A linear C=Ge=C heteroallene with a di-coordinated germanium atom

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Abstract
Allenes (>C≡C≡C<) are classified as cumulated dienes that have a linear structure with an sp-hybridized central carbon atom. We have succeeded in synthesizing and isolating a stable 2-germapropadiene derivative with bulky silyl substituents. The 2-germapropadiene allene moiety adopts a linear structure both in the solid state and in solution. In addition, an X-ray diffraction electron-density-distribution analysis of this 2-germapropadiene revealed a linear C=Ge=C geometry with a formally sp-hybridized germanium atom bearing two orthogonal C=Ge π-bonds. Based on detailed structural and computational studies, it can be concluded that the linear geometry of the isolated 2-germapropadiene most likely arises from the negative hyperconjugation of the silyl substituents at the terminal carbon atoms. The 2-germapropadiene reacts rapidly with nucleophiles, indicating that the linearly oriented germanium atom is highly electrophilic.

Keywords

Introduction
Allenes (R₂C≡C≡CR₂) contain one central carbon atom that shares two double bonds with two adjacent carbon atoms.¹ The central carbon atom in an allene is sp-hybridized, which results in the formation of a linear structure. Allenes in possession of strong electron-donating ligands, such as N-heterocyclic carbenes (NHC, R₂C moieties), at the terminal carbon atoms are known to have a bent structure (Chart 1).² These structures are known as “carbones”, i.e., carbene-stabilized C(0) species. The central carbon atom of a carbone possesses four valence electrons in the form of two lone pairs that are stabilized by donor-acceptor interactions between the central atom and the adjacent carbene moieties. Accordingly, the characteristic bent structure of a carbone is best interpreted in terms of the bonding character of the carbone, R₂C:→C(0)←:CR₂. Thus, the electron-donating R₂C: carbene moieties with weak π-accepting ability
enhance the electron density on the central carbon atom, which results in the bent structure due to two lone pairs on the C(0) center. In addition, heavy zero-valent group-14 compounds, so-called “tetrylones,” with the general formula \( \text{R}_2\text{E} \rightarrow \text{E}(0) \rightarrow \text{ER}_2 \) (\( \text{E} = \text{Si}: \text{silylone}; \text{Ge}: \text{germylone}; \text{Sn}: \text{stannylone}; \text{Pb}: \text{plumbylone} \)) are heavy congeners of carbones that have attracted considerable interest. Recently, the synthesis of the tin\(^4\) and lead\(^5\) analogues has been achieved, completing the synthesis of the entire series of tetrylones. Given that the central atom of the tetrylones has lone pairs with both \( s \)-character and \( p \)-character, their \( \text{E} \text{-E} \text{-E} \) angles should be close to 90° due to the \( p \)-character \( \text{E} \text{-E} \) bonds. However, the inclusion of more \( s \)-character in the \( \text{E} \text{-E} \) bonds could result in a widening of the \( \text{E} \text{-E} \text{-E} \) angle, resulting in a more \( sp \)-hybridized central atom together with \( p \)-character lone pairs. Accordingly, the lone pairs should donate electron density much more effectively to the ligands of the \( :\text{ER}_2 \) moieties, resulting in the pronounced \( \pi \)-bonding character of the \( \text{E} \text{-E} \) moieties. Germylones represent an isolable class of tetrylones characterized by a central germanium atom accompanied by a variety of ligands. The \( \text{E-Ge-E} \) angle of germylone \( \text{B}^6 \) (86.5(1)°) shown in Chart 1 is close to 90°, while the \( \text{E-Ge-E} \) bond angles in \( \text{C}^7 \) (114.71(6) - 115.27(6)°) and \( \text{D}^8 \) (\( \text{Si-Ge-Si}: 132.38(2)°, \text{Ge-Ge-Ge}: 122.61(6)° \)) are wider than that of \( \text{B} \), suggesting that they possess effective \( \pi \)-bonding character.

However, unlike all-carbon allenes, tetrylones with a linear structure have not yet been reported, probably due to the intrinsically unfavorable hybridization of heavier main-group elements caused by the large differences between the size of their \( ns \) and \( np \) orbitals. The previously reported tetrylones shown in Chart 1 have lone pairs with \( s \)-character and \( p \)-character on account of the electron-donating character of the terminal ligands. Thus, a tetrylone bearing an electron-accepting carbene moiety could exhibit a linear structure with two \( \pi \)-bonds as is the case in all-carbon allenes.

