Introduction

Silyl cations in general and silylium ions in particular can be classified as Lewis super acids due to their exceptionally high Lewis acidity.[1] Examples for tricoordinated silylium ions of the type \([R_3Si]^+\) are rare,[2–4] but their immense reactivity and Lewis acidity are attenuated by coordination of donor molecules, for example anions or solvent molecules, or by the intramolecular coordination of Lewis basic groups.[5] In this way, their Lewis acidity and reactivity can be controlled and, in some cases, even fine-tuned to suit the desired application.[6] An interesting mode, which conserves much of the original reactivity, is the stabilization of silylium ions by silanes through the formation of inter- or intramolecular 3c2e Si–H–Si bridges. Historically, the cyclic silyl cation 1 (Figure 1), obtained by a hydride transfer reaction from an \(\alpha,\omega\)-dihydridosilyl carbosilane, was the first well-documented example for such an interaction between a silane and a silylium ion.[7] During the last twenty years, additional examples of silylium ions that are stabilized by intramolecular 3c2e Si–H–Si bridges were characterized by NMR spectroscopy or X-ray diffraction (XRD) analysis.[11–15] It became also evident that the hydride transfer reaction of trialkylhydridosilanes in an excess of silane as solvent does not lead to the respective silylium ions, as initially proposed,[16,17] but results in the formation of the intermolecularly Si–H–Si bridged species.[18,19] This result underlined the general importance of this stabilization mode in silylium ion chemistry and the parallels to the activation of silanes by neutral boron or aluminum Lewis acids are obvious.[20–24] In further studies, the utility of 3c2e Si–H–Si bridges was demonstrated by using Si–H functionalities to trap intramolecularly silylium intermediates in sila-Wagner–Meerwein rearrangements of oligosilanes.[12,13] Although the silane/silylium ion interaction has been well studied by several research groups, the interaction between silylium ions and multiple Si–H groups (polyagostic interaction) has been investigated only in the case of spatially restricted polysilylarene derived cations 2 and 3 (Figure 1).[25,26] Cyclic Si–H–Si bridged cations seemed to be perfect precursors for the synthesis of bissilylium ions, a novel class of bidentate Lewis acids.[27–29] First attempts to use the Si–H–Si stabilized cation 4 undergoes at low temperatures a fast degenerate rearrangement, which exchanges the Si–H groups with a barrier of 31 kJ mol\(^{-1}\) via an antarafacial transition state. Reaction of the branched monocation 9 with a second equivalent of trityl cation or of the branched oligosilane 13 with two equivalents of trityl cation, gives at \(-80^\circ\)C the corresponding bissilylium ion 10, an example for a new class of highly reactive poly-Lewis acids.

Figure 1. Selected examples of Si–H–Si bridged silyl monocations 1–4 and examples for anion stabilized bissilylium ions 5–7.

Hydrogen-Bridged Oligosilanyl(silyl) Mono- and Oligosilanyl(silyl) Dications

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(Figure 1) as precursor for a potent bidentate bis(silyl) Lewis acid were unsuccessful in so far as the high reactivity of the generated dication decomposed the weakly coordinating [B-(C$_6$F$_5$)$_4$]$^-$ anion.[$^{14}$]

Recently, the Oestreich group succeeded in taming bis(silylium) ions 5–7 (Figure 1) by using halogenated carborate anions as external stabilizing donors, starting from either spatially well separated bis(hydridosilanes (for dications 5 and 6) or small cyclic Si–H–Si bridged cations (in the case of 7).[$^{30}$]

In the present work, we describe the results of our systematic study on a series of intramolecularly stabilized silyl cations, all featuring one or two six-membered cationic [Si$_5$H]$^+$ rings. This includes the persila-variant 8 of cation 1, the interaction of the cationic Si–H–Si bridge with additional Si–H functionalities in the branched oligosilylsilyl cation 9 and its transformation to dication 10 as an example for a bis(silyl) Lewis acid that is stabilized only by silane/silylium interaction (Figure 2).[$^{30–32}$]

