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Cesium Carbonate-Catalyzed Oxidation of Substituted Phenylsilanes for the Efficient Synthesis of Polyhedral Oligomeric Silsesquioxanes

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Supporting Information

ABSTRACT: Cesium carbonate-catalyzed oxidation of substituted phenylsilanes (ArSiH₃) in $N_{1}N_{2}$ -dimethylformamide (DMF) at room temperature for the efficient synthesis of polyhedral oligomeric silsesquioxanes (POSS) was described. This protocol allowed the rapid and selective access to several types of new POSS cages in modest to good yields under nonaqueous conditions. Depending on the bulkiness of the substituents on the phenyl rings, hexa- (T_6) , octa- (T_8) , and dodecaphenylsilsesquioxanes (T_{12}) can be selectively obtained. With the more bulky 2-(2',4',6'-trimethylphenyl)phenyl group, the cyclic tetrasiloxane (D_4) bearing four hydroxyl groups was isolated. Mechanism studies disclosed that the initial step involved the



Cs₂CO₃-catalyzed hydrosilylation of DMF with a hydrosilane to generate a siloxymethylamine intermediate followed by the dehydrocarbonative cross-coupling of the hydrosilane with the siloxymethylamine.

INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) of the general formula $(RSiO_{1,5})_n$ (n = 6, 8, 10, 12) (Chart 1) have attracted widespread interesting due to their rigid well-defined structure, unique molecular symmetry, and potential to offer high degrees of functionalization.¹ They have been one of the most promising nanoscopic organic-inorganic hybrid materials in a wide range of research fields including catalysts, nanocomposites,³ and biomaterials⁴ and continue to receive considerable attention in the preparation of novel functional materials.⁵

The most common synthetic method to produce POSS is the hydrolytic condensation of trifunctional silicon monomers $RSiX_3$ (X = Cl, OR', OH etc) using acid or base catalysis (Scheme 1).^{1,6} The cube-like T_8 cage was in general found as a major product owing to the high-degree of symmetry in the T₈ cube (octahedral symmetry, $O_{\rm h}$). However, this synthetic strategy may also yield other symmetric silsesquioxanes of T_n (n = 6, 10, 12 etc) cages, incompletely condensed silsesquioxane species,⁸ and polymeric siloxane byproducts.⁹ The isolation and purification of each pure form of the silsesquioxanes are further complicated by the coexistence of multiple isomers. In addition, these reactions often take days to months to reach completion and suffer from poor yield (<50%). On the other hand, many variables such as pH values, temperature, monomer type and the concentration of a monomer are known to mutually influence the hydrolytic condensation and any change in them may make a great difference to the constituents of the final products.^{1b,6b} Owing to the inherent disadvantages of the reaction, there is no straightforward route to obtain POSS with high efficiency and

selectivity. In recent years, some methods have been developed to improve yields and selectivity.¹⁰ Pietschnig et al. reported the synthesis of bulky alkyl-substituted POSS cages by the condensation reaction of silanetriols in the presence of trifluoroacetic acid.^{10b} Catalytic rearrangement of a mixture of silsesquioxanes for the preparation of a POSS has been reported by Koželj et al., but the rearrangements are characterized by high temperatures and the selectivity is not satisfactory in many cases.^{foc} Hwang et al. reported on a high yield synthesis of dodecaphenylsilsesquioxane (T₁₂-phenyl), but the reaction takes a long time (14 days) and the substrate suitability is very limited.¹⁰

Phenylsilsesquioxanes, known for their easily modified functionality¹¹ and superior thermal stability,¹² have been the focus of attention since Barry's earliest studies on the synthesis of $(PhSiO_{1,5})_n$ in 1955.¹³ Substituted phenylsilsesquioxanes are of great interest because of the availability of the substituents for the further functionalization and modification of their properties. However, they have been much less studied probably because of the limitations of traditional synthetic methods such as sensitivity to the steric and electronic effects of the substituents. In addition, multiple isomeric products may be generated during the preparation, and the different isomers could only be isolated in low yields.^{7b} Therefore, efficient methodologies for the selective formation of single substituted phenylsilsesquioxane products are highly desirable.

In recent years, catalytic oxidation of hydrosilanes has become a promising approach to produce siloxanes. There has

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Scheme 1. Traditional Hydrolytic Condensation vs Catalytic Oxidation

Previous work:		This work:		
$RSiX_3 \xrightarrow[H_2O]{\text{acid / base}} T_nR_n$	VS.	$RSiH_3 \xrightarrow{Cs_2CO_3} T_nR_n$		
X = -CI, -OR', -OH etc		R = Substituted Phenyl		

been extensive research on the oxidation of hydrosilanes with oxygen or water as oxidants catalyzed by transition metal-based catalysts.¹⁴ In particular, *N*,*N*-dimethylformamide (DMF) as a mild oxidant has also been employed for the catalytic oxidation of tertiary silanes (R_3SiH) with Mo and Pt-based catalysts.¹⁵ However, most of these investigations have been focused on the oxidation of tertiary silanes (R_3SiH)^{14b} and secondary silanes (R_2SiH_2).^{14e,16} The oxidation of primary silanes ($RSiH_3$) has been virtually unexplored probably due to the complexity of the reaction along with complex products. Therefore, efficient catalysts for the oxidation of primary silanes to yield a single product selectively are greatly favorable.

