



Transition Metal-Catalyzed Direct Arylation of Caged Silsesquioxanes: Substrate Scope and Mechanistic Study

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Abstract: Caged silsesquioxane (polyhedral oligomeric silsesquioxane: POSS) is an important class of organic-inorganic hybrid molecules. The electronic properties of POSS have gradually attracted attention from experimental and computational perspectives, while POSS is generally utilized for reinforcement of polymer materials. Practical synthetic routes to access to arylsubstituted POSS are effective tools for the systematic studies. Recently, we reported Rh-catalyzed direct arylation of heptaisobutyl-POSS with electron-rich aryl iodides. Herein substrates for the Rhcatalyzed direct arylation were widely examined: electron-deficient, sterically-hindered, and heteroatom-containing aryl halides, and heptaphenyl-POSS. Pd-catalyzed direct arylation of POSS was developed as well. Notably, thiophene was introduced by the Pdcatalyst, whereas the Rh-system did not work for the substrate. In addition, the reaction mechanism of the Rh-catalyzed reaction was elucidated by density functional theory calculations.

Introduction

Caged silsesquioxane, denoted as POSS (polyhedral oligomeric silsesquioxane), is one of the representative building blocks for inorganic-organic hybrid materials.^[1] The siloxane core of POSS is covered with organic substituents, and hence it has advantages derived from organic and inorganic materials; good designability and solubility due to the organic substituents and excellent materials properties due to the inorganic components. These characteristic natures are beneficial for reinforcement of polymer materials, and POSS has been introduced to polymer matrices as nano-fillers^[2] or cross-linking agents.^[3] In addition, polymers containing POSS in the end groups,^[4] side chains,^[5] or main chains^[6] were synthesized. Incorporation of POSS gives high thermal stability to organic polymers without diminishing intrinsic transparency of the polymers. In these traditional researches, electronic properties of POSS tend to be ignored. On the other hand, three-

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dimensional functional molecules have played important roles in optoelectronic materials due to their unique morphologies and intermolecular communications: fullerene, carbon nanotube, carborane, etc. In the case of POSS, there are a few experimental and computational studies on the electronic properties as well. Electron accepting behavior of POSS was previously observed in the studies on optical properties of octaaryl-substituted POSSs.^[7] Kieffer's group conducted calculations to show that the LUMO is located at the POSS core, and can interact to the aryl groups directly attached to the Si atoms.^[8] Laine's group developed synthetic methods to construct octaaryl-substituted POSS derivatives, and the electron acceptance of the POSS core was shown.^[9] In spite of these pioneering works, there are insufficient experimental studies on structure-property relationship of aryl-substituted POSSs. This is because systematic studies are still difficult due to the lack of synthetic routes towards the aryl-substituted POSSs.





Conventionally, aryl-substituted POSSs have been synthesized via condensation of an incompletely-condensed POSS with a silane-coupling agent having an aryl group (Scheme 1a), though silane-coupling agents are typically unstable under ambient condition due to theirs moisturesensitivity. Cross coupling or metathesis reactions (Schemes 1b and 1c) are effective for this end, but phenylene or vinylene linkers should be inserted between POSS and the aryl moieties.^[9,10] Recently, we have developed Rh-catalyzed direct arylation of monohydro-POSS by using aryl halides (Scheme 1d).^[11] This reaction is a promising tool for the systematic investigation of the aryl-substituted POSSs. In that previous paper, only limited substrates are examined for proof of concept; the substituents of the POSS core are isobutyl group, and the aryl halides possess electron-donating groups.

Herein, we have examined Pd catalysts for the direct arylation of POSSs besides the Rh catalyst. Furthermore, the scope of the substrates has been widened; heptaisobutyl- and heptaphenyl-POSSs were reacted with electron-donating, electron-withdrawing, sterically hindered, or heteroatomcontaining aryl halides. In addition, the reaction mechanism of the Rh-catalyzed direct arylation was computationally studied.

Results and Discussion

Rh-catalyzed direct arylation

Heptaisobutyland heptaphenyl-POSSs (1 and 2. respectively) were prepared as the reaction substrates. In the previous paper, we have optimized the reaction condition of the Rh-catalyzed direct arylation of 1 with aryl halides.^[11] We firstly focused on scope of the substrates for the Rh-catalyzed direct arylation. POSS derivatives 1 and 2 were reacted with aryl halides including electron-rich, electron-deficient, sterically hindered, heteroatom-containing aryl halides. Yields of aryl-POSSs 4a-k and 5a-f under the optimized reaction condition in hand are summarized in Table 1. The NMR yields were evaluated by the ¹H-NMR spectra, and isolation was carried out with column chromatography over silica gel or high performance liquid chromatography (HPLC).