**Chart 1.** Previously reported tetrylones A-D.

Recently, we have reported the synthesis of a stable \( \lambda^4 \)-sulfane \( \text{R}^\text{S}^2 \text{C}=\text{S}=\text{CR}^\text{S}^2, \text{R}^\text{S} = \text{Pb}_2\text{MeSi} \) which represents the first example of a heteroallene centered with a group-16 atom that uses bulky silyl substituents. Moreover, the corresponding \( \lambda^4 \)-selane and \( \lambda^4 \)-tellane were successfully synthesized using the same substituents. These heteroallenes exhibit allene-
type structures with pseudo $C_{\infty v}$ symmetric bent $>\text{C}=$Ch=$=\text{C}<_{\text{ (Ch = S, Se, Te)}}$ moieties that contain a 3-center-4-electron $\pi$-bond, similar to ozone ($O_3$). These results differ significantly from those reported by Arduego$^{11}$ and co-workers in which a bis(methylene)-$\lambda^4$-sulfane with $\pi$-donor and $\pi$-acceptor substituents on the carbon atoms result in an asymmetric ylide-type structure. The difference between the electronic structure of our bis(methylene)-$\lambda^4$-sulfane and theirs may be explained in terms of the character of the terminal ligands, i.e., the disilylcarbene ligands in our case can appropriately stabilize the $S=$C $\pi$ electrons due to the negative hyper conjugation of the silyl substituents. Accordingly, we expected that allene-type molecules centered with heavy group-14 elements and in possession of disilylcarbene moieties ($R^2_{\text{Si:C}}$) would also exhibit unique structures and properties. Herein, we report the isolation of a stable 2-germapropadiene with a linear $>\text{C}=$Ge=$=\text{C}<_{\text{ moiety and a formally } sp\text{-hybridized Ge atom. Moreover, we discuss both its reactivity and its electronic structure based on the results of a single-crystal X-ray electron-density-distribution (EDD) analysis.}}$

Results and discussion

Synthesis


Disilylcarbenoid $(\text{Ph}_2\text{MeSi})_2\text{CBrLi}$ was generated in situ by treating $(\text{Ph}_2\text{MeSi})_2\text{CBr}_2$ with tBuLi (2.1 equiv.) in THF at $-95^\circ\text{C}$. Subsequently adding dichlorogermylene dioxane complex (1.0 equiv.) at the same temperature afforded 2-germapropadiene 1 as pale-yellow crystals in a 50% yield (Scheme 1).

Structural characterization of 2-germapropadiene 1
Figure 1. a) Molecular structure of 2-germapropadiene I and b) its side view with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for I: C1-Ge1: 1.7764(2), C2-Ge1: 1.7740(2), C1-Si1: 1.8570(2), C1-Si2: 1.8577(2), C2-Si3: 1.8521(2), C2-Si4: 1.8524(2), C1-Ge-C2: 178.16(1), Si1-C1-Si2: 131.00(1), Si1-C1-Ge1: 115.44(1), Si2-C1-Ge1: 113.33(1), Si3-C2-Si4: 128.28(1), Si3-C2-Ge1: 115.73(1), Si4-C2-Ge1: 115.74(1).

