ORGANOMETALLICS

Interconversion among Dianionic, Anionic, and Neutral Compounds Bearing a Bond between Two Pentacoordinated Germanium Atoms

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Ⓢ Supporting Information

ABSTRACT: The first dianionic compounds bearing a bond between two pentacoordinated germanium atoms have been synthesized in a stable form as candidates for a core unit to construct unprecedented structures in group 14 element chemistry. X-ray crystallographic analysis and computational study indicated the single-bond character of the Ge−Ge bond. They were reversibly converted to the anionic and neutral Ge−Ge-bonded compounds while maintaining the coordination number of the germanium atoms. The interconversion features changes in structures around the germanium atoms, including changes from a staggered conformation of the Ge−O bonds to a parallel conformation.
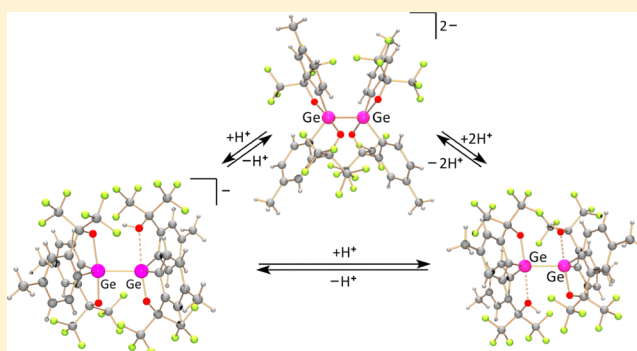
INTRODUCTION

Homonuclear E−E bonds of heavier group 14 elements E, where E is silicon, germanium, and tin, are fundamental and principal core units of the compounds containing these elements, such as polymers.[1] The heavier group 14 elements can be pentacoordinated, and such a species of trigonal-bipyramidal (TBP) structure is found as both a reactive intermediate and an isolated stable compound.[2] A homonuclear bond consisting of two pentacoordinated group 14 elements may provide compounds with characteristics of both the E−E bond and pentacoordinated species, and it will be a good candidate for a core unit to construct unprecedented structures in group 14 element chemistry. For silicon, there are increasing numbers of neutral Si−Si compounds bearing a highly coordinated silicon atom using chelate or bridging ligands,[3] including a polysilane of a hexacoordinated silicon chain.[4] In addition, even a dianionic species with a bond between two pentacoordinated ate-type silicon atoms is accessible.[5] For germanium, in contrast, the study on such a species is more difficult because of the unavailability of ^{73}Ge NMR spectroscopy for practical structure determination. Another difficulty arises from its instability; as Zaitsev and Karlov described, "*Ge−Ge compounds with a hypercoordinate Ge atom are the most unstable among the group 14 compounds.*"[6] Indeed, a Ge−Ge bond including one or two pentacoordinated atoms has been found only in a limited number of neutral compounds using an atrane framework[6] or trichloroacetate[7] or triflate[8] ligands that bridge two germanium atoms (Chart 1). We report here the synthesis and crystal structure of dianionic compounds with a bond between pentacoordinated germanium atoms, digerma-

Chart 1
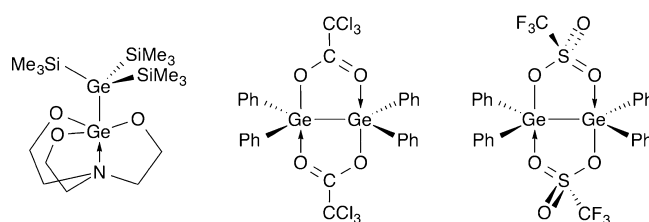
nates.[9,10] We also describe their interconversion into the anionic and neutral Ge−Ge-bonded compounds to demonstrate the reactivities of the pentacoordinated Ge−Ge-bonded compounds.

RESULTS AND DISCUSSION

Tetracoordinated spirogermane **1**, bearing two sets of a bidentate ligand, −C$_6$H$_3$-4-CH$_3$-2-C(CF$_3$)$_2$O−,[11−13] was reduced with lithium (1.2 equiv) in DME at −78 °C and warmed to room temperature to give **2a**, which was isolated as a hexahydrate, in 36% yield (Scheme 1). Its treatment with benzyltrimethylammonium chloride in acetone/water exchanged the countercation to give **2b** in 77% yield. No decomposition was observed after handling **2a**·6H$_2$O in air and even after heating in water at 100 °C for several hours, showing its thermal stability and its resistance against hydrolysis. The

Scheme 1. Synthesis of Digermanates 2a,b from Spirogermane 1
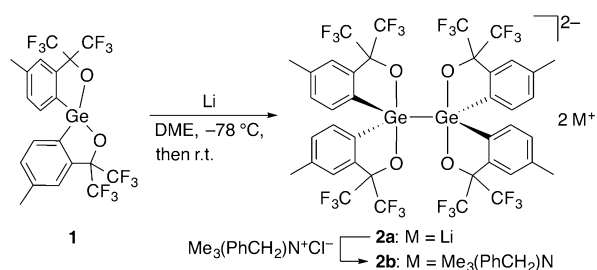
persistence of the Ge−Ge bond in the gas phase was confirmed by detection of an ion peak of m/z 1177, $[\mathrm{M}(\mathbf{2a}) - \mathrm{Li}]^{-}$, in the FAB mass spectrum. Compounds **2a,b** are the first examples of pentacoordinated digermanates with a Ge−Ge bond, as far as we know.

