²⁹Si{¹H} NMR (CDCl₃): δ –19.8 (*SiO*). IR (KBr, cm⁻¹): 3062, 3011 (ν CH, aromatic), 2135 (ν SiH), 1067 (ν SiO). GC-MS: *m*/*z* = 382, retention time (t_R) = 31.5 min.

(MePh₂Si)₂O, 8. Compound 8 was isolated as a colorless liquid from the hydrolytic oxidation of MePh₂SiH by following a procedure described above.

B.p. 157 °C/2 mmHg, yield = 97%. ¹H NMR (CDCl₃): δ 7.52, 7.27 (m, 10H, *Ph*), 0.56 (s, 3H, *Me*). ²⁹Si{¹H} NMR (CDCl₃): δ –9.8 (*SiO*). IR (KBr, cm⁻¹): 3063 (ν CH, aromatic), 2959, 2900 (ν CH, aliphatic), 1426 (δ CH), 1059 cm⁻¹ (ν SiO). GC-MS: *m*/*z* = 410, retention time ($t_{\rm R}$) = 31.7 min.

Conflicts of interest

There are no conflicts to declare.

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