**Results and Discussion**

The synthesis of starting material HMe$_2$Si(SiMe$_2$)$_3$SiMe$_2$H (11) was achieved by a series of salt metathesis steps involving PhMe$_2$SiLi[$^{33}$] followed by a protiodephenylation reaction of oligosilane 12 via silyl triflates and final introduction of the Si–H functionalities by lithium alanate (Scheme 1).[$^{34}$] Similarly, the branched oligosilane Si(SiMe$_2$SiMe$_2$H)$_4$ (13) was obtained via protiodephenylation of the tetraphenyl substituted oligosilane 14 followed by triflate to hydride substitution. The latter was synthesized in excellent yields (up to 86%) and high purity by multiple silyl group exchange, a protocol reported previously by the Marschner group (Scheme 1).[$^{35}$]

The newly synthesized silanes 11 and 13 were characterized by NMR spectroscopy, and mass spectrometry. The molecular structure of oligosilane 14 was further examined by XRD analysis (see Supporting Information for details). UV/vis analysis of 14 revealed an intensive long wavelength absorption at 252 nm reminiscent of the 255 nm reported for 12 (Scheme 1).[$^{36}$] This result rules out a significant influence of the branching at the central Si atom on the σ-conjugation.[$^{37,38}$]

The isolated oligosilanes 11 and 13 were used for cation synthesis by reaction with [Ph$_3$C][B(C$_6$F$_5$)$_4$] to form the respective oligosilylsilyl borates (Corey reaction, Scheme 2). All reactions had to be performed at low temperatures as the reactions of both oligosilanes with trityl borate using standard Corey conditions (room temperature, aromatic hydrocarbons or halo-hydrocarbons) resulted in intractable product mixtures.

After reaction of the linear silane 11 with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in chlorobenzene-$d_5$ at T = −40°C (Scheme 2), we observed the selective formation of the intramolecularly silane-stabilized silylium ion 8. Only three NMR signals are detected in the $^{29}$Si NMR spectrum at this temperature (Table 1, Figures S31–S34). While the $^{29}$Si nuclei of the SiMe$_2$ groups in position 1 and 2 of

![Figure 2. Oligosilylsilyl cations 8, 9 and dication 10 discussed in this work.](image-url)
the six-membered [Si,H]⁺ cycle resonate at very similar frequencies as the respective groups in the neutral precursor. The 29Si NMR chemical shifts in both solvents are practically identical (Table 1). Based on these results, we rule out structure-determining interactions between silyl cation 8 and chlorinated hydrocarbons, in agreement with previous studies on intramolecularly Si-H-Si bridged cations.[10,12,14]

At temperatures slightly higher than −80 °C, we observed in dichloromethane-d₆, the selective formation of the corresponding bis(silyl)chlorororn boreate 15([B(C₆F₅)₃]⁺) from the Si–H–Si bridged cation 8. This observation demonstrates the high reactivity of 8 (Scheme 3, see Supporting Information for details).

Subsequently, the hydride transfer reaction between the branched oligosilane 13 and one equivalent of [Ph₃C][B(C₆F₅)₃] was performed in dichloromethane-d₆ at T = −90 °C (Scheme 2). The obtained NMR spectroscopic data are in accordance with a highly dynamic behavior of cation 9 on the NMR time scale even at T = −90 °C. The ¹H NMR and ¹³C(¹H) NMR spectra are dominated by broad featureless signals that prevent a detailed analysis (Figures S52–S54). Therefore, the structural assignment of the formed silyl cation primarily relies on the 29Si NMR spectroscopic data (Table 1). In the 29Si[¹H] NMR spectrum of cation 9 (Figure 4, top spectrum), five signals are detected. The most upfield-shifted signal at δ²⁹Si = −124.8 is assigned to the central silicon atom Si¹ by comparison with the starting material 13 (δ²⁹Si = −119.2). The broad resonance of the Si³ atoms appear at δ²⁹Si = 89.1 (line width at half height, ω₁/₂ = 62 Hz) and it shows no detectable J₁H₂/₁H₃ splitting in the 29Si NMR spectrum at the same temperature (Figure 4, bottom spectrum). Upon cooling of the sample down to T = −93 °C, the downfield signal

