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Synthesis and Characterization of Functionalizable Silsesquioxanes with Ladder-type Structures

Yujia Liu,^a Kazuki Onodera,^b Nobuhiro Takeda,^b Armelle Ouali,^{*a,c} and Masafumi Unno^{*a,b}

^a Gunma University Initiative for Advanced Research (GIAR)-International Open Laboratory with Institute Charles Gerhardt Montpellier (UMR5253 CNRS-UM-ENSCM), Gunma University, Kiryu 376-8515, Japan

^b Department of Chemistry and Chemical Biology, Graduate School of Science and Technology, Gunma University, Kiryu 376-8515, Japan

^c Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM. ENSCM, 8 rue de l'École Normale, 34296 Montpellier Cedex 05, France

ABSTRACT: Novel tetra vinyl- and tetra allyl- substituted laddersiloxanes were synthesized and characterized. It was shown that peripheral olefins could successfully undergo hydrosilylation quantitatively, possibly leading to tetrahalide ladder structures. All

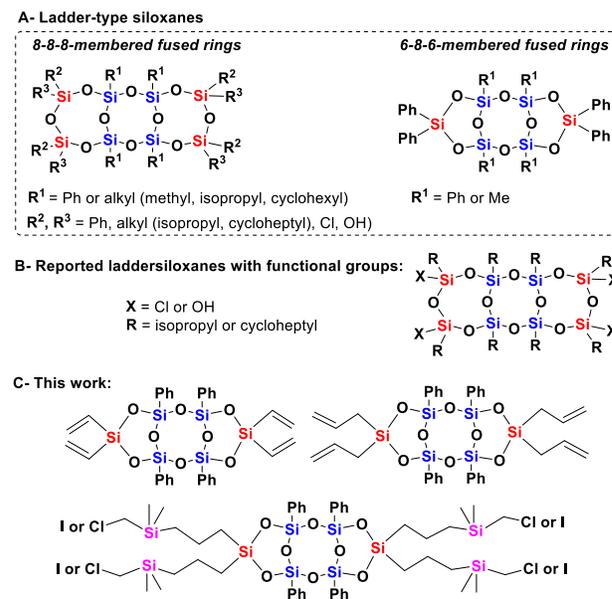
reported functional laddersiloxanes LS (LS-Vinyl₄, LS-Allyl₄, LS-Cl₄ and LS-I₄) thus constitute promising building blocks for more complex inorganic-organic hybrid materials.

Silsesquioxanes, organosilicon compounds with the empirical formulas $\text{RSiO}_{3/2}$ ($\text{R} = \text{H}$, alkyl, aryl), have been extensively studied due to their interesting properties such as thermal stability, low dielectric constant and water repellency.¹ Several types of well-defined silsesquioxanes have been reported and they include partially condensed, cages² (e. g. T₈, T₁₀ and T₁₂) or ladder structures (so called “laddersiloxanes”). The latter, possessing highly ordered double-chain structures and possibly presenting polymeric forms are of particular interest.³ For example, they appear as attractive candidates in the field of electronic devices where highly thermally stable and well-defined structures without defects are required to improve the physical properties without altering the electronic properties of the organic semiconducting fragment.⁴ Since the preparation of the first bicyclic and tricyclic laddersiloxanes about 50 years ago, many efforts have been devoted to improve synthetic routes to these compounds as well as the characterization methods,³ but also to reach pentacyclic,⁵ heptacyclic^{5c,6} and even nonacyclic⁷ ladder structures from our group.