Cesium carbonate (Cs_2CO_3) has been extensively used as a base in organic synthesis owing to its good stability, ease of handling, commercial availability, and high solubility in organic solvents.¹⁷ We have shown that Cs_2CO_3 could efficiently catalyze the reduction of tertiary amides, aldehydes, and ketones with silanes.¹⁸ In the course of our investigations, we found that some siloxane byproducts can also be isolated.^{18b} Herein, we report on the Cs_2CO_3 -catalyzed oxidation of substituted phenylsilanes with DMF to produce a POSS selectively at room temperature with only 1.0% molar loading of the catalyst. Compared with the traditional hydrolytic condensation method, this protocol represents the most efficient, rapid, and general process, leading to the synthesis of a series of new phenyl-substituted POSS in modest to high yields.

EXPERIMENTAL SECTION

General Considerations. DMF was purchased from Sigma-Aldrich, dried over $CaH_{2^{j}}$ and distilled prior to use. PhSiH₃ and Cs_2CO_3 were purchased from Alpha and used without additional purification. The other hydrosilanes were prepared via modified procedures.¹⁹ The ¹H, ¹³C, and ²⁹Si NMR spectroscopic data were recorded on a Bruker Mercury Plus 400 NMR spectrometer. The chemical shifts are referenced against external Me₄Si (¹H, ¹³C, ²⁹Si). The mass spectrometric data were obtained with a Varian 7.0T FTMS. Fourier transform infrared (FT-IR) spectra were recorded with a Bruker TENSOR II infrared spectrophotometer using KBr discs. The thermogravimetric analysis (TGA) measurement was performed with a Netzsch STA449F3 thermogravimetric analyzer over the temperature range 20–800 °C in air. GC-MS data were obtained with a Thermo Scientific TRACE 1300 & ISQ QD system, equipped with a TG-5MS column.

Synthesis of 4-Bromo-2,6-dimethylphenylsilane. 5-Bromo-2iodo-1,3-dimethylbenzene (5.97 g, 19.2 mmol) was dissolved in 100 mL of n-hexane. To the stirred solution was added n-BuLi (8 mL, 2.4 M in hexane, 19.2 mmol) at room temperature.^{19c} The reaction mixture was stirred for 5 h. After cooling to -78 °C, Si(OMe)₄ (3.21 g, 21.2 mmol) was added. The reaction was allowed to warm up to room temperature over 10 h. The resulting mixture was filtered and the filtrate was concentrated in vacuo. The filtrate was added to a solution of LiAlH₄ (821 mg, 21.6 mmoL, 100 mL Et_2O) at -78 °C. The reaction was allowed to warm up to room temperature over 10 h and was then quenched with methanol (10 mL) and water (50 mL) followed by the extraction of the aqueous layer with *n*-hexane (2×60) mL). The combined organic layers were dried over Na₂SO₄. It was filtered, and the filtrate was evaporated to dryness. Purification by distillation afforded 4-bromo-2,6-dimethylphenylsilane as a colorless liquid (2.8 g, 68%). ¹H NMR (400 MHz, CDCl₃): δ 7.04 (s, 2H, Ar-H), 4.00 (s, 3H, -SiH₃), 2.27 (s, 6H, -CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 146.8, 130.0, 126.1, 124.7, 23.5. ²⁹Si NMR (79 MHz, $CDCl_{2}$): δ -75.9.

Synthesis of 2-(2',4',6'-trimethylphenyl)phenylsilane. 1-Iodo-2-(2',4',6'-trimethylphenyl)benzene (11.2 g, 34.7 mmol)^{19a} was dissolved in 50 mL of Et₂O. To the stirred solution was added n-BuLi (16 mL, 2.4 M in hexane, 38.4 mmol) at -78 °C. The reaction mixture was stirred for 2 h and then added to HSiCl₃(6.8 mL, 69.4 mmol) at -78 °C. The reaction was allowed to warm up to room temperature over 10 h. The resulting mixture was filtered and the filtrate was concentrated in vacuo. The filtrate was added dropwise to a solution of LiAlH₄ (988 mg, 26.03 mmol, 100 mL Et₂O) at -78 °C. The reaction was allowed to warm up to room temperature over 10 h and was then quenched with methanol (10 mL) and water (50 mL) followed by the extraction of the aqueous layer with *n*-hexane (2×60) mL). The combined organic layers were dried over Na₂SO₄. It was filtered, and the filtrate was evaporated to dryness. Purification by distillation afforded 2-(2',4',6'-trimethylphenyl)phenylsilane as a colorless solid (7.9 g, 50%). ¹H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H, Ar-H), 7.65 (s, 1H, Ar-H), 7.51 (s, 1H, Ar-H), 7.32 (s, 1H, Ar-H), 7.15 (s, 2H, Ar-H), 4.01 (s, 3H, -SiH₃), 2.54 (s, 3H, -CH₃), 2.14 (s, 6H, -CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 149.0, 139.2, 137.6, 137.2, 135.9, 131.0, 128.9, 128.4, 128.3, 126.6, 21.4, 20.7. ²⁹Si NMR (79 MHz, CDCl₃): δ -61.7.

