

One-Pot Condensation of a Bicyclo[1.1.1]pentasilane through Elimination of Iodotrimethylsilane Assisted by a Lewis Base

Yuki Yokouchi and Takeaki Iwamoto*



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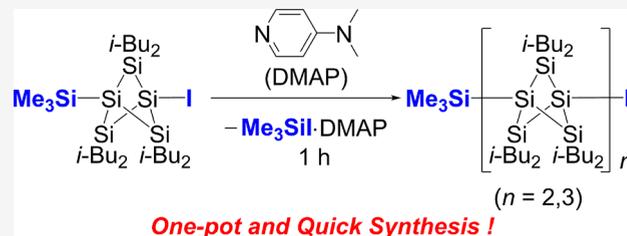


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ABSTRACT: Development of efficient bond formation reactions remains important in organic and main-group-element chemistry. Herein, we report the metal-free one-pot condensation reaction of 1-iodo-3-(trimethylsilyl)-substituted bicyclo[1.1.1]pentasilane (BPS) in the presence of 4-(dimethylamino)pyridine (DMAP) providing oligomers of BPS, persila[*n*]staffanes (*n* = 2, 3), which involves the successive Si–Si bond formation reaction accompanied by the concomitant formation of iodotrimethylsilane (TMSI) in the form of a DMAP complex. The computational study suggests that the formation of a pentasila[1.1.1]propellane–DMAP complex resulting from the elimination of TMSI from the BPS is a key intermediate.



Cyclic oligosilanes, silicon compounds with two or three-dimensional frameworks such as cage-, polyhedron-, ladder-, bowl-, and sphere-shaped structures, exhibit the electronic structures due to the σ conjugation depending on their fixed conformation^{1–13} and should be potential units for large σ conjugated systems.^{14–24} Such cyclic oligosilanes have recently been demonstrated as units for judiciously designed molecular wires that can be conductive materials and molecular electronic devices.^{25–27} To increase the diversity of the structures and properties of highly ordered silicon materials based on the cyclic oligosilanes, development of the efficient condensation reactions of cyclic oligosilanes to form Si–Si bonds under milder conditions remains crucial. Various silicon skeletons are generally synthesized through the following reactions: the metathesis of halosilanes or alkoxy-silanes with metal silanides, the Wurtz-type coupling reactions of halosilanes, the disproportionation reactions of polyhalogenated silanes with chloride ion,^{21,28–30} the rearrangement of polymethyloligosilanes with aluminum trichloride,^{31–34} the dehydrogenative coupling reaction of di- or trihydrosilanes, and the living polymerization of masked disilenes.³⁵ Despite the abundant ways to form the Si–Si bonds, however, direct incorporation of cyclic oligosilanes to the highly ordered polycyclic oligosilanes remains scarce. Marschner et al. developed a simple and versatile method to prepare potassium cyclooligosilanides via the site-selective elimination of trimethylsilyl or dimethylphenylsilyl groups by *t*-BuOK and applied this method to synthesize catenated cyclic oligosilanes.^{14,36–41} Recently Klausen et al. have achieved the condensation reactions of 1,1,4,4-tetrahydrocyclohexasilanes by the dehydrogenative coupling reactions.^{42,43}

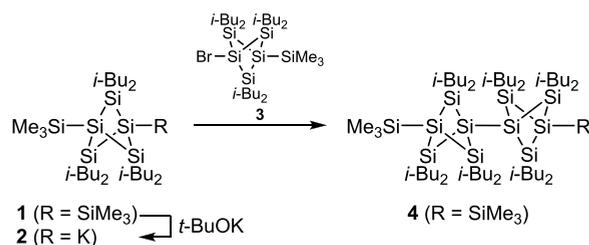
We have previously reported highly ordered polycyclic oligosilanes comprising a bicyclo[1.1.1]pentasilane (BPS) unit,