2-Germapropadiene I was characterized using NMR and ultraviolet-visible (UV-vis) spectroscopy, Infrared (IR) spectroscopy, mass spectrometry, and single-crystal X-ray diffraction analysis (Figure 1). The central C-Ge-C moiety of I exhibits a linear geometry (C-Ge-C angle: 178.16(1)°) with two C-Ge bonds that are almost identical in length [C1-Ge1: 1.7764(2) Å; C2-Ge1: 1.7740(2) Å]. The structural features of I are almost identical to those of the theoretical studies on H₂C=Ge=CH₂ reported by Apeloig.¹³ These bond lengths are some of the shortest among typical C-Ge double bonds, which generally range from 1.80 to 1.84 Å in hitherto reported germenes.¹⁴ The C-Ge bonds in I are about 10% shorter than the C-Ge single bonds (1.979(9) Å) in bis(trimethylsilyl)methyl-substituted digermene¹⁵ and significantly shorter than those of the carbene-coordinated germynes B (1.965(3)-1.961(3) Å)⁶ and C (1.9386(16)-1.9417(15) Å)⁷ in Chart 1. This reduction in bond length is slightly larger than those reported for germenes (about 6-8%), which suggests that the double-bond character in R₂C=Ge=CR₂ is more pronounced than in germenes. This bond length is also slightly shorter than that of 1-germapropadiene (1.783(2) Å),¹⁶ and significantly shorter than that of 2-germapropadiene with a tetra-coordinated germanium atom (1.882(2) Å).¹⁷ The allenic moiety of the previously reported 1-germapropadiene and 2-germapropadiene exhibit a bent structure and a pyramidal germanium atom, respectively. In contrast, the two terminal carbons of I are almost planar (sum of the bond angles for C1: 359.8(1)° and for C2: 359.8(1)°), indicating that the structural properties of 2-germapropadiene I are considerably different from those of the 1-germapropadiene. Furthermore, the planes of C1-Si1-Si2 and C2-Si3-Si4 deviate slightly from being perpendicular to each other (78.99°) due
to the steric repulsion among the silyl groups. The C-Ge bond distances for bis(carbene)germylone (1.965(3) Å and 1.961(3) Å) are much longer than those of 1. The C-Ge-C angles of acyclic germylone C, where no allenic character was identified, fall in the range 114.71(6)-115.27(6)°.

Figure 2. Static model maps of 1 on the section of the a) C1-Ge1 and b) Ge1-C2 bonds including the top of each C-Ge bonding electron density. Contours were drawn at 0.005, 0.05, and −0.02 e Å⁻³ intervals for dashed-blue, blue, and red lines, respectively.

To obtain experimental information on the electronic structure of 1, we performed an X-ray EDD analysis based on the Hansen-Coppens formalism. The EDD analysis revealed that the C-Ge-C sites have mutually nearly orthogonal (ca. 94°) π-electron clouds as electron density spreads on each C-Ge bond almost perpendicular to the adjacent C-Si₂ plane (Figure 2). An apparent electron density of lone pairs on the Ge atom was not observed on the static model maps. As a result of the atoms-in-molecule (AIM) analysis, the C-Ge bonds are characterized by the positive electron density (ρ_{BCP}: 1.112(8) e Å⁻³ for C1-Ge1 and 1.102(8) e Å⁻³ for C2-Ge1) and the small positive Laplacian (\nabla²ρ_{BCP}: 1.519(19) e Å⁻⁵ for C1-Ge1 and 1.599(19) e Å⁻⁵ for C2-Ge1) values at the bond critical points (BCPs). Moreover, the negative values of the total energy density H at the BCPs of the C-Ge bonds (C1-Ge1: −0.92 Hartree Å⁻³; C2-Ge1: −0.91 Hartree Å⁻³) exhibit the polar and covalent nature of the C-Ge bonds. The bond ellipticity at the bond critical point of the C-Ge bond was 0.14 for both C1-Ge1 and C2-Ge1. For comparison, the same parameter for the C-C bond in the benzene ring is 0.13-0.23, suggesting that the C-Ge bonds in 1 have considerable π-bonding properties. These results suggest that the central atom of 1 is a simple di-coordinated germanium atom with formally sp-hybridized C-Ge bonds. Furthermore, the bonding electron density on the Si₃-C2 (Figure 2a) and Si2-C1 (Figure 2b) bonds are spread over each of the adjacent electron densities on the C-Ge bonds.
This electron delocalization may come from the negative hyperconjugation from the Si atom to the C-Ge bond. To investigate the multiple-bond character of 1 by vibrational spectroscopy, we recorded the IR spectrum (KBr, pellet) of 1 in the solid state (Figure S38), which the C=Ge=C asymmetric stretching frequency of 1 at 973 cm\(^{-1}\) and the assignment of this IR shift was supported by DFT calculations (1024 cm\(^{-1}\)) at the B3PW91/6-311G(2d,p) level. The C=C=C asymmetric stretching frequency of 1,1,3,3-tetrakis(trimethylsilyl)allene appears at 1870 cm\(^{-1}\). Consequently, the frequency of the stretching vibration reflects the bond strength of the allene moieties.