Yields of the reaction with heptaisobutyl-POSS 1 (run 1-11) were moderate except for run 7 and 10. The present reaction can be applied to electron-rich (3a,b,d), electron-deficient (3e,f), sterically hindered (3d,i), reactive (3h) and heteroatom-containing (3k) aryl halides. In run 7 and 10, no reaction proceeded with 3g and 3j probably because the nitrogen and sulfur atoms worked as a catalytic poison through coordination to the metal center.

In the case of heptaphenyl-POSS **2** (run 12-17), the NMR yields were hard to be evaluated because the crude products contained complicating mixtures of oligomeric silsesquioxanes. As a result, the isolated yields were significantly lowered from those of **1**. In particular, **5c** and **5d** failed to be isolated due to large amounts of oligomeric products. These results suggests that heptapheyl-POSS is sensitive to the present reaction condition; in general, the substituents affect hydrolysis behavior of POSS.^[12] In our previous paper, even heptaisobutyl-POSS

[Rh(cod)(MeCN)2]BF2

iPr₂EtN, DMF 80 °C, 1.5h

Ar-X

OMe

X (3)

-I (3a)

(3b)

(3c)

(3d)

-I (3e)

(**3f**)

(3g)

(**3h**)

(3i)

Ar

-R

MeO

MeOC

1: R = *i*Bu

2: R = Ph

POSS

1

1

Run

1*°*

2°

4

5

6

7^c

8

9

1

1

^{-I} (3j) 10 1 4j n.d.) Br (**3k**) 11 1 4k 60 (52) 75 (20) 12 2 3a 5a (11) 13 2 3b 5b 14 2 3c 5c n.d. 15 2 3d 5d n.d. 16 2 3e 5e (28) 17 2 3f 5f (32) ^a[POSS] = 0.15 M, [aryl halide] = 0.225 M, [Rh] = 7.5 mM, [*I*Pr₂EtN] = 1.15 M. ^bNMR yield (bare) and isolated yield (in a parenthesis). °Cited from reference 11.

were partially decomposed by using strongly nucleophilic amines as well. $\ensuremath{^{[11]}}$

Then, we measured the UV-vis absorption spectrum of octaphenyl-POSS **5c** to examine the electronic effect of the POSS core, though we failed to synthesize **5c** by the present reaction (**5c** is commercially available). However, the three

4: R = *i*Bu

5: R = Ph

Product

4a

4b

4c

4d

4e

4f

4g

4h

4i

WILEY-VCH

″Ar∮

Yield^b

[%]

87 (78)

87 (62)

81 (74)

78 (71)

76 (43)

81 (79)

n.d.

81 (79)

69 (53)

dimensional unoccupied orbital of the POSS did not contributed to the LUMO of **5c** as we have already reported the same phenomenon in the case of **4c**. For the detail, see supporting information (Figure S31).

Pd-catalyzed direct arylation

Masuda and coworkers reported Pd(0)-catalyzed silylation of aryl halides with triethoxysilane.^[13] Inspired by this closely related report, plladium was chosen in order to expand the scope of applicable metals for the direct arylation. The reaction condition of 1 with *p*-iodoanisole was firstly optimized (Table 2). In run 1, P(o-tol)₃ iPr₂EtN, and DMF were selected as ligand, base, and solvent, respectively in reference to the Masuda's paper^[13] and our previous paper on the Rh-catalyzed direct arylation.^[11] DMF, NMP, toluene, and THF were examined in run 1-4, and DMF and NMP were suitable for the reaction (78%). Reaction temperature was changed from 50 °C to 120 °C (run 1, 5, and 6), and the reaction at 80 °C offered the highest yield. Amines were investigated in run 6 and 7. Et₃N (62%, run 7) and *i*Pr₂HN (65%, run 8) gave lower yields than *i*Pr₂EtN (78%, run 1). Finally we investigated phosphine ligands. DeShong and coworkers employed biphenyl-di-tert-butylphosphine (JohnPhos) for improvement of the Pd-catalyzed silylation.^[14] Here, we examined Cy JohnPhos (run 9) and PPh₃ (run 10), but the yields were lower than that of run 1. Hence, we have concluded that the reaction condition of run 1 is the best for the present reaction.