General Procedure for Catalytic Oxidation of Primary Phenylsilanes in DMF. In a glovebox, Cs_2CO_3 (1.0% mol, 16 mg, 0.05 mmol), 4 mL of DMF and a phenylsilane (5.0 mmol) were added into a 10 mL Schlenk tube. The tube was removed from the glovebox and then connected with a balloon to avoid pungent trimethylamine gas from leakage. The reaction mixture was stirred for 24 h at room temperature. After the reaction was complete, the volume of the solvent was concentrated to about 1.0 mL. It was filtered and the remaining crude product was washed several times with methanol to give analytically pure product (the crude product of T_8 -1 was washed with toluene).

Synthesis of $(PhSiO_{1,5})_8$ $(T_8^{-1}).^{20}$ Using 541 mg of PhSiH₃, T₈-1 was isolated (251 mg, 39%) as a white powder. ¹H NMR (400 MHz, CDCl₃): δ 7.79–7.72 (d, 2H, Ar-H), 7.45 (t, J = 7.4 Hz, 1H, Ar-H), 7.36 (t, J = 7.3 Hz, 2H, Ar-H).

Synthesis of $(2,4-Me_2C_6H_3SiO_{1.5})_8$ (T_8 -2). Using 681 mg of 2,4dimethylphenylsilane, T_8 -2 was isolated (613 mg, 78%) as a white

Table 1. Crystallographic Data for T₈-2, T₈-4, T₁₂-1, and D₄-1

	T ₈ -2	T ₈ -4	T ₁₂ -1	D ₄ -1
Formula	$C_{64}H_{72}O_{12}Si_8$	C64H64Br8O12Si8	C ₉₆ H ₁₀₈ O ₁₈ Si ₁₂	C68H80O10Si4
Fw	1257.93	1889.15	1886.90	1169.68
T/K	113	113	113	113
Space group	Pcab	Pbca	P1	P-421c
a/Å	15.307(3)	24.9229(7)	18.0221(5)	13.3014(2)
b/Å	24.534(4)	23.5176(5)	18.5288(4)	13.3014(2)
c/Å	37.280(6)	28.8663(7)	19.1226(4)	18.0425(5)
lpha/deg	90.00	90.00	96.9593(19)	90.00
β /deg	90.00	90.00	105.188(2)	90.00
γ/deg	90.00	90.00	105.211(2)	90.00
$V/Å^3$	14000(4)	16919.3(7)	5821.7(3)	3192.21(13)
Ζ	8	8	2	2
$d_{\rm calc} {\rm g/cm^3}$	1.194	1.483	1.076	1.217
F(000)	5312.0	7488.0	1992.0	1248.0
GOF	1.026	1.009	1.017	1.051
R1 (I > 2σ (I))	0.0575, 0.1156	0.0546, 0.1218	0.0435, 0.1127	0.0595, 0.1647
wR2 (all data)	0.1135, 0.1397	0.0783, 0.1342	0.0541, 0.1195	0.0680, 0.1717
CCDC number	1818769	1818770	1818779	1818781

powder. ¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 7.3 Hz, 1H, Ar-H), 7.19–6.92 (m, 2H, Ar-H), 2.53 (s, *J* = 17.4 Hz, 3H, o-CH₃), 2.39 (s, 3H, p-CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 144.2, 140.8, 135.6, 130.8, 126.4, 125.6, 22.6, 21.5. ²⁹Si NMR (79 MHz, CDCl₃): δ -77.7. HRMS (MALDI): calcd for [C₆₄H₇₂NaO₁₂Si₈]⁺[M + Na]⁺, *m/z* 1279.3075; found, *m/z* 1280.3101. TGA (in air): mass loss of 5 wt % at 411 °C; total mass loss: 64%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2800, 1606, 1445, 1095 (Si–O–Si), 682.

Synthesis of $(2,5-Me_2C_6H_3SiO_{1.5})_8$ (T_8 -3). Using 681 mg of 2,5-dimethylphenylsilane, T_8 -3 was isolated (555 mg, 70%) as a white powder.¹H NMR (400 MHz, CDCl₃): δ 7.64 (s, 1H, Ar-H), 7.20 (d, J = 7.5 Hz, 1H, Ar-H), 7.15 (d, J = 7.6 Hz, 1H, Ar-H), 2.53 (s, 3H, m-CH₃), 2.29 (s, 3H, o-CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 140.9, 136.3, 133.9, 131.6, 129.8, 129.4, 22.2, 20.9. ²⁹Si NMR (79 MHz, CDCl₃): δ -77.8. HRMS (MALDI): calcd for $[C_{64}H_{72}NaO_{12}Si_8]^+$ [M + Na]⁺, m/z 1279.3075; found, m/z 1280.3077. TGA (in air): mass loss of 5 wt % at 431 °C; total mass loss: 66%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2800, 1604, 1452, 1089 (Si–O–Si), 658.