**Scheme 3.** Formation of 15([B(C₆F₅)₃]⁺) in dichloromethane.
sharpens ($\omega_{\text{J}} = 43$ Hz) and a doublet splitting of $^{1}J_{\text{SiH}} = 31$ Hz becomes visible (Figure 4, insert in the bottom spectrum). Even at this temperature, the broad signals in the $^{1}H$ and $^{13}C(1^H)$ NMR spectra of 9 make an exact assignment of the signals impossible. Hence, the position of the signal of the bridging hydrogen atom cannot be detected by either 1D or 2D NMR spectroscopy. The silicon atom Si$^i$ resonates at $\delta^{29}\text{Si} = -34.3$ and splits up into a doublet in the hydrogen-coupled $^{29}\text{Si}$ NMR spectrum ($^{1}J_{\text{SiH}} = 170$ Hz, see Supporting Information for details). The observed $^{1}J_{\text{SiH}}$ coupling is almost identical to the one detected for the neutral starting material 12 ($^{1}J_{\text{SiH}} = 178$ Hz). The remaining two signals are broad singlets in the $^{29}\text{Si}$ NMR spectrum at $T = -90$ °C and are assigned to the silicon atoms Si$^i$ and Si$^i$. A distinction based on the experimental data is not possible. The results of $^{29}\text{Si}$ NMR chemical shift calculations support our structural assignment (Table 1).

We note here that the decisive NMR spectroscopic parameters of branched cation 9 are very similar to those of the monocyclic cation 8 (Table 1). There is no indication of an additional interaction of the non-bridging Si–H groups with the cationic Si–H–Si bridge in the ground state. For example, no reduced Si–H coupling constant is detected for the additional hydridosilane groups. Variable temperature (VT) $^{29}\text{Si}(1^H)$ NMR experiments reveal a strong dependency of the number of signals on the temperature (Figure 5).

With increasing temperature, the signals at $\delta^{29}\text{Si} = 89.0$ (Si$^i$) and $-34.2$ (Si$^i$) broaden and finally disappear at $T = -70$ °C. No averaged $^{29}\text{Si}$ NMR signal is detected for Si$^{15}$ up to $T = 20$ °C. At the same time, the signal at $\delta^{29}\text{Si} = -37.2$ and $-35.1$ (Si$^i$ and Si$^i$) broaden and an averaged signal at $\delta^{29}\text{Si} = -36.6$ appears (Figure 5). The underlying process is shown to be reversible upon renewed cooling (see Supporting Information for details). These observations suggest an intramolecular, reversible hydride transfer between the terminal dimethylsilyl groups and the dimethylsilyl groups that are involved in the Si–H–Si moieties of cation 9. This process equilibrates the Si atoms in $\alpha$ position (Si$^i$ and Si$^i$) and atoms in $\beta$ position (Si$^i$ and Si$^i$), respectively (Scheme 4).

The barrier of this process can be estimated from the VT $^{29}\text{Si}$ NMR data to be as low as $\Delta G^\text{IRR} = 31$ kJ mol$^{-1}$ (see Supporting Information, ch. 5). At $T = -20$ °C, the $^{1}H$ NMR spectrum shows first signs of decomposition which becomes rapid around $T = 0$ °C and results in a mixture of unidentifiable products (see Figure S113). The $^{1}H$ NMR data at increased temperatures support the dynamic process. Thus, three signals are visible in the $^{1}H$ NMR spectrum at $T = -30$ °C (see Figures S109–S111): A broad singlet at $\delta^{1}H = 2.89$ and two singlets at $\delta^{1}H = 0.45/0.55$ whose integral ratio of 3H ($\delta^{1}H = 2.89$):24H ($\delta^{1}H = 0.45/0.55$):24H ($\delta^{1}H = 0.45$) agrees with an averaging of all four disilyl units of cation 9 (Scheme 4).

The formation of cation 9 was further verified by a trapping reaction between silyl borate 9[B(C$_5$F$_5$)$_3$] and $^8$Bu$_3$SnD at $T = -40$ °C in toluene which resulted in the formation of the neutral, monodeuterated starting material 13-D$_1$ (Scheme 5, Supporting Information material, ch. 4).