Under the reaction condition optimized above, several kinds of substrates were examined (Table 3). The yields of **4a-e** of the

 Table 2. Optimization of reaction condition for Pd-catalyzed direct arylation.^a



^a[POSS] = 0.15 M, [*p*-iodoanisole] = 0.225 M, [Pd] = 7.5 mM, [ligand] = 30 mM, [amine] = 1.15 M. ^bNMR yield.

Pd-catalyzed reaction were lower than those of the Rh-catalyzed one. In particular, the reaction with sterically-hindered substrate



^aReaction condition of run 1 in Table 2. ^bNMR yield (bare) and isolated yield (in a parenthesis).

3d did not proceed. On the other hand, it is worth noting that the thienyl group was introduced in moderate yield by utilizing the Pd catalyst (run 6), whereas the Rh catalyst did not work for **3j** (Run 11 in Table 1). This result corresponds to the case of arylation of triethoxysilane,^[15] though the reason remains to be clear. It has been demonstrated that adequate selection from the present Rh and Pd catalysts can expand the scope of applicable substrates.

Reaction mechanism

Xu and coworkers reported mechanism of the Pd-catalyzed silylation of aryl iodides with hydrosilanes by density functional theory (DFT) calculations, $^{\left[16\right] }$ whereas that of the Rh-catalyzed reaction is still unclear. In addition, mechanistic studies on catalytic reactions for POSS substrates have never been performed despite their recent progress. Therefore, we decided to conduct DFT calculations for understanding of the mechanism of the Rh-catalyzed direct arylation. A relevant previous study of Murata group indicates that a RhI complex is formed prior to starting the direct arylation.^[13] Following the previous paper, a plausible reaction mechanism is given in Scheme 2. A Si-H bond in a POSS is clearly indicated by H-Si(POSS). The reaction is initiated by insertion of the RhI complex into a H-Si(POSS) bond to form a silvl hydride species, (H-RhI-Si(POSS)) by the H(POSS) atom migration to the Rh atom (Path A). From the resultant silvl hydride species, H and X atoms are removed by triethylamine NEt₃ to form a silyl rhodium complex (Rh-Si(POSS)) together with I·HNEt₃ (Path B). After that event, the resultant Rh-Si(POSS) complex reacts with an

aryl halide (Arl) leads to an arylrhodium intermediate (Ar-RhI-Si(POSS)) *via* a transition state for I-atom migration from Arl to the Rh atom (**Path C**). In the arylrhodium intermediate, a C atom of the Ar group is bound to the Si(POSS) atom to form a Si-C bond. The Si-C bond formation results in an Ar-POSS species bound by RhI. After that, the product complex dissociates into an Ar-Si(POSS) species and RhI. The resultant RhI complex serves a species reacting with POSS, and thus the reaction continuously proceeds in the same pathway along Scheme 2.



Scheme 2. Plausible mechanism of Rh-catalyzed direct arylation of POSS.

Following reaction mechanisms in Scheme 2, we obtained local minima and transition states. Detailed discussion on the energetics of the Rh-catalyzed direct arylation of POSS is described in Supporting Information (SI), including Figures S33-S35. Briefly, the DFT calculations found that all local minima and transition states are energetically stable relative to the initial state (POSS, RhI, ArI, and NEt₃). The results indicated that the Rh-catalyzed direct arylation of POSS easily proceeds in an exothermic manner. Importantly, the rate-determining step of the overall reaction is removal of I-HNEt₃ from the Rh center in Path B ($E_a = 23.2 \text{ kcal/mol}$), while the reductive elimination in Path C needs similar activation energy ($E_a = 21.3 \text{ kcal/mol}$). The electron donating or accepting groups on the aryl halides modulate the activation energy in the reductive elimination; electron withdrawing groups slightly raise the activation energy,^[17] resulting in slightly lower yields in the experimental study summarized in Table 1.