Synthesis of (4-Br-2,6-Me₂C₆H₂SiO_{1.5})₈ (T₈-4). Using 1.08 g of 4bromo-2,6-dimethylphenylsilane, T₈-4 was isolated (731 mg, 62%) as a white powder. ¹H NMR (400 MHz, CDCl₃): δ 7.02 (s, 2H, Ar-H), 2.12 (s, 6H, Ar-CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 146.5, 131.0, 126.5, 125.4, 23.4. ²⁹Si NMR (79 MHz, CDCl₃): δ -80.4. TGA (in air): mass loss of 5 wt % at 371 °C; total mass loss: 68%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2800, 1566, 1457, 1099 (Si–O–Si), 660, 563 (C– Br), 503(C–Br).

Synthesis of $(3,5-iPr_2C_6H_3SiO_{1.5})_8$ (T_8 -5). Using 960 mg of 3,5diisopropylphenylsilane, T_8 -5 was isolated (626 mg, 58%) as a white powder.¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, J = 12.3 Hz, 2H, Ar-H), 7.17 (d, J = 11.8 Hz, 1H, Ar-H), 2.88 (m, J = 12.2, 6.1 Hz, 2H, CH(CH₃)₂), 1.45–1.00 (m, 12H, CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃): δ 148.0, 130.5, 130.1, 126.7, 34.3, 24.1. ²⁹Si NMR (79 MHz, CDCl₃): δ –77.9. HRMS (MALDI): calcd for [$C_{96}H_{136}NaO_{12}Si_8$]⁺ [M + Na]⁺, m/z 1727.8083; found, m/z 1728.8104. TGA (in air): mass loss of 5 wt % at 187 °C; total mass loss: 66%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2800, 1606, 1460, 1092 (Si–O–Si), 681.

Synthesis of $(3,5-tBu_2C_6H_3SiO_{1.5})_8$ (T_8 -6). Using 1.10 g of 3,5-di (*tert*-butyl)phenylsilane, T_8 -6 was isolated (701 mg, 58%) as a white powder.¹H NMR (400 MHz, CDCl₃): δ 7.73–7.44 (d, 1H, Ar-H), 7.44–6.90 (m, 2H, Ar-H), 1.53–0.59 (m, 18H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃): δ 149.7, 129.5, 128.0, 125.1, 34.7, 31.5. ²⁹Si NMR (79 MHz, CDCl₃): δ –77.5. HRMS (MALDI): calcd for [C₁₁₂H₁₆₈NaO₁₂Si₈]⁺[M + Na]⁺, m/z 1952.0587; found, m/z 1954.0622. TGA (in air): mass loss of 5 wt % at 182 °C; total mass loss: 69%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2800, 1588, 1460, 1095 (Si–O–Si), 711.

Synthesis of $(2\text{-}iPrC_6H_4SiO_{1.5})_8$ ($T_8\text{-}7$). Using 751 mg of 2isopropylphenylsilane, $T_8\text{-}7$ was isolated (588 mg, 68%) as a white powder.¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, J = 7.3 Hz, 1H, Ar-H), 7.44 (t, J = 7.3 Hz, 1H, Ar-H), 7.34 (d, J = 7.9 Hz, 1H, Ar-H), 7.13 (t, J = 7.1 Hz, 1H, Ar-H), 3.41 (m, J = 12.7, 6.2 Hz, 1H, CH(CH₃)₂), 1.00 (d, J = 6.4 Hz, 6H, CH(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃): δ 155.5, 135.7, 131.3, 128.3, 125.2, 124.9, 34.2, 24.3. ²⁹Si NMR (79 MHz, CDCl₃): δ -77.7. HRMS (MALDI): calcd for [C₇₂H₈₈NaO₁₂Si₈]⁺ [M + Na]⁺, m/z 1391.4327; found, m/z1392.4348. TGA (in air): mass loss of 5 wt % at 457 °C; total mass loss: 61%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2800, 1603, 1459, 1125 (Si–O–Si), 657.

Synthesis of $(2-tBuC_6H_4SiO_{1.5})_8$ (T_8 -8). Using 822 mg of 2-(*tert*butyl)phenylsilane, T_8 -8 was isolated (546 mg, 59%) as a white powder. ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, J = 7.6, 1.1 Hz, 1H, Ar-H), 7.36 (d, J = 7.9 Hz, 1H, Ar-H), 7.29–7.21 (t, 1H, Ar-H), 6.86 (t, J = 7.2 Hz, 1H, Ar-H), 1.16–1.09 (s, 9H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃): δ 157.5, 138.2, 130.4, 127.6, 126.4, 124.4, 37.0, 32.2. ²⁹Si NMR (79 MHz, CDCl₃): δ –78.5. HRMS (MALDI): calcd for [C₈₀H₁₀₄NaO₁₂Si₈]⁺ [M + Na]⁺, m/z 1503.5579; found, m/z1504.5612. TGA (in air): mass loss of 5 wt % at 395 °C; total mass loss: 70%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2800, 1607, 1558, 1099 (Si– O–Si), 675.