persila[*n*]staffanes (*n* = 1–3) that exhibit substantial σ -conjugation through the BPS cages.¹⁷ These persila[*n*]staffanes were synthesized by the step-by-step extension of the BPS cages through a combination of the reported functionalization reactions at the bridgehead positions such as the selective transmetalation (Marschner's method) of **1** (or **4**) with *t*-BuOK providing the corresponding metalated species such as **2** and the subsequent addition of brominated BPS (**3**) (Figure 1a). The yields of the persila[*n*]staffanes in this method decreased with increasing the number of the BPS units due to the multistep reactions as well as the low solubility of the resulting products. Herein, we report the metal-free one-pot synthesis of persila[*n*]staffanes (*n* = 2 (**6**) and 3 (**7**)) by condensation of 1-iodo-3-(trimethylsilyl)bicyclo[1.1.1]pentasilane **5** (Figure 1b). This reaction involves the unprecedented efficient Si–Si bond formation reaction through elimination of iodotrimethylsilane (TMSI) assisted by 4-(dimethylamino)pyridine (DMAP).

1-Iodobicyclo[1.1.1]pentasilane **5** was newly synthesized by iodination of **2** (for details, see the Supporting Information and Figure 2). The reaction of **5** with 3 equiv of DMAP in benzene at room temperature for 1 h afforded a yellow solution including 1-iodopersila[*n*]staffanes **6** (*n* = 2) and **7** (*n* = 3), which were observed with high-resolution mass spectrometry (HRMS) (Figures S24–S26), together with a precipitate of

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(a) Previous Work: Step-by-step Extension



(b) This Work: One-pot Condensation

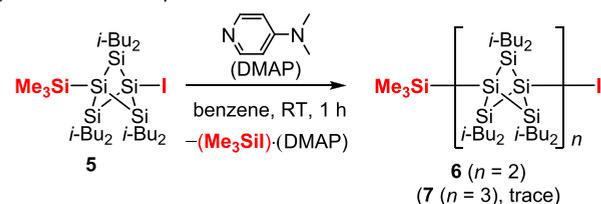


Figure 1. (a) Step-by-step extension and (b) one-pot condensation of bicyclo[1.1.1]pentasilanes.

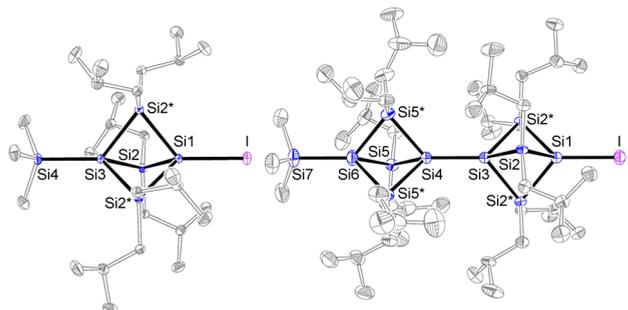


Figure 2. Molecular structures of **5** (left) and **6** (right) (atomic displacement parameters are set at the 50% possibility; hydrogen atoms are omitted for clarity).

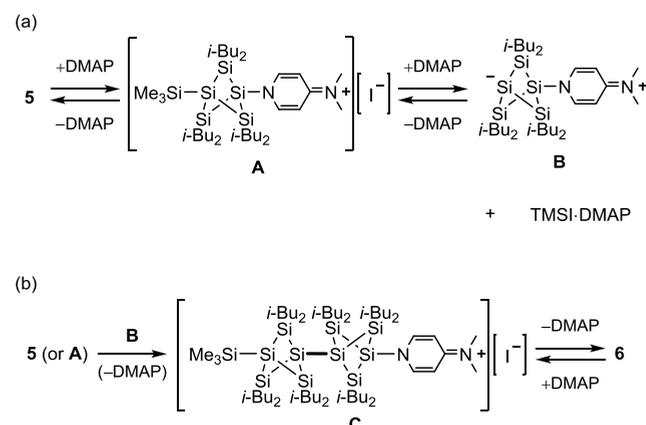
TMSI-DMAP⁴⁴ (Figure 1b). The resulting TMSI-DMAP can be easily removed by filtration from the reaction mixture, as it is insoluble in benzene. The resulting filtrate was subjected to preparative gel permeation chromatography (GPC) to furnish **6** (56%).⁴⁵ The molecular structure of **6** was determined by a combination of multinuclear NMR spectra and single-crystal X-ray diffraction analysis (Figure 2). The GPC analysis indicated that the crude mixture contained two other components with molecular weights higher than **6**, which is consistent with the results of the HRMS (Figure S1). Although the fraction with the second longer retention time could be identified as **7** ($n = 3$), its further characterization was unsuccessful due to its very low amount and low solubility. The condensation reaction also proceeded in toluene and benzotrifluoride, while the reaction in CD₂Cl₂ afforded a complex mixture including *i*-Bu₂SiCl₂,⁴⁶ indicating that the BPS cage decomposed in this condition.^{47,48} Notably, DMAP is a suitable Lewis base in the condensation of the BPS: when other Lewis bases such as *Pt*-Bu₃, PPh₃, and NEt₃ were used, the reactions in C₆D₆ did not complete even at 80 °C for 24 h, although the formation of **6** (and **7**) were observed in ¹H NMR spectra. The observed slower reactions probably emerged from high solubility of the corresponding base-TMSI complexes, which would cause the corresponding reverse reactions.