Conclusions

In summary, we have investigated scope of substrates for our previously reported Rh-catalyzed direct arylation of POSS, and newly developed Pd-catalyzed one. Wide variety of aryl groups can be introduced to the POSS backbones with isobutyl or phenyl groups; electron-rich, electron-deficient, sterically hindered, heteroatom-containing aryl halides were applicable. The Rh-catalyzed direct arylation was computationally studied, and the energetically preferable reaction mechanisms, obtained from the DFT calculations, can support the above experimental findings. Though the effect of the three dimensional unoccupied molecular orbital located in the POSS core has not been observed yet, further investigation will open a way to creation of POSS-based electronic materials. We are now trying to optimize the substituents of POSS, and to introduce various conjugated systems. These results will be reported in future publications.

Experimental Section

1. Materials

Bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate ([Rh(cod)(MeCN)₂]BF₄) and (2-biphenyl)dicyclohexylphosphine (Cv JohnPhos) were purchased from Sigma Aldrich. Toluene, hexane, ethyl methanol (MeOH), acetate (EtOAc), triethylamine (Et₃N), diisopropylethylamine (iPr2EtN), iodobenzene, and triphenylphosphine (PPh₃) were purchased from Nacalai Tesque, Inc. Tetrahydrofuran (THF, super dehydrated grade), N,N-dimethylformamide (DMF, super dehydrated grade), 1-methyl-2-pyrrolidone (NMP, super dehydrated grade), and toluene (super dehydrated grade) were purchased from Wako Pure Chemical Industry, Ltd. Trichlorosilane, 4-iodotoluene, 4iodoanisole, 2-iodoanisole, 4-iodoacetophenone, 3-iodobenzotrifluoride, 4-iodobenzonitrile, 4-diiodobenzene, 4-bromoiodobenzene, 4hydoroxviodobenzene, 4-iodophenol, 2-iodobiphenyl, 2-iosovhiophene, 3-bromopylidine, tris(dibanzylideneacetone)dipalladium(0) (Pd₂(dba)₃) and tris(2-metylphenyl)phosphine ($P(o-tol)_3$) were purchased from Tokyo Chemical Industry Co., Ltd. Heptaisobutyl-trisilanol-POSS and heptaphenyl-trisilanol-POSS were purchased from Hybrid Plastics. Heptaisobutyl-POSS (1)^[18] and heptaphenyl-POSS (2)^[19] were prepared according to the literature procedures.

2. Instruments

¹H- (400 MHz), ¹³C- (100 MHz), and ²⁹Si- (80 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer. The samples were analyzed in CDCl₃ using Me₄Si as an internal standard. The following abbreviations are used; s: singlet, d: doublet, dd: doubledoublet, dt: doublet of triplets, t: triplet, qd: quartet of doublets, m: multiplet. Preparative high-performance liquid chromatography (HPLC) for purification was performed on LC-6AD (SHIMADZU) with a Shodex KF-2001 column (SHOWADENKO, Tokyo, Japan) using CHCl₃ as an eluent.

3. Synthetic procedure and characterization data

General Procedure A: A DMF solution (2 mL) of **1** (245 mg, 0.3 mmol), aryl halide (0.45 mmol), [Rh(cod)(MeCN)₂]BF₄ (6 mg, 0.015 mmol), and *i*Pr₂EtN (2.3 mmol) was stirred for 1.5 h under nitrogen atmosphere. After the reaction, toluene (75 mL) was added to the reaction mixture, and the organic layer was washed with water. The volatiles were removed under reduced pressure, and the residue was subjected to short column chromatography over silica gel (eluent: hexane/EtOAc = 9/1). The product including small amounts of impurities was recrystallized from CH₂Cl₂, EtOAc, and MeOH to obtain colorless crystals.

4a-d: The characterization data are shown in the previous paper.[11]

4e: ¹H-NMR (CDCl₃, 400 MHz) δ 7.95 (d, 2H, J = 8.0 Hz), 7.77 (d, 2H, J = 8.4 Hz), 2.62 (s, 3H), 1.93-1.81 (m, 7H), 0.99-0.94 (m, 42H), 0.67-0.60 (m, 14H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 198.4 138.3 137.8 127.2 26.7 25.7 25.7 23.9 23.8 22.5 22.4 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ - 67.0 -67.7 -81.4 ppm. HR-FAB-MS (m/z): calcd for C₃₆H₇₀O₁₃Si₈ [M+H]⁺, 935.3049; obs, 935.3041.