X-ray crystallographic analysis of **2b** shows that it exists as a racemic mixture of the digermanate which has two germanium atoms of the same chirality together with benzyltrimethylammonium parts in the unit cell (Figure 1A). Two pentacoordinated germanium atoms, situated in the TBP geometry, are bonded to two apical oxygens, two equatorial carbons, and one germanium to form a pentacoordinated state. In other words,
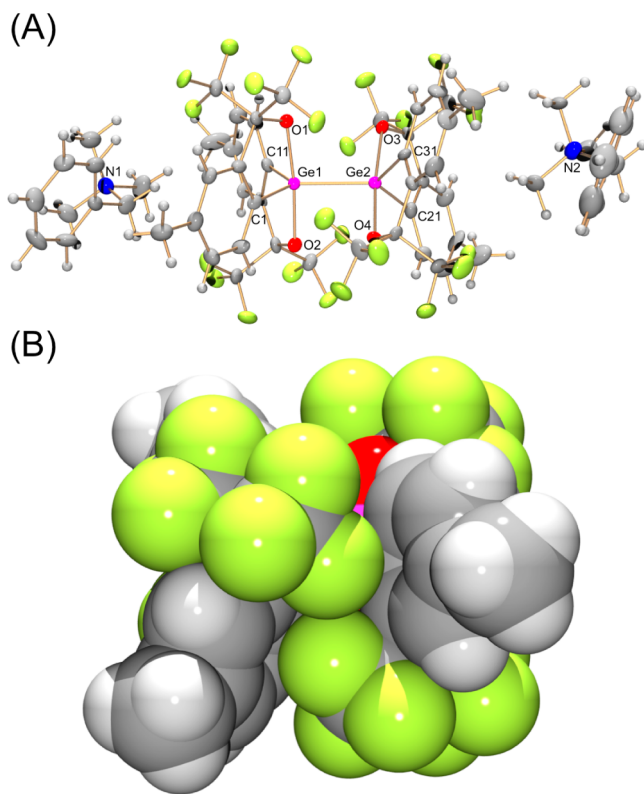

Figure 1. (A) ORTEP drawing of digermanate **2b** (thermal ellipsoid plots with 50% probability). (B) CPK model view of the dianion moiety of **2b** (white, hydrogen; gray, carbon; red, oxygen; yellow-green, fluorine; magenta, germanium). Solvent molecules in the crystal are omitted. Selected bond lengths (Å) and angles (deg): Ge1−Ge2 2.414(2), Ge1−O1 2.036(5), Ge1−O2 2.054(5), Ge1−C1 1.937(7), Ge1−C11 1.947(7), Ge2−O3 2.056(5), Ge2−O4 2.017(5), Ge2−C21 1.968(8), Ge2−C31 1.958(8), O1−Ge1−Ge2 92.93(14), O1−Ge1−C1 82.9(2), O1−Ge1−C11 93.3(3), O3−Ge2−Ge1 93.52(14), O3−Ge2−C21 82.7(3), O3−Ge2−C31 93.5(3), O4−Ge2−Ge1 92.53(15).