In the single crystals, both **5** and **6** contain BPS units on a crystallographic 3-fold axis through the bridgehead Si atoms. The Si1–I bond lengths [2.5045(6) Å (**5**) and 2.505(3) Å (**6**)] lie within the reported values on four-coordinate Si atoms [2.410(1)–2.6413(6) Å].^{49,50} Distances between the bridgehead Si atoms in the iodo-substituted BPS cages (Si1⋯Si3) [2.8488(8) Å (**5**); 2.839(3) Å (**6**)] are significantly shorter than that in the disilylated BPS cage in **6** (Si4⋯Si6) [2.935(4) Å], which can be explained by the inductive effects of the iodo substituent at the bridgehead positions. The iodine atom that has higher electronegativity than the silicon atom should shorten the endocyclic Si1–Si2(*) bonds of **5** and **6** due to the increased *s* character of the orbitals on the Si1 atoms for the Si1–Si2(*) bonds compared with those of the other Si–Si bonds.⁵¹

To understand the mechanism for this reaction, we examined the effects of halides and silyl groups at the bridgehead silicon atom on the reactions. The condensation of 1-bromo and 1-chloro-substituted BPSs **3** and **8** using DMAP occurred as well to provide the corresponding persila[*n*]staffanes ($n = 2$ –4), which were detected by HRMS (APCI) (Figures S31–S38). However, the reactions proceeded substantially slowly [half-life, 27 h for **3**; 19 h for **8**; <4 min for **5** (Figure S2)], and some unidentified byproducts were observed in ¹H NMR spectra (Figures S3 and S4). These results indicate that the iodo substituent is important for the efficient Si–Si bond formation. Furthermore, comparison of reactivity between iodinated BPSs that contain trimethylsilyl (TMS) (**5**) and bulkier *t*-butyldimethylsilyl (TBS) group (**9**)⁵² provided an insight into the elimination process of TMSI. The reaction of **5** (5 mM) with DMAP (50 mM) in C₆D₆ at room temperature provided **6** in 50% yield even after 4 min as observed in the ¹H NMR spectrum, while that of **9** on the same condition did not provide the corresponding persila[*n*]staffanes. Eventually 85% of **9** remained intact even after 14 days but TBSI-DMAP formed in 8% yield with concomitant formation of unidentified compounds. These results clearly indicate that the increase of the steric bulk of the silyl group at the bridgehead position prevents the further reaction.

As halosilanes and Lewis bases such as pyridine and NHC react reversibly to form the corresponding *N*-silylpyridinium and *N*-silylimidazolium halides,^{44,53} it is reasonable to consider that the DMAP-adduct of **5** (A) is a possible initial intermediate for the condensation reaction (Scheme 1a).^{54,55}

Scheme 1. Possible Mechanism for the Initial Steps of the Reaction of **5** and DMAP



The intermediate **A** can further react with an extra DMAP to afford a zwitterionic pentasila[1.1.1]propellane–DMAP complex (**B**) and TMSI·DMAP.⁵⁶ As these species should exist in equilibrium, coupling reactions between **5** (or **A**) and **B** could occur to provide persila[2]staffane **C**, which should also equilibrate with **6** (Scheme 1b). This scenario can also explain the formation of **7** by the coupling reactions between **C** (or **6**) and **B**.