4f: ¹H-NMR (CDCl₃, 400 MHz) δ 7.93 (s, 1H), 7.84 (d, 1H, *J* = 7.6 Hz), 7.68 (d, 1H, *J* = 8.0 Hz), 7.48 (t, 1H, *J* = 7.8 Hz), 1.94-1.82 (m, 7H), 0.99-0.94 (m, 42H), 0.68-0.60(m, 14H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 137.2 133.1 130.8 130.8 127.9 126.9 126.9 25.7 25.6 23.9 22.5 22.4 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ -66.9 -67.7 -67.8 -81.5 ppm. HR-FAB-MS (m/z): calcd for C₃₅H₆₇F₃O₁₂Si₈ [M+H]⁺, 961.2817; obs, 961.2820.

4h: ¹H-NMR (CDCl₃, 400 MHz) δ 7.51 (s, 4H), 1.91-1.82 (m, 7H), 0.98-0.93 (m, 42H), 0.65-0.62 (m, 14H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ135.6 130.9 130.7 125.2 25.7 23.9 22.5 22.4 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ -67.1 -67.8 -67.9 -80.6 ppm. nano-ESI (m/z): calcd for $C_{34}H_{67}BrO_{12}Si_8Na$ [M+Na]*: 993.2; obs, 993.1.

4i: ¹H-NMR (CDCl₃, 400 MHz) δ 7.89 (d, 1H, *J* = 7.2 Hz), 7.49-7.24 (m, 8H), 1.86-1.74 (m, 7H), 0.96-0.90 (m, 42H), 0.63-0.43 (m, 14H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 148.9 143.8 136.1 130.4 130.3 129.9 129.2 127.8 127.0 126.0 25.8 25.8 25.7 23.9 23.9 23.8 22.6 22.6 22.4 22.3 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ -66.8 -67.7 -67.9 -67.9 -87.1 ppm. HR-FAB-MS (m/z): calcd for C₄₀H₇₂O₁₂Si₈ [M+H]⁺, 969.3257; obs, 969.3253.

4k: ¹H-NMR (CDCl₃, 400 MHz) δ 8.81 (dd, 1H, J = 1.6 and 1.2 Hz), 8.64 (dd, 1H, J = 4.8 and 1.6 Hz), 7.92 (dt, 1H, J = 7.6 and 1.6 Hz), 7.28 (qd, 1H, J = 4.8 and 0.8 Hz), 1.90-1.80 (m, 7H), 0.98-0.94 (m, 42H), 0.65-0.60 (m, 14H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 154.4 151.1 141.7 127.2 123.0 25.7 25.7 23.9 22.5 22.3 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ -66.8 - 67.0 -67.7 -81.1 ppm. HR-FAB-MS (m/z): calcd for C₃₃H₆₇NO₁₂Si₈ [M+H]⁺, 894.2896; obs, 894.2886.

General Procedure B: A DMF solution (2 mL) of **1** (245 mg, 0.3 mmol), aryl halide (0.45 mmol), [Rh(cod)(MeCN)₂]BF₄ (6 mg, 0.015 mmol), and *i*Pr₂EtN (2.3 mmol) was stirred for 1.5 h under nitrogen atmosphere. After the reaction, toluene (75 mL) was added to the reaction mixture, and the organic layer was washed with water. The volatiles were removed under reduced pressure, and the residue was subjected to flash column chromatography over silica gel (eluent: hexane/EtOAc = 1/1). The product was purified by preparative HPLC using CHCl₃ as an eluent.

5a: ¹H-NMR (CDCl₃, 400 MHz) δ 7.77-7.74 (m, 14H), 7.70 (d, 2H, J = 8.4 Hz), 7.46-7.42 (m, 7H), 7.37-7.34 (m, 14H), 6.91 (d, 2H, J = 8.8 Hz), 3.79 (s, 3H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 161.7 135.9 134.2 130.8 130.3 130.3 127.9 121.3 113.6 55.0 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ - 77.4 -78.2 -78.3 ppm. HR-FAB-MS (m/z): calcd for C₄₉H₄₂O₁₃Si₈ [M+H]⁺, 1063.0858; obs, 1063.0868.