The current work concerns tricyclic laddersiloxanes. These compounds can be composed of three eight-membered rings (8-8-8-membered fused rings) or possess two external six-membered rings (6-8-6-membered fused rings) (Scheme 1, A). The first ones could be obtained e.g. by reaction of dihydroxysiloxanes with cyclotetrasiloxanes bearing isocyanate substituents⁸ or by oxidation of the corresponding preformed tricyclic ladder oligosilanes.⁹ Ladder-type siloxanes with 6-8-6-membered fused rings can also be synthesized by reaction of cyclic tetrabromide and diphenylsilanediol.¹⁰ Both 8-8-8 and 6-8-6 laddersiloxanes have also been prepared from cyclic tetrasilanol by using dichlorosiloxanes^{5a} or dichlorosilanes,¹¹ respectively. It is noteworthy that for all these tricyclic compounds, most of the peripheral groups present on the silicon atoms (Scheme 1, A, R¹, R² and R³) consist of non-reactive phenyl or alkyl groups. Interestingly, hydrolytic condensation of cycloheptyltrichlorosilane or opening of cage hexasilsesquioxanes under basic conditions allows generation of tricyclic 8-8-8 ladder structures having four reactive peripheral silanols (Scheme 1, B, R = cycloheptyl, X = OH).¹² Several of us reported the preparation of more stable phenyl counterparts (R = Ph, X = OH) from the corresponding tetraphenyl substituted cyclic 8-8-8 laddersiloxanes in two steps and high yields: i) cleavage of the Si-

phenyl bond by HCl leading to tetrachloro ladder siloxanes (Scheme 1, B, X = Cl); ii) hydrolysis of the Si-Cl bonds to yield Si-OH bonds.^{5a,c} Therefore and to the best of our knowledge, the functionalizable laddersiloxanes reported to date possess either peripheral chlorosilanes or silanols (Scheme 1, B). The former ones were shown to react with silanols and the second with chlorosil(ox)anes, both via dehydrochlorinations, going pentacyclic ladder structures.^{5a,c}

Scheme 1. Structures of ladder-type siloxanes.



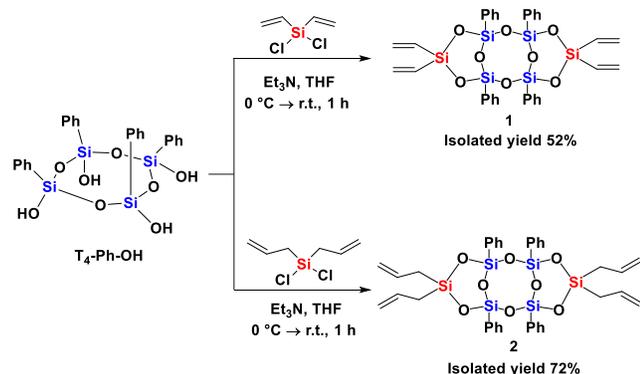
The possibilities of using laddersiloxanes as building blocks in more complex structures are thus quite limited due to the lack of available peripheral functional groups. In an effort to enlarge the scope of functionalizable laddersiloxanes and broaden the number of pathways to introduce new functionalities around the tricyclic inorganic skeletons, a synthetic route to tetra vinyl- and tetra allyl-decorated ladder structures is herein reported (Scheme 1, C). In this work, tetraallyl laddersiloxanes are shown to undergo hydrosilylation with dimethylphenylsilane and chloromethyldimethylsilane. In the latter case, the tetra-

chloro- tricyclic ladder structure obtained successfully undergoes halogen exchange to form the corresponding tetra-iodo-laddersiloxane (Scheme 1, C).

RESULTS AND DISCUSSION

The precursor, all-*cis*-tetraphenyl-cyclotetrasiloxanetetraol (**T₄-Ph-OH**), was synthesized according to Kawakami *et al.*¹³ Noteworthy, the phenyl substituents are preferred to alkyl ones to ensure higher thermal stability of the targeted laddersiloxanes.¹¹ Therefore, the solution of divinylchlorosilane in anhydrous THF was added dropwise into a solution of cyclic silanol **T₄-Ph-OH**, distilled triethylamine and anhydrous THF at 0 °C under an argon atmosphere. The mixture was then warmed to room temperature (25 °C) and allowed to stir for one hour. The desired tricyclic laddersiloxane **1** was obtained in 52% isolated yield after washing with hexane and purification through a silica plug. The tricyclic laddersiloxane **2** was prepared using the same protocol from cyclic silanol **T₄-Ph-OH** with diallyldichlorosilane and isolated with 72% yield (Scheme 2). It is worth noting that no polymers were observed at the end of reaction. Addition rates and reaction times of the dichlorosilane solution were found to be key factors for the success and selectivity of this synthesis.