The formation of a DMAP-adduct such as **A** was suggested in the reaction of **9** and DMAP in CD₂Cl₂. In the ²⁹Si NMR spectrum of the reaction mixture at −40 °C, four major signals at −167.3, −44.3, −11.5, and 13.0 ppm were observed, which are assignable to a DMAP-adduct of **9** (**A**^{TBS}) and well-reproduced by the GIAO calculation (Table 1). These signals

Table 1. Observed and Calculated ²⁹Si Chemical Shifts of **A**^{TBS}

A^{TBS}

Si nuclei	chemical shift $\delta(^{29}\text{Si})$	
	observed ^a	calculated ^b
Si ¹	−44.3	−49.9
Si ²	−11.5	−2.7 (averaged)
Si ³	−167.3	−169.9
Si ⁴	13.0	15.9

^aIn CD₂Cl₂. ^bGIAO/HCTH407/6-311G+(3d)[Si], 6-31G+(d,p)-[C,H,N] level of theory.

gradually disappeared with increasing temperature (Figures S12–S23). In the case of **5**, however, **A** was not observed in a similar condition probably due to the facile subsequent reactions such as the elimination of the less hindered Me₃Si group (Figures S5–S7).

To understand the details of the reaction mechanism, we calculated a possible reaction route from **5'** that is a model compound substituted by Me groups instead of *i*-Bu groups in benzene (Scheme 2).^{57–61} As the first step, the substitution of

I atom with DMAP to generate *N*-silylpyridinium iodide **A1'** was calculated to be endergonic (+28.4 kJ mol^{−1}) with an activation barrier of 51.3 kJ mol^{−1} (298.15 K).⁶² After an inter- or intramolecular migration of iodide from around the coordinating DMAP (**A1'**) to around TMS (**A2'**), which is endergonic (+56.9 kJ mol^{−1}), the elimination of TMSI provides complex **B'**.⁶³ In this step, the iodide ion approaches the backside of the TMS group with the activation energy of 40.2 kJ mol^{−1}.⁶⁴ Finally, a coupling reaction of **B'** and **5'** to form persila[2]staffane **C'** followed by the substitution of DMAP with iodide to afford **6'**, both of which are exergonic with the small activation energies. This calculated reaction route is applicable to explain the formation of trimer **7** and the larger oligomers. Although each reaction described in Scheme 2 should be reversible, the low solubility of TMSI·DMAP in benzene can prevent the reverse reaction from **B'** to **A2'** to result in the efficient condensation reaction. In addition to the aforementioned reactions, a side-reaction from **A1'** was calculated. After addition of the iodide ion to the bridge silicon atom (SiMe₂), the Si–Si bond between the bridge and bridgehead Si atoms in **A1'** is cleaved with an activation barrier of 38.2 kJ mol^{−1} (Figures S76). This process should be prevented due to the steric demand around the bridge silicon atoms in the real system.

In summary, we have found a one-pot condensation of iodinated BPS **5** assisted by DMAP affords persila[*n*]staffanes (*n* = 2 and 3). The computational study suggests that the zwitterionic pentasilapropellane–DMAP complex **B** generated by the elimination of TMSI from **5** should play an important role in the Si–Si bond formation between the BPS cages. The metal-free condensation reaction of oligosilanes through elimination of TMSI as found in the present study could offer an alternative route to highly ordered silicon clusters involving cyclic oligosilane units similar to covalent organic frameworks (COF).