5b: ¹H-NMR (CDCl₃, 400 MHz) δ 7.76-7.74 (m, 14H), 7.65 (d, 2H, J = 8.0 Hz), 7.46-7.42 (m, 7H), 7.37-7.34 (m, 14H), 7.17 (d, 2H, J = 7.6 Hz), 2.34 (s, 3H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 140.9 134.3 134.2 130.8 130.3 130.2 128.7 127.9 126.7 21.6 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ - 77.7 -78.3 -78.3 ppm. HR-FAB-MS (m/z): calcd for C₄₉H₄₂O₁₂Si₈ [M+H]⁺, 1047.0909; obs, 1047.9003.

5e: ¹H-NMR (CDCl₃, 400 MHz) δ 7.92 (d, 2H, J = 8.0 Hz), 7.86 (d, 2H, J = 8.0 Hz), 7.77-7.74 (m, 14H), 7.45-7.43 (m, 7H), 7.38-7.34 (m, 14H), 2.58 (s, 3H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 198.3 138.8 136.0 134.5 134.2 134.2 131.0 130.9 130.1 130.0 130.0 128.0 127.9 127.4 26.7 ppm;

 $^{29}\text{Si-NMR}$ (CDCl₃, 80 MHz) δ -78.1 -78.2 -79.2 ppm. HR-FAB-MS (m/z): calcd for C_{50}H_{42}O_{13}Si_8 [M+H]+, 1078.0858; obs, 1075.0853.

5f: ¹H-NMR (CDCl₃, 400 MHz) δ 8.06 (s, 1H), 7.92 (d, 1H, *J* = 7.6 Hz), 7.77-7.68 (m, 14H), 7.68 (d, 1H), 7.45 (d, 1H, *J* = 7.6 Hz), 7.46-7.43 (m, 7H), 7.38-7.35 (m, 14H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 137.5 134.3 134.2 131.6 131.0 130.9 130.4 130.1 130.0 129.9 128.4 128.0 128.0 127.5 127.5 125.5 122.8 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ -78.0 -78.2 ppm. HR-FAB-MS (m/z): calcd for $C_{49}H_{39}F_3O_{12}Si_8$ [M+H]⁺, 1101.0626; obs, 1101.0637.

General Procedure C: A DMF solution (2 mL) of **1** (245 mg, 0.3 mmol), aryl halide (0.45 mmol), $Pd_2(dba)_3$ (14 mg, 0.015 mmol), $P(o-tol)_3$ (18 mg, 0.06 mmol) and *i*Pr₂EtN (2.3 mmol) was stirred for 1.5 h under nitrogen atmosphere. After the reaction, toluene (75 mL) was added to the reaction mixture, and the organic layer was washed with water. The volatiles were removed under reduced pressure, and the residue was subjected to flash column chromatography over silica gel (eluent: hexane/EtOAc = 9/1). The product was purified by preparative HPLC using CHCl₃ as an eluent.

4j: ¹H-NMR (CDCl₃, 400 MHz) δ 7.62 (d, 1H, J = 4.8 Hz), 7.64 (d, 1H, J = 2.4 Hz), 7.18 (dd, 1H, J = 4.8 and 3.6 Hz), 1.91-1.84 (m, 7H), 0.97-0.94 (m, 42H), 0.66-0.60 (m, 14H) ppm; ¹³C-NMR (CDCl₃, 100 MHz) δ 136.5 131.5 130.3 127.8 25.7 25.7 23.9 22.5 22.4 ppm; ²⁹Si-NMR (CDCl₃, 80 MHz) δ -67.2 -67.5 -67.8 -83.7 ppm. HR-FAB-MS (m/z): calcd for C₃₂H₆₆O₁₂SSi₈ [M+H]⁺, 899.2508; obs, 899.2507.