The UV-vis spectrum of 1 in THF shows absorption maxima at \(\lambda_{\text{max}} = 265\) nm (\(\epsilon = 11000\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)), 272 nm (\(\epsilon = 12000\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)), and 283 nm (\(\epsilon = 11000\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)), indicating isolated \(\pi\)-bonding without any conjugation, as is the case with all-carbon allenes (Figure S37). Time-dependent density-functional theory (TD-DFT) calculations at the TD-B3PW91/6-311++G(2d,p)/B3PW91/6-311G(2d,p) level for 1 suggest that a mixture of two \(\pi-\pi^*\) transitions (HOMO-1 \(\rightarrow\) LUMO and HOMO \(\rightarrow\) LUMO+2; Figure 3) result in one strong absorption peak at 272 nm (\(f = 0.3218\)), which is comparable to the observed \(\lambda_{\text{max}}\) values for 1. The \(\lambda_{\text{max}}\) values of 1 are significantly different from those of the trisilaallene (584 nm, \(\epsilon = 700\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)) with a bent structure. Our previously reported RSi\(_2\)C=CH=CR\(_2\)Si\(_2\) compounds (Ch = S, Se, Te) have bent structures both in the solid state and in solution and show characteristic absorptions at \(\lambda_{\text{max}} = 449\) nm (Ch = S), 523 nm (Ch = Se), and 610 nm (Ch = Te), indicating the presence of strong interactions between each of the C-Ch multiple bonds due to their bent structures. In the \(^1\)H NMR spectrum of 1 in benzene-\(d_6\) at room temperature, the methyl protons of the silyl substituents were observed as a sharp singlet, suggesting that 1 adopts a highly symmetric structure in solution. The \(^{13}\)C NMR spectrum of 1 at room temperature showed a signal at 85.2 ppm, which is consistent with that of allene carbons. Gauge-independent atomic orbital (GIAO) \(^{13}\)C NMR calculations for 1 afforded a value of 86.0 ppm, which is also consistent with the experimental results, albeit that this value is slightly down-field shifted relative to that of tetrakis(trimethylsilyl)allene (\(\delta = 64.0\)).\(^{19}\) In their entirety, these results indicate that the allene structure is maintained in solution.
Figure 3. Kohn-Sham molecular orbitals of 2-germapropadiene 1, calculated at the B3PW91/6-311G(2d,p) level. The HOMO and HOMO-1 involve the two C-Ge π-bonds. The LUMO and LUMO+2 involve the two C-Ge π*-bonds.