Synthesis of $(C_{12}H_9SiO_{1.5})_8$ (T_8 -9). Using 916 mg of 2-phenylphenylsilane, T_8 -9 was isolated (523 mg, 51%) as a white powder.¹H NMR (400 MHz, CDCl₃): δ 7.45 (t, J = 7.5 Hz, 1H, Ar-H), 7.33 (d, J = 8.3 Hz, 1H, Ar-H), 7.28–7.14 (m, 3H, Ar-H), 6.98 (d, J = 7.9 Hz, 2H, Ar-H), 6.73 (t, J = 14.9, 7.3 Hz, 1H, Ar-H), 6.60 (t, J = 15.2, 7.7 Hz, 1H, Ar-H). ¹³C NMR (101 MHz, CDCl₃): δ 148.7, 142.5, 136.5, 130.1, 129.5, 129.1, 128.9, 127.1, 126.6, 125.6. ²⁹Si NMR (79 MHz, CDCl₃): δ –80.6. HRMS (MALDI): calcd for $[C_{96}H_{72}NaO_{12}Si_8]^+$ [M + Na]⁺, m/z 1663.3076; found, m/z 1664.3091. TGA (in air): mass loss of 5 wt % at 461 °C; total mass loss: 33%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3150–2900, 1588, 1469, 1094 (Si–O–Si), 698.

Synthesis of $(C_{15}H_{15}SiO)_4(OH)_4$ (D_4 -1). Using 1.13 g of 2- $(2',4',6'-trimethylphenyl)phenylsilane, <math>D_4$ -1 was isolated (856 mg, 67%) as a white powder. ¹H NMR (400 MHz, d_8 -THF): δ 5.60–5.41 (m, 2H, Ar-H), 5.24 (m, J = 11.5, 7.5 Hz, 1H, Ar-H), 5.00 (d, J = 7.3 Hz, 1H, Ar-H), 4.97–4.81 (m, 2H, Ar-H), 0.46–0.25 (s, 3H, p-CH₃), 0.09 – -0.08 (s, 6H, o-CH₃). ¹³C NMR (101 MHz, d_8 -THF): δ 145.5, 138.3, 135.2, 134.3, 133.4, 130.7, 127.6, 126.6, 125.7, 123.2. HRMS (MALDI): calcd for $[C_{60}H_{64}NaO_8Si_4]^+$ [M + Na]⁺, m/z 1047.3576; found, m/z 1047.4047. TGA (in air): mass loss of 5 wt % at 85 °C; total mass loss: 75%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3700–3300 (Si–OH), 3100–2800, 1612, 1430, 1350, 1040 (Si–O–Si), 752.

Synthesis of (2,6-Et₂C₆H₃SiO_{1.5})₆ (T₆-1). Using 821 mg of 2,6-diethylphenylsilane, T₆-1 was isolated (511 mg, 55%) as a white powder. ¹H NMR (400 MHz, CDCl₃): δ 7.34–7.17 (t, 1H, Ar-H), 6.99 (d, *J* = 15.9, 7.9 Hz, 2H, Ar-H), 2.91 (q, *J* = 7.3 Hz, 4H, CH₂CH₃), 0.93 (t, *J* = 7.4 Hz, 6H, CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 151.9, 130.9, 126.6, 126.1, 29.8, 17.3. ²⁹Si NMR (79 MHz, CDCl₃): δ -68.8. HRMS (MALDI): calcd for [C₆₀H₇₈NaO₉Si₆] ⁺[M + Na]⁺, *m*/*z* 1133.4159; found, *m*/*z* 1133.4158. TGA (in air): mass loss of 5 wt % at 366 °C; total mass loss: 66%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2900, 1595, 1492, 1443, 1070 (Si–O–Si), 696.

Synthesis of $(3,5-Me_2C_6H_3SiO_{1.5})_{12}$ (T_{12} -1). Using 681 mg of 3,5-dimethylphenylsilane, T_{12} -1 was isolated (537 mg, 68%) as a white powder. ¹H NMR (400 MHz, CDCl₃): δ 7.34 (s, 2H, Ar-H), 7.09 (s, 1H, Ar-H), 2.27 (s, 6H, Ar-CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 136.8, 136.7, 132.4, 132.0, 131.8, 131.6, 131.3, 21.2. ²⁹Si NMR (79 MHz, CDCl₃): δ -79.4, -81.7. HRMS (MALDI): calcd for [C₉₆H₁₀₈NaO₁₈Si₁₂]⁺[M + Na]⁺, m/z 1909.9118; found, m/z 1909.4683. TGA (in air): mass loss of 5 wt % at 429 °C; total mass loss: 69%. FT-IR (KBr, cm⁻¹): $\tilde{\nu}$ 3100–2800, 1596, 1447, 1097 (Si–O–Si), 695.

X-ray Single Crystal Analysis. All intensity data were collected with a Bruker SMART CCD diffractometer using graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 113(2) K. The structure was solved by direct methods (SHELXS-97)²¹ and refined by full-matrix least-squares on F² with Olex2. All nonhydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97)²² with Olex2.²³ Single crystals of these compounds suitable for X-ray diffraction studies were obtained in THF at room temperature. Crystallographic data are shown in Table 1.