Scheme 2. Synthesis of laddersiloxanes **1** and **2** from **T₄-Ph-OH**.

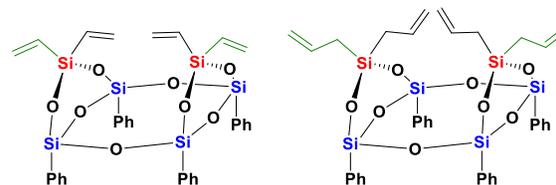


Multinuclear NMR spectroscopies were performed to characterize laddersiloxanes **1** and **2**. Both ²⁹Si NMR spectra (Supporting Information Fig. S3 and S6) clearly displayed signals corresponding to the T-group silicon atoms (**Si** in blue) and to the D-group silicon atoms (**Si** in red). For the laddersiloxane **1**, the ²⁹Si resonances at -67.8 and -34.5 ppm have respectively been assigned to T- and D-groups silicon atoms. For **2**, the chemical shift of T-group silicon atoms δ -67.7 was found to be almost the same as that of **1** while the signal of D-group silicon atoms was significantly shifted to the left, δ -15.2 (against 34.5 ppm in the case of **1**). Such awkward observation, related to the enhanced electro-donating properties of the allyl substituents compared to the vinyl ones, has already been reported in the case of double-decker siloxanes bearing vinyl or allyl groups.¹⁴ It is worth noting that ¹H and ¹³C NMR spectra highlighted that vinyl- (resp. allyl-) moieties bound to each peripheral D-group silicon atom (Scheme 3, **Si** in red) were not magnetically equivalent, each expected signal for methylene or olefinic moieties giving rise to two distinct patterns (see Supporting Information Fig. S1, S2, S4 and S5). These data are thus in accordance with the expected all-*cis* configuration of the cyclotetrasiloxanetetraol **T₄-Ph-OH** in laddersiloxanes **1** and **2** (Scheme 3).

Both compounds **1** and **2** were also analyzed by matrix-assisted laser desorption/ionization coupled time-of-flight

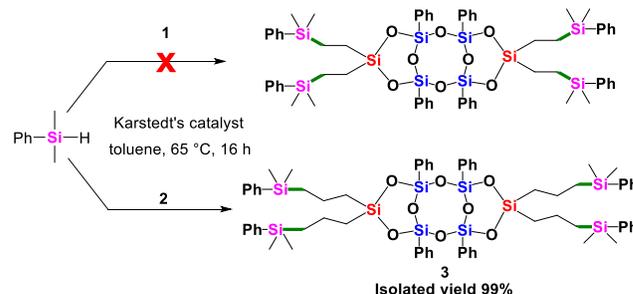
(MALDI-TOF) mass spectroscopy and the experimental mass spectra were in good agreement with the calculated molecular weight (see SI). Along the same lines, elemental analyses results matched very well to the theoretical values.

Scheme 3. All-*cis*-configuration of the laddersiloxanes: non-equivalence of the substituents beared by the peripheral D-group silicon atoms.