Electronic structure of 1

To investigate the electronic structure of 1, we performed theoretical calculations. Geometry optimization of the structure of 1 at the B3PW91/6-311G(2d,p) level afforded parameters that are in good agreement with those obtained from the X-ray crystallographic analysis. Natural-bond-orbital (NBO) calculations\textsuperscript{20} on the optimized structure of 1 showed that the C-Ge bonds have two almost degenerate π orbitals (HOMO and HOMO-1) and two corresponding π* orbitals (LOMO and LUMO+2) (Figure 3). The molecular orbital occupancy for 1 is consistent with predictions made for both the parent allene \((\text{Me}_3\text{Si})_2\text{C}=:\text{C}=(\text{SiMe}_3)_2\) and its germanium analogue \((\text{H}_3\text{Si})_2\text{C}=:\text{Ge}=:\text{C}(\text{SiH}_3)_2\) (Figures S35 and S36). These calculations are consistent with an allene molecule in possession of \(sp\)-hybridized C–Ge bonds together with the corresponding π-bonds. The estimated bond order of the two C-Ge bonds in 1, based on its Wiberg bond index (WBI) of 1.384, which is by a factor of 1.89 higher than the value of 0.7316 obtained for the C-Ge single bond in 2 (\textit{vide infra}), indicating that the C-Ge bonds in 1 have significant π-bond character. The calculated natural-
population-analysis (NPA) charge on the germanium atom was +1.76, while the charge on each of the adjacent carbon atoms was −1.86. The theoretically optimized structure of the less bulky (H₃Si)₂C≡Ge≡C(SiH₃)₂ shows a linear structure (Figure 3a), indicating that the silyl groups on the carbon atoms are essential to obtain the linear structure. This is a result of the localized negative charge on the allene carbons that arises from the α-effect of the silyl substituents.²¹ The C(allene)-Si bonds (1.8521(2) - 1.8577(2) Å) are shorter than the C(phenyl)-Si bonds (1.8734(5) – 1.8845(2) Å) in 1. In general, silyl-substituted carbanions exhibit almost planar structures and their C-Si bond lengths (ca. 1.80 Å) are approximately 5% shorter than those of neutral species (~ 1.90 Å).²² The shorter Si-C bonds found in the carbanions and the planarity of the ion can be attributed to the delocalization of the charge on the carbanionic carbon via negative hyperconjugation, which endows them with partial double-bond character. Thus, the electronic structure of a 2-germapropadiene bearing silyl groups can be rationalized by the contribution of resonance structures possessing two localized positive charges on the germanium atom and negative charges on each terminal carbon atom (Figure 4a). In contrast, the optimized structure of (H₂N)₂C≡Ge≡C(NH₂)₂, which is found in zero-valent germylones, has a bent form (Figure 4b). This can be attributed to the strong electron donation of the diaminocarbene s to the germanium atom. In addition, the resonance structures of germylones localize the negative charge on the germanium and the positive charge on the carbon atoms. The electronic structure of (H₂N)₂C≡Ge≡C(NH₂)₂ is the complete opposite to that of the silyl-substituted 2-germapropadiene. We found that the electronic properties of the substituents on the carbon atoms have a significant influence on the overall molecule, and that the silyl substituents play an active role in obtaining such novel linear heavy allenes.

Figure 4. a) Resonance structures suggested for the description of bonding in (H₃Si)₂C≡Ge≡C(SiH₃)₂ and b) (H₂N)₂C≡Ge≡C(NH₂)₂.
Figure 5. a) Thermolysis of 1 and b) the molecular structure of 3-sila-1-germacyclobutene 2 with thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for 2: C1-Ge1: 1.800(2), C2-Ge1: 1.987(2), C1-Si1: 1.982(2), C2-Si1: 1.852(2), C1-Ge1-C2: 95.18(6), Ge1-C1-Si1: 89.95(7), C1-Si1-C2: 93.70(7), C1-Ge1-C3: 134.31(7), C2-Ge1-C3: 130.32(6), Ge1-C1-Si4: 135.29(9), Si1-C1-Si4: 134.66(9). c) DFT-derived energy diagram for the isomerization between 1 and 2, calculated at the B3PW91/6-311G(2d,p) level.

In contrast to the considerable thermal stability observed, both in the solid state and in solution, for the trisilaallene⁸ and tetrakis(trimethylsilyl)allene,¹⁸ 1 decomposes in solution gradually at room temperature or after 2 h at 60 °C to quantitatively furnish the corresponding cyclic isomer 3-sila-1-germacyclobutene 2 after 1,3-migration of the phenyl group (Figure 5a,b). To investigate the reaction mechanism for this thermal isomerization, we performed theoretical calculations and a kinetic study. The potential energy surface (Figure 5c) contains two transition states (TS1 and TS2) and one intermediate (Int). The first step is the formation of an intermediate via 1,3-migration of the phenyl group with an energy barrier of 23.6 kcal mol⁻¹ for the generation of Int. The experimental activation barrier of ΔG‡ = 24.9 kcal mol⁻¹ (ΔH‡ = 20.4 kcal mol⁻¹; ΔS‡ = −15.2 kcal mol⁻¹), which was estimated based on an Eyring plot, leads to the 1-sila-3-germabutadiene as an intermediate (Figure S39). The negative value for ΔS‡ is acceptable as the intramolecular rearrangements and consistent with the calculated values of the isomerization. Subsequently, Int produces cyclic isomer 2 via TS2. Other forms of thermal isomerization that give the corresponding three-membered rings of tetrasiyl-substituted trisilaallene²¹ and tristannaallene²² have also been reported. These products arise from the large contribution of the metallylene-substituted vinylidenes heavier analogues. Thus, it seems that 2-germapropadiene 1 exhibits an electronic structure that is different
from these compounds.