The reaction of 13 with two equivalents of [Ph$_3$C]B(C$_5$F$_5$)$_3$ led even at $T = -80$ °C to a spontaneous decoloration of the reaction mixture which indicates the complete consumption of the trityl cation and the formation of the dication 10 (Scheme 6).
are detected at spectrum into a doublet with a coupling constant of 41 Hz (Figure 6, insert). The spectroscopic assignment is supported by 

\[ \text{[B(C_6F_5)_4]^2+} \] with one additional equivalent of trityl borate occurred immediately, even at \( T = -80^\circ \text{C} \) (Scheme 6). This suggests that the second hydride transfer from silyl cation 9 to trityl cation is fast, which contrast reports on the related carbosilane based dications 4–7, which are formed only at elevated temperatures and extended reaction times.\[14,30\] Similarly, the reaction of silyl borate 9 \([\text{B(C_6F_5)_4}]_2\) with one additional equivalent of trityl borate occurred immediately, even at \( T = -80^\circ \text{C} \) (Scheme 6). This suggests that the second hydride transfer from silyl cation 9 to trityl cation is fast, which contrast reports on the related carbosilane based dications 4–7, which are formed only at elevated temperatures and extended reaction times.\[14,30\] The NMR spectroscopic investigations verify that both reactions give the same product, \(10 \equal [\text{B(C_6F_5)_4}]_2\) which decomposes in dichloromethane at temperatures higher than \( T = -80^\circ \text{C} \). The NMR spectroscopic data indicate the high symmetry of the obtained oligosilanylsilyl dication 8 (\( \delta_{\text{Si-H}} = 0.55 \)) of the bridging Si–H–Si bridged hydrogen atom is observed by \(1^H \) NMR spectroscopy (Figure S90). The \(^{13}\text{C} [^1\text{H}] \) NMR spectrum of the reaction product also shows only two signals (Figure S87). In the \(^{29}\text{Si}[^1\text{H}] \) NMR spectrum, three singlet signals are detected at \( \delta^{29}\text{Si} = -121.4 \) (\( \text{Si}^1 \)), \(-34.4 \) (\( \text{Si}^2 \)) and 88.1 (\( \text{Si}^0 \)) (Figure 6). The latter splits in the hydrogen-coupled \(^{29}\text{Si} \) NMR spectrum into a doublet with a coupling constant of \( J_{\text{Si-H}} = 41 \) Hz (Figure 6, insert). The spectroscopic assignment is supported by \(^{29}\text{Si} \) NMR chemical shift calculations for a DFT-optimized molecular structure of 10 (Table 1).

Comparison of the NMR spectroscopic parameters of the cations 8–10 reveals \(^{29}\text{Si} \) NMR chemical shifts for the Si–H–Si silicon atoms in a very narrow range between \( \delta^{29}\text{Si} = 87–89 \) (Table 1). The \( J_{\text{Si-H}} \) coupling constants in these Si–H–Si bridges are small (\( J_{\text{Si-H}} = 31–41 \) Hz) as expected from the reduced bond order.\[10,14\] Finally, the \( ^1\text{H} \) NMR chemical resonances of the bridging hydrogen atoms in cations 8 (\( \delta^{29}\text{Si} = 0.73 \) in \( \text{CDCl}_3 \)) and in dication 10 (\( \delta^{29}\text{Si} = 0.81 \) in \( \text{CDCl}_3 \)) are found in a confined spectral region (Table 1). These NMR spectroscopic parameters are in the typically range reported for cationic 3c2e Si–H–Si bridges.\[9\] Interestingly, the presence of two positive charges in dication 10 does not influence its NMR parameters in any significant manner when compared to the monocaticonic silyl species 8 and 9.

For all three cations, the good agreement between calculated and experimental \(^{29}\text{Si} \) NMR chemical shifts is a sign of the quality of the molecular structures predicted by the DFT calculations. This allows a detailed discussion of structural and energetic parameters based on the DFT results. Cation 8 adopts a chair-like conformation of the Si,H ring, with a bent symmetric Si–H–Si bond (\( \alpha_{\text{Si-H-Si}} = 158^\circ \)), both silicon atoms are separated by 319 pm and the Si–H bond length is 163 pm. These structural parameters are typical for silane-stabilized silylium ions\[36\] and similar values are obtained for the 3c2e Si–H–Si groups of cations 9 and 10 (see Supporting Information for details). The strength of the Si–H–Si bond in silyl cation 8 is predicted to be 81 kJ mol\(^{-1}\) as calculated from the energy difference between an artificial linear silylium ion 16 and Si–H–Si bridged cation 8 (Scheme 7, see Figure S121 for computed structures).