RESULTS AND DISCUSSION

Initially, we studied the Cs_2CO_3 -catalyzed oxidation of commercially available PhSiH₃ with DMF as the oxidant and

Table 2. Optimization of the Reaction Conditions for the Oxidation of PhSiH₃



Entry	Cat	Catalyst Loading (mol %)	Temp (°C)	Time (h)	Yield (%) ^a
1	Cs ₂ CO ₃	1	RT	24	39
2	Na_2CO_3	1	RT	24	0
3	K_2CO_3	1	RT	24	0
4	Cs_2CO_3	0	RT	24	0
5	Cs_2CO_3	0.5	RT	24	34
6	Cs ₂ CO ₃	5	RT	24	36
7	Cs ₂ CO ₃	1	50	18	33
8	Cs_2CO_3	1	100	16	21
^a Isolated yield.					

solvent (Table 2, entry1), and the reaction was monitored by ¹H NMR spectroscopy. It was observed that the reaction was complete in *ca.* 24 h and T_8 -1 could be isolated in 39% yield. Other alkali carbonates, including Na₂CO₃ and K₂CO₃, have also been tested under the same conditions (Table 2, entries 2–3). However, no conversions were observed with these carbonates probably due to their low solubility in DMF.^{17d} The oxidation of PhSiH₃ with different loadings of Cs₂CO₃

was also investigated (Table 2, entries 4–6). It was found that the catalyst loadings can be reduced to as low as 0.5 mol % without noticeable decrease of the yield (Table 2, entry 5) while the increase of the catalyst loadings did not lead to the improvement of the yields (Table 2, entry 6). In the absence of Cs_2CO_3 , no reaction was observed (Table 2, entry 4). The influence of temperature on the reaction was also studied. At high temperatures, the decreased yields were observed under similar conditions (Table 2, entries 7–8). On the basis of these results, the catalytic reaction was conducted at room temperature with 1.0 mol % of Cs_2CO_3 as the catalyst to extend substrates. The results are summarized in Table 3.

Table 3. Results for the Catalytic Oxidation of Phenyl silanes in DMF^a

	RSiH ₃ <u>1 mol% Cs₂CO₃, 4 mL DMF</u> - NMe ₃ (RSiO _{1.5}) _n				
Entry	R	POSS (Yield,%) ^b	²⁹ Si NMR	Other T cages present	
1	÷	T ₈ -1 (39)	_ c	-	
2	$+ \rightarrow$	T₈-2 (78)	-77.7	T10	
3	$+ \bigcirc$	T₈-3 (70)	-77.8	T10	
4	-kBr	T₈-4 (62)	-80.4	-	
5	₽r	T ₈ -5 (58)	-77.9	-	
6	÷ → tBu tBu	T₈-6 (58)	-77.5	-	
7	^{iPr}	T 8-7 (68)	-77.7	-	
8	fBu →	T₈-8 (59)	-78.5	-	
9	Ph +	T₈-9 (51)	-80.6	-	
10	Et Et	T ₆ -1 (55)	-68.8	T ₈	
11	÷	T ₁₂ -1 (68)	-79.4, -81.7	-	

^{*a*}Reaction conditions: silane (5.0 mmol) and Cs_2CO_3 (16 mg, 0.05 mmol) in 4 mL DMF at room temperature in 24 h. ^{*b*}Isolated yield. ^{*c*29}Si NMR chemical shift could not be obtained due to low solubility of the product.

As shown in Table 3, in most cases, the reaction selectively yielded T_8 in modest to good yields (Table 3, entries 2–9). The low yield obtained with PhSiH₃ is due to the formation of polymeric materials. All the POSS except T_8 -1 are soluble in organic solvents such as THF, chloroform, and toluene but sparsely soluble in methanol or acetonitrile. Therefore, these crude products can be easily purified by washing with methanol without further purification.

It has been observed that the oxidation of $PhSiH_3$ yielded a significant amount of high molecular weight products, and T_8 -1 was only isolated in 39% yield. However, the alkyl and aryl-substituted phenyl silanes (Table 3, entries 2–9) gave T_8 as the major products with much less high molecular weight products. This indicated that the substituents on the phenyl rings have substantial effects on the reaction outcomes and the products might be controlled by the steric effects of the phenyl rings. It is noted that the oxidation of phenylsilane with bulky

2,6-diethylphenyl group yielded the hexamer T_{6} -1 (Table 3, entry 10) as a major product, which can be isolated in 55% yield. In contrast, the oxidation of less hindered 3,5dimethylphenylsilane gave the T_{12} in 68% yield (Table 3, entry 11). The reaction is in general selective for the formation of a certain cage, and only trace isomeric products were detected in a few cases (Table 3, entries 2–3 and 9). These results indicated that the introduction of alkyl substituents on the phenyl ring could improve yields and selectivity. In contrast, the oxidation of PhSiH₃ gave a relatively low yield T_8 cage with the contamination of a significant amount of polymers. We reasoned that the substituents on the phenyl rings could prevent the formation of polymeric materials and thus facilitate the formation of the cages.