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- a) R. M. Laine, C. Zhang, A. Sellinger, L. Viculis, *Appl. Organometal. Chem.* **1998**, *12*, 715; b) R. M. Laine, *J. Mater. Chem.* **2005**, *15*, 3725;
 c) D. B. Cordes, P. D. Lickiss, F. Rataboul, *Chem. Rev.* **2010**, *110*, 2081; d) K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2013**, *86*, 1231; e)
 Q. Ye, H. Zhou, J. Xu, *Chem. Asian J.* **2016**, *11*, 1322; f) K. Naka, Y. Irie, *Polym. Int.* **2017**, *66*, 187; g) Z. Li, J. Kong, F. Wang, C. He, *J. Mater. Chem. C* **2017**, *5*, 5283; h) H. Zhou, Q. Ye, J. Xu, *Mater. Chem. Front.* **2017**, *1*, 212; i) H. Imoto, *Polym. J.* **2018**, *50*, 837.
- [2] a) K. Tanaka, S. Adachi, Y. Chujo, J. Polym. Sci., Part A: Polym. Chem.
 2009, 47, 5690; b) K. Tanaka, S. Adachi, Y. Chujo, J. Polym. Sci., Part A: Polym. Chem.
 2019, 47, 5690; b) K. Tanaka, S. Adachi, Y. Chujo, J. Polym. Sci., Part A: Polym. Chem.
 2010, 48, 5712; c) J.-H. Jeon, K. Tanaka, Y. Chujo, J. Polym. Sci., Part A: Polym. Chem.
 2013, 51, 3583; e) J.-H. Jeon, K. Tanaka, Y. Chujo, J. Polym. Sci., Part A: Polym. Chem. 2014, 2, 624; f) K. Ueda, K. Tanaka, Y. Chujo, Polym. J. 2016, 48, 1133; g) K. Ueda, K. Tanaka, Y. Chujo, Bull. Chem. Soc. Jpn. 2017, 90, 205; h) K. Tanaka, H. Kozuka, K. Ueda, J.-H. Jeon, Y. Chujo, Mater. Lett. 2017, 203, 62; i) S. Yuasa, Y. Sato, H. Imoto, K. Naka, J. Appl. Polym. Sci. 2018, 135, 46033.
- [3] For recent papers, see: a) Y. Fang, H. Ha, K. Shanmuganathan, C. J. Ellison, ACS Appl. Mater. Interfaces 2016, 8, 11050; b) X. Zhou, X. Fan, C. He, Macromolecules 2016 49, 4236; c) E. Carbonell, L. A. Bivona, L. Fusaro, C. Aprile, Inorg. Chem. 2017, 56, 6393; d) D. Wang, R. Sun, S. Feng, W. Li, H. Liu, Polymer 2017, 130, 218; e) A. Raghuvanshi, C. Strohmann, J.-B. Tissot, S. Clément, A. Mehdi, S. Richeter, L. Viau, M. Knorr, Chem. Eur. J. 2017, 23, 16479; f) C. Xing, L. Wang, L. Xian, Y.

Wang, L. Zhang, K. Xi, Q. Zhang, X. Jia, *Macromol. Chem. Phys.* 2018, 219. 1800042.

- [4] For recent papers, see: a) L. Li, C. Zhang, S. Zheng, J. Polym. Sci., Part A: Polym. Chem. 2017, 55, 223; b) Z. Qin, B. Qu, L. Yuan, X. Yu, J. Li, J. Wang, H. Lv, X. Yang, Polym. Chem. 2017, 8, 1607; c) Y. Cao, S. Xu, L. Li, S. Zheng, J. Polym. Sci., Part B: Polym. Phys. 2017, 55, 587.
- [5] a) R. Goseki, A. Hirao, M. Kakimoto, T. Hayakawa, ACS Macro Lett.
 2013, 2, 625; b) L. Hong, Z. Zhang, W. Zhang, Ind. Eng. Chem. Res.
 2014, 53, 10673; c) T. Suzuki, A. Yoshida, S. Ando, K. Nagai, Polym. Int. 2015, 64, 1209; d) F. Kato, A. Chandra, S. Horiuchi, T. Hayakawa, RSC Adv. 2016, 6, 62172; e) T. Seshimo, Y. Utsumi, T. Dazai, T.
 Maehashi, T. Matsumiya, Y. Suzuki, C. Hirano, R. Maeda, K. Ohmori, T.
 Hayakawa, Polym. J. 2016, 48, 407.
- [6] For recent papers, see: a) K. Wei, L. Wang, L. Li, S. Zheng, *Polym. Chem.* 2015, *6*, 256; b) P. Wang, Y. Tang, Z. Yu, J. Gu, J. Kong, *ACS Appl. Mater. Interfaces* 2015, *7*, 20144; c) T. Maegawa, Y. Irie, H. Imoto, H. Fueno, K. Tanaka, K. Naka, *Polym. Chem.* 2015, *6*, 7500; d) P. Żak, B. Dudziec, M. Dutkiewicz, M. Ludwiczak, B. Marciniec, M. Nowicki, *J. Polym. Sci., Part A: Polym. Chem.* 2016, *54*, 1044; e) J. Hao, Y. Wei, J. Mu, *RSC Adv.* 2016, *6*, 87433; f) T. Maegawa, O. Miyashita, Y. Irie, H. Imoto, K. Naka, *RSC Adv.* 2016, *6*, 31751; g) Y.-T. Liao, Y.-C. Lin, S.-W. Kuo, *Macromolecules* 2017, *50*, 5739; h) S. Fujii, S. Minami, K. Urayama, Y. Suenaga, H. Naito, O. Miyashita, H. Imoto, K. Naka, *ACS Macro Lett.* 2018, *7*, 641; i) H. Imoto, R. Katoh and K. Naka, *Polym. Chem.* 2018, *9*, 4108.
- [7] F. J. Feher and T. A. Budzichowski, J. Organomet. Chem. 1989, 379, 33.
- [8] C.-G. Zhen, U. Becker, J. Kieffer, J. Phys. Chem. A 2009, 113, 9707.
- [9] a) S. Sulaiman, A. Bhaskar, J. Zhang, R. Guda, T. Goodson III, R. M. Laine, *Chem. Mater.* 2008, 20, 5563; b) R. M. Laine, S. Sulaiman, C.