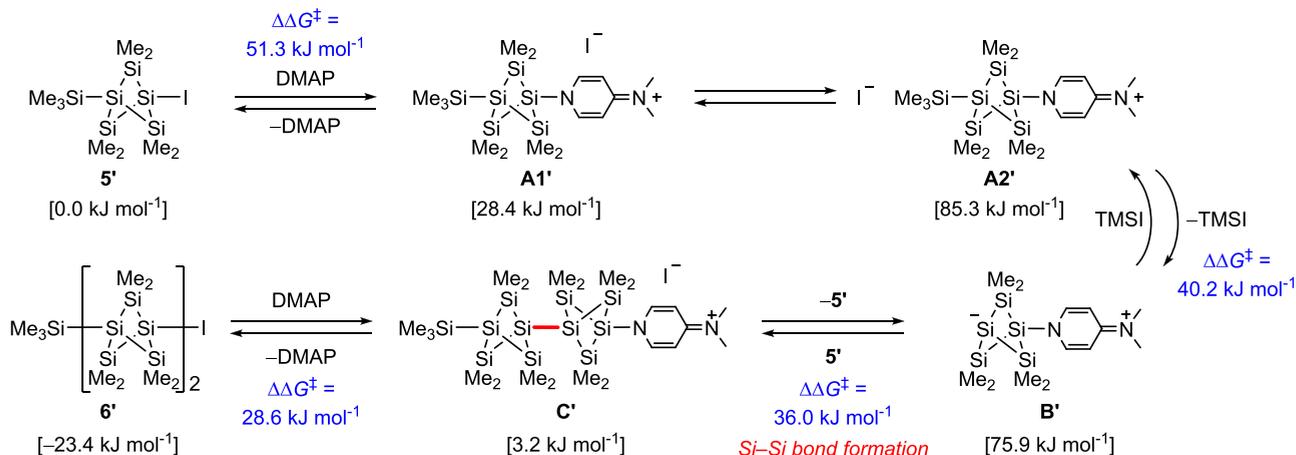
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00514>.

Experimental and computational details (PDF)

Scheme 2. Possible Route for the Formation of **6'** from **5'** Predicted by DFT Calculations^a



^aThe values in the brackets are relative Gibbs free energies (kJ mol^{−1}; 298.15 K) calculated at the PCM(benzene)/B3PW91-D3/6-311+G(d,p)^{C,H,N,Si}-LANL2DZDp^I level of theory.

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 2006779–2006785 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.

AUTHOR INFORMATION

Corresponding Author

Takeaki Iwamoto – Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan;

orcid.org/0000-0002-8556-5785;

Email: takeaki.iwamoto@tohoku.ac.jp

Author

Yuki Yokouchi – Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Complete contact information is available at:

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Notes

The authors declare no competing financial interest.

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- (55) The halophilic attack of DMAP to the iodo substituent of **5** providing the corresponding silanide and N-iodopyridinium is less likely to occur because persila[2]staffane **4**, which should be formed by the reaction of the resulting silanide and **5**, was not observed.
- (56) The addition of nitrogenous bases to pentasila[1.1.1]propellane has been unknown to our knowledge, although several 1,3-addition reactions have been reported. (a) Nied, D.; Koppe, R.; Kloppe, W.; Schnockel, H.; Breher, F. Synthesis of a Pentasilapropellane. Exploring the Nature of a Stretched Silicon-Silicon Bond in a Nonclassical Molecule. *J. Am. Chem. Soc.* **2010**, *132*, 10264–10265. (b) Nied, D.; Breher, F. New Perspectives for “Non-classical” Molecules: Heavy [1.1.1]propellanes of Group 14. *Chem. Soc. Rev.* **2011**, *40*, 3455–3466.
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- (61) DFT calculations were performed at the B3PW91-D3/6-311+G(d,p)^{C,H,N,Si}-LANLDZdp¹//B3PW91-D3/6-31+G(d,p)^{C,H,N,Si}-LANLDZdp¹ with effective core potential (ECP) for I atom and polarizable continuum model (PCM) as a solvent effect of benzene.
- (62) The abstraction of the TMS group of **5** with DMAP was calculated to be unfavorable compared with the substitution reaction. The activation energy was 119.3 kJ mol⁻¹ through the transition state (TS6).
- (63) As the reactions are conducted in benzene, the solvent separated ion pair is less likely to be formed, which is supported by DFT calculations: the energy of the solvent separated ion pair corresponding to **A1'** is calculated to be higher in energy than those of the contact ion pairs **A1'** [by 99.1 kJ mol⁻¹] and **A2'** [by 42.2 kJ mol⁻¹]. Conversely, two or more molecules of **A1'** may form a weak aggregate in benzene to undergo the reactions whereby extra I⁻ ions participate, such as the attack of a second I⁻ ion to the TMS group of **A1'**.
- (64) The calculated energy levels for *n* orbitals of free DMAP, iodide ion of **A1'**, and iodide ion of **A2'** were –7.04 eV, –5.02 eV, and –4.52 eV, respectively, which indicates that the iodide ion is more reactive than DMAP.