**Reactivity of 2-germapropadiene 1**

The results of some reactions of 2-germapropadiene 1 are summarized in Scheme 2. The products are formed quantitatively in all cases, as determined via a $^1$H NMR analysis (for details, see the Supplementary Information). Reactions of 1 with various nucleophiles were performed to investigate the electrophilicity of the germanium atom as indicated by the canonical structure shown in Figure 4. The reactions of 1 with the H$_2$O, CH$_3$OH, and EtOH proceeded smoothly to produce germanediol 3, dialkoxygermane 4, and 5, respectively, via nucleophilic additions to the germanium center. It should also be noted here that the germanium atom is always the most electrophilic atom in the C=Ge=C allene moiety. These reactions reflect the electronic structure of the silyl-substituted 2-germapropadiene and stand in contrast to the reported reactivity of trisilaallenes with cyclic alkyl groups while similar reactivity has been shown in the case of a tetrASYl-substituted trisilaallene. The structure of the tetrasy1-substituted trisilaallene has not been determined via X-ray analysis, but its central Si-Si-Si angle was theoretically estimated to be $164.3^\circ$. Thus, the electronic structure of 2-germapropadiene 1 is similar to that of a tetrasy1-substituted trisilaallene.

Furthermore, the reaction of 1 with the nucleophilic reagent CH$_3$Li resulted in the formation of dimethylgermanium dianion 6, which was structurally characterized via single-crystal X-ray diffraction analysis. The addition of H$_2$O or CH$_3$I to 6 resulted in the quantitative formation of protonated 7 or methylated 8, respectively. In contrast, 1 was found to be inert toward electrophilic res such as CH$_3$I or C$_2$H$_5$Br, where heating of 1 with these electrophiles gave only thermal decomposition product 2. These results indicate that the germanium atom of 1 is strongly electrophilic and that the reactivity of 1 reflects its predicted canonical structures.

**Scheme 2.** Reactions of 2-germapropadiene 1 with H$_2$O, CH$_3$OH, C$_2$H$_5$OH, and CH$_3$Li to produce the corresponding addition products (3-8).

**Conclusions**

We have reported the synthesis, structure, and properties of stable 2-germapropadiene
(Ph₂MeSi)₂C=Ge=C(SiMePh₂)₂ (1), which exhibits a linear structure. The allene-bond character of 1 was fully examined using spectroscopic means and single-crystal X-ray diffraction analysis, theoretical calculations, and a reactivity study. The principal features of 1 are the almost linear C-Ge-C moiety and its planar tricoordinate carbon atoms. We have demonstrated that electron-accepting carbenes such as a disilyl carbene result in a C=Ge=C allene with C–Ge bonds that have higher sp-character, which results in the formation of a linear structure. Heavier analogs of allenes, which had previously been considered to adopt a bent structure, were found to adopt a linear structure depending on their substituents. The title compound, with its high reactivity and high stability, has the potential to open up new avenues in the chemistry of the main-group elements.

Funding Sources
This research was funded by JSPS KAKENHI grants JP18K14204 and 20K05468 from MEXT (Japan).

Supporting Information
Experimental procedures, NMR data, X-ray crystallographic analysis, computational details, kinetic experiments, and electrochemical experiments (PDF). Computational data of coordinates (xyz).

Accession Codes
CCDC 2220028, 2218722-2218727 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, 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.

ACKNOWLEDGMENTS
We would like to thank Dr. Nobuhiro Yasuda, Dr. Kunihisa Sugimoto, and Dr. Yuiga Nakamura at JASRI BL02B1 of SPring-8 (2020A0557, 2020A0834, 2020A1056, 2020A1644, 2020A1650, 2020A1656, 2021A1592, 2021A1578, 2021B1435, 2021B1833, 2021B132, 2021B1798, and 2022A1200). Furthermore, the authors would like to thank Prof. T. Sasamori (University of Tsukuba) for his kind assistance and helpful discussions. The authors are also grateful to Dr. U. F. J. Mayer from Mayer Scientific Editing (http://www.mayerscientificediting.com/) for his assistance and the kind discussions during the preparation of this manuscript.

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