The ²⁹Si NMR chemical shifts of POSS are also listed in Table 3. They are all in the expected region around -78 ppm for phenyl-substitued T₈ cages^{7b,24} and -68 ppm for phenyl-substitued T₆ cages.²⁵ T₁₂-1 shows two singlets at -79.4 ppm and -81.7 ppm consistent with its lower symmetry (D_{2d}).^{10c,26}

The IR spectra of POSS show a strong characteristic band of Si-O-Si at 1000-1200 cm⁻¹ and aromatic C-H region at 3100-2800 cm⁻¹, 1500-1250 cm⁻¹, and 800-600 cm⁻¹ which are consistent with former reports.^{11a,c}

For the functionalization of phenyl POSS, para-octaiodophenylsilsesquioxane (I₈OPS) was prepared via iodination of octaphenylsilsesquioxane (≥93% regioselectvity) by Laine.^{11d} However, many efforts to obtain octabromophenylsilsesquioxane selectively via bromination of phenyl POSS were unsuccessful.^{11e,g} In 2011, Laine reported on the synthesis of ortho-octabromophenylsilsesquioxane with only ca. 85% regioselectivity.^{11c} It is noteworthy that the oxidation of 4bromo-2,6-dimethylphenylsilane gave para-octabromophenylsilsesquioxane (T_8-4) (Table 3, entry 4). The successful synthesis of T₈-4 indicated the catalytic system is tolerant to the carbon-halide bonds. The X-ray diffraction analysis showed that T₈-4 crystallized in the orthorhombic space group Pbca. The X-ray crystal structure of T₈-4 is shown in Figure 1. The O-Si-O angles are in the range 106.6(2)- $109.9(2)^{\circ}$, the Si-O-Si angles are in the range 146.3(3)-155.1(3)°, and the Si-O and Si-C bond lengths are in the ranges 1.609(4)-1.626(4) Å and 1.852(5)-1.866(5) Å. The structure of T₈-4 is a little distorted due to the larger steric bulk of the ligands; however, the distortion is not great compared with the former reports.^{10e,27} This compound offers perfect cubic symmetry and allows the addition of diverse functional groups. Therefore, it has great potential to develop diverse nanobuilding blocks.

The oxidation of 3,5-dimethylphenylsilane gave T_{12} -1 in 68% yield (Table 3, entry 11). The X-ray diffraction analysis shows that T_{12} -1 crystallized in the triclinic space group PI. The O–Si–O angles are in the range 107.52(9)–111.04(8)°, the Si–O–Si angles are in the range 146.32(11)–166.65(11)°, and the Si–O and Si–C bond lengths are in the ranges 1.6103(16)–1.6247(16) Å and 1.842(2)–1.857(2) Å. The X-ray crystal structure of T_{12} -1 is shown in Figure 2; it is a little more distorted than the (PhSiO_{1.5})₁₂.²⁸ Only a few high-yield routes to pure T_{12} have been reported.^{10d,26} They could be prepared by the cage rearrangement via the nucleophilic substitution of T_8 .²⁹ The reactions often lead to a mixture of T_{12} , and their pure forms could only be obtained in low yield by silica gel column chromatography or recrystallization. Compared with the traditional methods, the



Figure 1. ORTEP-representation of $(4-Br-2,6-Me_2C_6H_2SiO_{1.5})_8$ (T₈-4). Ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: Si7–O10 1.609(4), Si6–O9 1.626(4), Si6–C40 1.852(5), Si3–C17 1.866(5), Si5–O9–Si6 146.3(3), Si7–O10–Si6 155.1(3), O4–Si1–O5 106.6(2), O6–Si6–O9 107.8(2), O10–Si7– O7 109.9(2), C1–Si1–O5 114.2(2), O10–Si6–C40 107.3(2).



Figure 2. ORTEP-representation of $(3,5-Me_2C_6H_3SiO_{1.5})_{12}$ (T_{12} -1). Ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: Si8–O10 1.6014(16), Si1–O1 1.6247(16), Si10– C73 1.842(2), Si7–C49 1.857(2), Si3–O2–Si2 146.32(11), Si1– O4–Si4 166.65(11), O18–Si2–C9 107.03(9), O9–Si8–C57 112.63(9), O10–Si9–O17 107.52(9), O4–Si1–O1 111.04(8).

present protocol provides a straightforward and efficient way to $\mathrm{T}_{\mathrm{12}}.$

The oxidation of 2-phenylphenylsilane gave the T_8 cage (Table 3, entry 9), while increasing ortho-hindrance of the phenylsilane from phenyl to 2,4,6-trimethylphenyl (mesityl) yielded the eight-membered ring cyclotetrasiloxanetetraol (($C_{15}H_{15}SiO$)₄(OH)₄, D₄-1) (Scheme 2). Cyclotetrasiloxanetetraols have been synthesized by acid/base catalyzed hydrolytic condensation of trifunctional silanes, which in general led to a mixture of stereoisomers.³⁰ However, the selective synthesis of an all-cis D₄-tetraol via hydrolysis of the all-cis