For cation 9, we located several cyclic Si–H–Si bridged conformers of very similar energy. The maximal free enthalpy
difference at $T = -90^\circ C$ between these conformers is $\Delta G^{*183} = 17 \text{kJ mol}^{-1}$ (see Table S6). Compared to the isomeric silylium ion with an open structure (17), the conformer of 9a of lowest energy is stabilized by $\Delta G^{*183} = 90 \text{kJ mol}^{-1}$ (Figure 7). In agreement with the NMR data, no interactions between the [Si–H–Si]$^+$ moiety and the two remaining Si–H functionalities are evident in the computed structure 9a.

A transition state TS1 for the intramolecular hydride transfer (Scheme 4) was located 27 kJ mol$^{-1}$ above the conformer of lowest energy (Figure 7). TS1 is characterized by a pentacoordinated silicon atom that adopts a trigonal-bipyramidal environment with the approaching and leaving Si–H groups in the apical positions (antarafacial arrangement, Figure 8). The computed activation barrier for this process agrees with the activation energy of 31 kJ mol$^{-1}$ that was estimated based on the experimental VT$^{29}$Si NMR data (Figure 3).

Additionally, an alternative transition state TS2 for the intramolecular hydride transfer, which interchanges the Si–H groups in a suprafacial process was located (Figure 8). This transition state is markedly higher in energy ($\Delta G^{*183} = 61 \text{kJ mol}^{-1}$) and was hence ruled out (Figure S124). The intramolecular antarafacial process involving TS1 with its pentacoordinated silicon atom agrees well with the similar structural motif suggested by Nikonov and co-workers for the arene based silyl cation 2 (Figure 1).

For dication 10, the calculations predict the expected spirocyclic structure of C$_2$ point group symmetry (Figure 9). The first Si–H–Si group stabilizes dication 18 by 85 kJ mol$^{-1}$ compared to its non-bridged isomer 19. Interestingly, dication 10 with two Si–H–Si bridges is lower in energy by additional 120 kJ mol$^{-1}$ compared to dication 18 (Figure 10, Figure S121).

Figure 7. Part of the potential energy surface of 9 that shows the intramolecular hydride transfer in 9 (Scheme 4) ($\Delta E$: electronic energy; $\Delta G^{*183}$: Gibbs energy at 183K, both calculated at M06-2X/6-311 + G(d,p)).

Figure 8. Schematic representation of the orbital interactions in the different transition states TS1 and TS2.

Figure 9. Computed C$_2$-symmetric structure of dication 10 and important parameters of the Si–H–Si bridge (at M06-2X/6-311 + G(d,p), all hydrogen atoms but the Si–H atoms are omitted for clarity, $\Sigma \alpha$: sum of the bond angles at Si$^3$ involving its three carbon substituents).

Figure 10. Comparison of the relative energies of carbodication 20 and silyl dication 10 with their non-bridged isomers. Tricoordinated carbon or silicon units are marked in red ($\Delta E$: electronic energy; $\Delta G^{*193}$: Gibbs energy at 193K, both calculated at M06-2X/6-311 + G(d,p)).

For dication 10, the calculations predict the expected spirocyclic structure of C$_2$ point group symmetry (Figure 9). The first Si–H–Si group stabilizes dication 18 by 85 kJ mol$^{-1}$ compared to its non-bridged isomer 19. Interestingly, dication 10 with two Si–H–Si bridges is lower in energy by additional 120 kJ mol$^{-1}$ compared to dication 18 (Figure 10, Figure S121). This strong stabilization rules out the possibility for hydrogen exchange between the two Si–H–Si groups and is in qualitative agreement with the static structure of 10 detected by NMR spectroscopy in solution. A comparison with the isostructural carbodication 20 synthesized by Sorensen is interesting.\cite{40} In contrast to the silicon species 10, carbodication 20 undergoes a
rapid mutual exchange between the two C–H–C groups via a non-hydrogen bridged cations, in agreement with the much smaller calculated stabilization of 20 by the hydrogen bridges (29–36 kJ mol−1 per C–H–C bridge, Figure 10, Table S4, Figure S122).