To our knowledge, the only previous example of tetrafunctionalizable DDSQ involved four reactive Si-Cl (or Si-OH) bonds (Scheme 1, B) likely to react with hydroxylated (or chlorosilane) compounds. The non-hydrolyzable unsaturated C-C bonds reported here open the way to other possibilities in terms of functionalizations including hydrosilylations, an important and efficient reaction for olefin functionalization¹⁵ that was chosen for functionalizing alkenyl laddersiloxanes **1** and **2**. Along these lines, **1** and **2** were allowed to react with dimethylphenylsilane as a model substrate in the presence of 2.5 mol% of Karstedt catalyst (Scheme 4). In the case of **1**, several non-identified products were formed, obviously resulting from the polymerization of the C=C bond, and the isolation of the expected laddersiloxane by GPC (Gel Permeation Chromatography) was not possible (Scheme 4, top). To our delight, hydrosilylation occurred cleanly and quantitatively starting from **2** and the desired laddersiloxane **3** was successfully isolated in 99% yield after purification through a plug of silica (Scheme 4, bottom).

Scheme 4. Hydrosilylation of laddersiloxanes **1** and **2** with dimethylphenylsilane in the presence of Karstedt's catalyst.



²⁹Si NMR spectrum of **3** displayed expected and previously described signals for T silicon atoms (**Si** in blue) corresponding to the **T₄** core (Figure 1). The chemical shift of D-group silicon atoms (**Si** in red) were shifted to δ -6.6 as compared to δ -15.2 in **2** which is in the favor of a successful reduction of the olefin. The appearance of two new singlets (**Si** in pink) at δ -3.7 and -4.0 respectively, was also consistent with the formation of the carbosilane moiety and the successful hydrosilylation of allyl fragments (Figure 1). The ¹H and ¹³C NMR spectra of compound **3** clearly demonstrated the quantitative disappearance of olefinic groups at around 5-6 ppm and 131 ppm (in ¹H NMR and ¹³C NMR respectively) and the appearance of new patterns corresponding to methylene groups formed during hydrosilylation (see SI). As in the case of laddersiloxanes **1** and **2**, both carbosilane groups (CH₂-CH₂-CH₂-**Si**(Me)₂Ph) bound to peripheral D-group silicon atoms (Scheme 4, **Si** in red) are not

magnetically equivalent and gave rise to two distinct patterns. Noteworthy, the results of MALDI-TOF mass spectroscopy of **3** supported very well the structure.

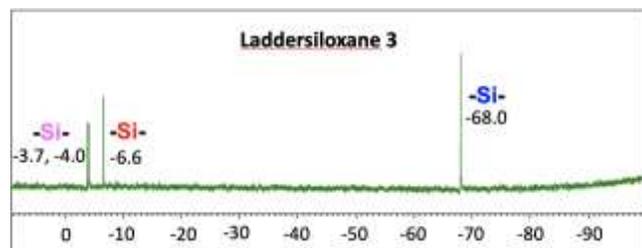
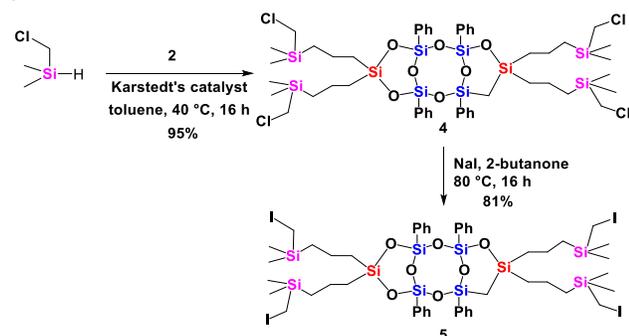


Figure 1. ^{29}Si NMR spectrum (CDCl_3) for the laddersiloxane **3**. Chemical shifts are in ppm unit.

More challenging chloromethyl(dimethyl)silane possessing a reactive chloro group was next tested as the hydrosilylation reagent (Scheme 5). Hydrosilylation occurred in quite similar reaction conditions as those used with dimethylphenylsilane. The expected laddersiloxane **4** could thus be quantitatively formed within 16h at 40 °C and isolated in 95% yield after purification over a plug of silica. A halogen exchange was next performed under typical conditions for Finkelstein reaction to lead to tetra-iodo laddersiloxane **5** in 81% yield (Scheme 5).¹⁶ The latter is expected to be highly reactive in further nucleophilic substitutions, thus opening the way to readily functionalizable ladder-type structures.