Scheme 2. Synthesis of D₄-1



D4-tetrachloride has been reported by Unno et al.^{30a} D_4 -1 is almost insoluble in toluene and chloroform but has a limited solubility in THF. It is envisioned that D_4 -1 could be an oligomer associated by hydrogen bonds in the absence of THF. Single crystals of D₄-1 suitable for X-ray diffraction studies were obtained from THF at room temperature. X-ray diffraction analysis showed that D_4-1 crystallized in the tetragonal space group $P\overline{4}21c$ and confirmed that it was alltrans configuration in the solid state. The two THF molecules form hydrogen bonds with the OH groups (Figure 3). The Si-O bond lengths (1.617-1.626(3) Å) and O-Si-O angle (108.5(2)) in D₄-1 are similar to those of the cyclic tetraphenyltetrasiloxanetetraols reported by Kawakami et al.,³⁰ ^b while the Si–O–Si angles $(138.6(2)^\circ)$ are smaller than those $(145-152^{\circ})$ for known tetrasiloxanetetraols probably because of the steric effects on the substituent.^{30b,c}

The oxidation of primary alkylsilanes under the same conditions has also been examined. However, all the reactions generated a mixture due to the low activity of the substrates. This observation is in accordance with a base-catalyzed hydrosilylation, in which the phenyl group could improve the Lewis acidity of the silanes.

Since oxidation of primary silanes may yield a mixture of siloxane intermediates which are difficult to identify, dimethylphenylsilane PhMe₂SiH (a) was selected to investigate the initial reaction pathway (Scheme 3). The oxidation of PhMe₂SiH yielded a small amount of siloxymethylamine PhMe₂SiOCH₂NMe₂ (b) as indicated by the ¹H NMR analysis (see Figure S1 in the SI, the comparison with literature spectrum^{15c}) and GC-MS (Figure S2). Therefore, it was concluded that the initial step in the oxidation process involved the Cs₂CO₃-catalyzed hydrosilylation of DMF to form siloxymethylamine. Since siloxymethylamine **b** cannot be obtained in pure form, it was synthesized according to the



PhMe ₂ SiH a	Cs ₂ CO ₃	PhMe ₂ SiOCH ₂ NMe ₂ b	Cs ₂ CO ₃	PhMe ₂ SiOSiMe ₂ Ph + c	NMe ₃
	hydrosilation	dehydroc	arbonative cro	ss-coupling	

literature.^{15c} Thus, the reaction of the siloxymethylamine with PhMe₂SiH catalyzed by Cs_2CO_3 under the catalytic oxidation conditions has been investigated for the understanding of the following step. It was found that this reaction resulted in the dehydrocarbonative Si–O cross-coupling with the formation of the disiloxane PhMe₂SiOSiMe₂Ph (c) and NMe₃ in high yield (see Table S1 in the SI).

On the basis of these experimental findings, we proposed the possible mechanism shown in Scheme 4. It is quite possible

Scheme 4. Proposed Mechanism for the Cs₂CO₃-Catalyzed Oxidation of Silanes



that a hydrosilane interacted with the "naked" $\rm CO_3^{2-}$ dianion to yield a hypervalent hydrosilicate intermediate **A**, which then transfers the hydride ligand to the carbonyl group to form the hydrosilylation product **B**. **B** reacted with **A** via the hydrogen transfer from the silicate to the carbon atom ($\rm CH_2NMe_2$) in **B** companied by Si–O coupling to give siloxane product and trimethylamine. The formation of **D**₄-1 with hydroxyl groups is reproducible, but the mechanism for the OH formation is not clear at present. All attempts to isolate and detect the possible intermediates were unsuccessful to date. This could be attributed to the bulky 2-(2',4',6'-trimethylphenyl)phenyl group, which may prevent further Si–O coupling once the D₄ skeleton was formed.



Figure 3. ORTEP-representation of all-trans ($C_{15}H_{15}SiO$)₄(OH)₄ (D_4 -1). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Si1a-O1 1.608(4), Si1a-O 2d 1.617(3), Si1a-O2a 1.626(3), Si1a-C1 1.851(4), O1-Si1a-O2a 109.03(19), O 2d-Si1a-O2a 108.5(2), O1-Si1a-C1 110.4(2), Si1a-O2a-Si1b 138.6(2).

CONCLUSION

In summary, we have performed systematic studies on the Cs₂CO₃-catalyzed oxidation of substituted phenylsilanes with DMF for the selective formation of several types of POSS such as T₆, T₈, and T₁₂ cages and a D₄ cyclosiloxane. The catalytic process is efficient, safe, and general for substituted phenylsilanes. For all the reactions described in this work, medium to high yields could be obtained under mild conditions. Therefore, it is practically useful for the synthesis of various substituted phenyl POSS in bench scale. This catalytic system also represents the first highly efficient and selective methodology for the oxidation of primary hydrosilanes. The substituents on the phenyl rings have significant effects on the product yields and to some extent control the structures of the POSS. Further studies on the Cs2CO3-catalyzed hydrosilane transformations and the applications of these substituted phenyl POSS are currently in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02107.

NMR spectra and mechanism study details (PDF)

Accession Codes

CCDC 1818769–1818770, 1818779, and 1818781 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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