Conclusion

The high utility of 3c2e Si–H–Si bridges to stabilize otherwise short-lived and highly reactive cationic oligosilane species at low temperatures was demonstrated. NMR data and the quantum mechanical derived structural parameters of cation 8 are very close to those determined for previously carbon based bissilylhydronium ions, such as 1 and 4; however, the high reactivity and the thermal instability of the persila-analogue 8 is remarkable. The installation of additional hydridodimethylsilyl groups as in the branched cation 9 leads to a highly dynamic situation due to the fast interchange between Si–H groups coordinated to the silylium ion and free Si–H groups. This intramolecular Si–H group exchange proceeds via an associative mechanism with a very low barrier of approx. 30 kJ mol−1 along a pentacoordinated transition state. The intramolecular process studied for cation 9 serves as a general model also for intermolecular [R3Si–H–SiR3]−/SiR3 group exchange in solutions of silylium ions in silanes.18 It is interesting to note that beside this dynamic process, there is no interaction between the free Si–H groups and the cationic Si–H–Si bridge in the sense of polyagostic interaction in the ground state of cation 9.

The second hydride transfer reaction between trityl cation and silyl cation 9 is remarkably facile. Even at −80 °C, it proceeds immediately to completion and yields exclusively dication 10. This suggests that the second ionization step occurs at silane groups that are spatially separated from the positively charged [Si–H–Si]2+ moiety and that the existing and the evolving cation are also electronically isolated by the oligosilane backbone. This is also supported by the close agreement of the NMR spectroscopic parameter for the cationic [Si–H–Si]2+ units in monocations 8 and 9 compared to those of dication 10. The formation of two independent [Si–H–Si]+ groups confers to 10 a high conformational stability. The mutual exchange of the Si–H groups is excluded due to the high binding energy of 85–120 kJ mol−1 between the individual silylium ions and the silane unit. This distinguishes dication 10 from the corresponding dicarbocation 20, which undergoes fast C–H/C–C bond exchange due to the lability of the 3c2e [C–H–C]+ bond.

The immediate synthesis of the silane-stabilized bissilylium ion 10 at low temperature contrasts recent results by the Oestreich group, who reported the preparation of carbonate-stabilized bissilylium ions 5–7 by hydride transfer from carbon-tethered bissilanes at room temperature with reaction times up to several days.26 In the case of compound 7, it is not completely clear whether the rate-retarding factor is the stability of the Si–H–Si bridge of the intermediate bissilylhydronium carbonate or its low solubility in the applied solvent. Our approach using tetrahydridosilanes as precursors and forming independently two silane-stabilized silylium ions is of advantage in respect of reaction temperature and time. Bissilylium ion 10 is a new example of a bidentate Lewis acid with largely unquenched silylium-ion character.27–29 The two intramolecular [Si–H–Si]+ units provide two electronically independent, highly Lewis acidic centers in one molecule. We expect this arrangement to be highly favorable for future catalytic application, for example, in hydrodefluorination reactions, and we will transfer it to other more robust molecular frameworks.6,41,42

Experimental Section

All hydride transfer reactions were performed as NMR experiments following the same protocol. The specified amount of [Ph3C][B-(C6F5)4] was directly weighted into an NMR tube which was then evacuated for 30 min and gently flushed with nitrogen. In the NMR tube, [Ph3C][B(C6F5)4] was then dissolved in the respective NMR solvent and the resulting solution was cooled to the temperature needed for the NMR experiment using a cooling bath. Subsequently, the hydrogen-substituted silane, dissolved in the used NMR solvent, was slowly added by syringe. The addition proceeded slowly so that the silane-containing solution cooled down while it went down on the glass walls of the cooled NMR tube. In this way, biphasic mixtures were obtained. The NMR tube was sealed, removed from the cooling bath, and thoroughly mixed. The mixing proceeded as fast as possible so that a warming-up of the reaction mixture was minimized. Directly after mixing, the NMR tube was put back into the cooling bath, transferred into the precooled spectrometer and measured.

The handling of the NMR tubes was performed in specially designed glassware that allowed for the evacuation of the NMR tube and the subsequent handling under nitrogen. To guarantee a good thermal conduction between cooling bath and the solution in the NMR tube, the room between the glassware and the inlying NMR tube was filled with n-hexane.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.