Brick, M. Roll, R. Tamaki, M. Z. Asuncion, M. Neurock, J.-S. Filhol, C.-Y. Lee, J. Zhang, T. Goodson III, M. Ronchi, M. Pizzotti, S. C. Rand, Y. Li, *J. Am. Chem. Soc.* **2010**, *13*2, 3708.

- [10] a) M. F. Roll, M. Z. Asuncion, J. Kampf, R. M. Laine, ACS Nano 2008, 2, 320; b) M. Z. Asuncion, M. F. Roll, R. M. Laine, *Macromolecules* 2008, 41, 8047.
- [11] H. Imoto, S. Wada, K. Naka, Dalton Trans. 2017, 46, 6168.
- [12] Z. Li, Y. Kawakami, *Chem. Lett.* **2008**, *37*, 804.
- [13] M. Murata, K. Suzuki, S. Watanabe, Y. Masuda, J. Org. Chem. 1997, 62, 8569.
- [14] A. S. Manoso, P. DeShong, J. Org. Chem. 2001, 66, 7449.
- [15] In the papers on Pd-catalyzed arylation of triethoxysilane, thienyl groups were introduced (see, references 12 and 13). However, in those on Rh catalyst, no investigation on thienyl groups were shown; for example, see following papers. a) M. Murata, M. Ishikura, M. Nagata, S. Watanabe, Y. Masuda, *Org. Lett.* **2002**, *4*, 1843; b) M. Murata, H. Yamasaki, T. Ueta, M. Nagata, M. Ishikura, S. Watanabe, Y. Masuda, *Tetrahedron* **2007**, 63, 4087.
- [16] Z, Zu, J.-Z. Xu, J. Zhang, Z.-J. Zheng, J. Cao, Y.-M. Cui, L.-W. Xu, *Chem. Asian J.* 2017, 12, 1749.
- [17] The activation energy in the reductive elimination, defined by the energy difference between Int_C and TS2_C in Figure S33 depends on types of aryl halide substrate. The activation energy values decline in the following order: 4-acetaldehyde-iodobenzene (22.4 kcal/mol) > iodobenzene (21.3 kca/mol) > 4-methoxyl-iodobenzene (19.2 kcal/mol).
- [18] C.-H. Lu, C.-H. Tsai, F.-C. Chang, K.-U. Jeong, S.-W. Kuo, J. Colloid Interface Sci. 2011, 358, 93.
- [19] Y. Liu, Y.Shi, D. Zhang, J. Li, G. Huang, Polymer 2013, 54, 6140.

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FULL PAPER



Functional cages: Pd- or Rh-catalyzed direct arylation of cage-silsesquioxane has been attained. Phenyl- and isobutyl-substituted cage-silsesquioxanes were applicable for the arylation with electron-donating, electron-withdrawing, heteroatom-containing, and reactive substrates. The reaction mechanism of the Rh-catalyzed direct arylation has been computationally studied in detail.

Functional cage

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Transition Metal-Catalyzed Direct Arylation of Caged Silsesquioxanes: Substrate Scope and Mechanistic Study