As expected, on the ^{29}Si NMR spectra of **4** and **5**, the chemical shifts of T- and D-group silicon atoms (**Si** in blue and **Si** in red respectively, Supporting Information, Fig. S12 and S15) were found to be very close to those of laddersiloxane **3**. The signals of the carbosilane silicon atoms (**Si** in pink) were found respectively at 3.1, 2.8 ppm for **4** and 4.7, 4.5 ppm for **5**. This observed shift to the left compared with laddersiloxane **3** is consistent with the stronger electro-withdrawing properties of phenyl groups in **3** (Figure 1). The slight shielding effect in the case of **5** relative to **4** is in accordance with the lower electronegativity of iodine. ^1H and ^{13}C NMR spectra were consistent with a quantitative hydrosilylation and as expected, the characteristic carbon atoms adjacent to the halides (Cl or I for **4** and **5** resp.) were quite different, δ -4.66, -4.33 ppm for **4** and δ -13.14, -13.06 ppm for **5** (Supporting Information, Fig. S11 and S14). The experimental MALDI-TOF mass spectroscopy and elemental analysis results of these two compounds were also found in good accordance with their calculated values.

Scheme 5. Hydrosilylation of **2** with chloromethyl(dimethyl)silane to lead to laddersiloxane **4** and halide exchange to yield laddersiloxane **5**.



The thermal stability of laddersiloxanes **1-5** was explored by thermogravimetric analysis (TGA) under a nitrogen stream.

The melting points of laddersiloxanes **1-3** which are solid compounds decreased from 196 to 81 °C with longer chains on the peripheral silicon atoms (See SI, Table S1). Besides, laddersiloxanes **1** and **2** displayed a T_{d5} (5 % weight loss) around 310 °C while the highest T_{d5} temperature (426 °C) was observed for laddersiloxane **3**. This higher thermal stability is likely due to the presence of phenyl groups on the peripheral chains.¹¹ Ladder structures **4** and **5** decorated with 4 chloro- or iodo-substituents respectively are viscous liquids and **4** was found to display a higher T_{d5} (357 °C) than **5** (315 °C).

In summary, novel 6-8-6 laddersiloxanes involving four reactive substituents - vinyl, allyl, chloride or iodide - were prepared and characterized by multinuclear ^1H , ^{13}C and ^{29}Si NMR, mass spectroscopy and elemental analysis. The synthetic method is simple and the expected laddersiloxanes are formed in high yields (81 to 99%) and purities. Olefin groups of the allyl-moieties from **2** were shown to react through hydrosilylation with various silanes including functional chloromethyl(dimethyl)silane. The resulting tetrachloro-substituted laddersiloxane **4** could be successfully transformed into the corresponding tetraiodo compound **5**. In summary, the various readily functionalizable tricyclic laddersiloxanes reported here for the first time constitute building blocks for preparing more complex organic-inorganic hybrid materials, the peripheral alkenes being moreover expected to react through various other reactions including metathesis, Heck or thiol-ene reactions. Potential areas of application range from the fields of electronics and optics to those of supported catalysis or nanocomposites. More generally, this work may open new opportunities to develop applications for ladder structures which remain underexplored to date compared to their double-decker or cage counterparts. Whatever the domain, original properties are expected due to the highly ordered double-chain structure that distinguishes laddersiloxanes from other polyhedral oligomeric silsesquioxanes.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data, ^1H , ^{13}C , and ^{29}Si NMR spectra, and Maldi-Tof MS spectra, and IR spectra, and TGA for all compounds **1-5**

AUTHOR INFORMATION

Corresponding Author

* E-mail: unno@gunma-u.ac.jp; armelle.ouali@enscm.fr.

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Conflict of Interest

The authors declare no conflict of interest.

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