eight atoms in total bind to this Ge−Ge bond. The germanium atoms are almost entirely surrounded by the ligands, as is apparent from the CPK model view (Figure 1B). The apical Ge1−O1 and Ge2−O3 bonds are staggered relative to each other, as shown by the O1−Ge1−Ge2−O3 torsion angle (−60.79(17)°) (Table 1). This conformation can avoid the potential steric repulsion of the ligands. The Ge1−Ge2 bond length (2.414(2) Å) is intermediate between those of the reported neutral pentacoordinated digermanes, in which two germanium atoms are bridged by trichloroacetate ligands (2.393(2) Å)[7] or triflate ligands (2.4635(12) Å),[8] and is almost the same as that of common tetracoordinated digermanes, such as $\mathrm{Ph_3Ge-GePh_3}$ (2.437(2) Å).[14] In contrast, the apical Ge−O bond lengths (2.017(5)−2.056(5) Å) are much longer than the sum of Ge−O covalent radii (1.86 Å).[15] Even though the apical bonds of the hypercoordinated species tend to be longer, the Ge−O bonds of **2b** are meaningfully longer than those of the previously reported butylgermanate bearing similar bidentate ligands (1.984(5), 1.994(5) Å).[12] The long Ge−O bond lengths indicate weakening of the Ge−O bonds because of considerable delocalization of the negative charges on the oxygen atoms.
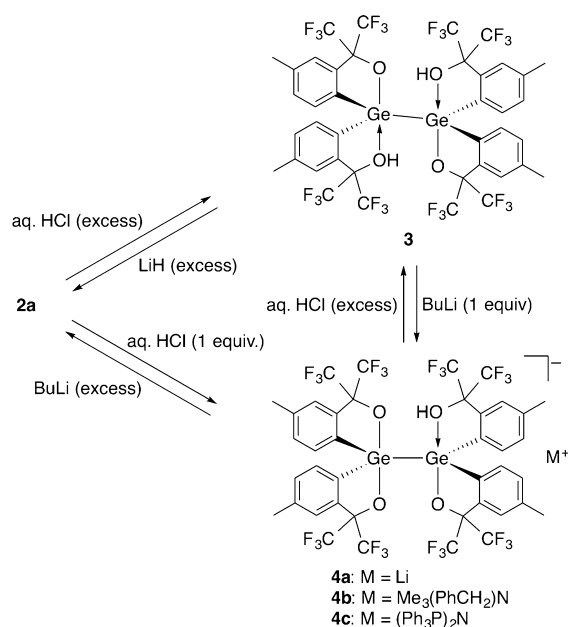
The weakening of the Ge−O bonds in the digermanate prompted us to investigate its protonation reactions. Reaction of digermanate **2a** with excess hydrochloric acid in THF caused its protonation at one oxygen atom for each germanium atom to give digermane **3**, similarly to protonation of the silicon analogue[5,16] (Scheme 2). Digermane **3** was reversed to **2a** by deprotonation with an excess amount of lithium hydride. In contrast, the reaction of digermanate **2a** with equimolar hydrochloric acid gave germylgermanate **4a**. Further protonation of **4a** with excess hydrochloric acid gave **3**. Deprotonation of **3** and **4a** with excess lithium hydride and butyllithium, respectively, could re-form digermanate **2a**. The reactivities are reasonable because both **3** and **4a** are protonated products of **2a**. Use of an equimolar amount of butyllithium in the reaction of **3** gave **4a**. Therefore, **4a** is recognized as an intermediate of the interconversion between **2a** and **3** in both the protonation and deprotonation. The interconversion among the dianionic, anionic, and neutral compounds bearing the Ge−Ge bond was achieved by acid−base reactions in this way. It makes a good contrast with the interconversion among the germyl cation, radical, and anion by redox reactions.[17]

A feature of the crystal structure of **3** differs apparently from that of **2b** in the conformation around the germanium atoms and Ge−Ge bond (Figure 2). In **3**, O2 and O3 atoms of the two hydroxy groups occupy the backside of the Ge1−O1 and Ge2−O4 bonds, respectively, making the germanium atoms pentacoordinated. These hydroxy groups form O1···H−O3 and O4···H−O2 hydrogen bonds in **3**, as evidenced by the O1···O3 and O2···O4 distances (2.622(6) and 2.613(6) Å, respectively). The pentacoordinated states are achieved by C,O-chelate ligands in **3**. The Ge···O distances in **3** (Ge1···O2, 2.305(4) Å; Ge2···O3, 2.304(4) Å) are much longer than the Ge−O bonds in **2b**, whereas they are considerably shorter than the sum of the van der Waals radii (3.65 Å). Both bond angles, O1−Ge1−Ge2 (98.06(12)°) and O4−Ge2−Ge1 (97.99(12)°), are definitely wider than the O−Ge−Ge bond angles (92.53(15)−93.52(14)°) of digermanate **2b**. These structural parameters show a trigonal-bipyramidal structure of **3** around both pentacoordinated germanium atoms. The hydrogen bonds, as mentioned above, may contribute to the conformation of the Ge−O bonds. The Ge1−O1 and Ge2−

Table 1. Selected Bond Lengths (Å) and Torsion Angles (deg) of the Optimized and Crystal Structures of the Ge−Ge-Bonded Compounds

	2^{2-} (calcd)	2b (X-ray)	3 (calcd)	3 (X-ray)	4^- (calcd)	4b (X-ray)[a]
Ge1−Ge2	2.464	2.414(2)	2.478	2.4444(9)	2.489	2.445(8)
Ge1−O1	2.018	2.036(5)	1.914	1.950(4)	2.127	2.189(4)
Ge1−O2	2.018	2.054(5)	2.343	2.305(4)	1.927	1.934(4)
Ge2−O3	2.018	2.056(5)	2.343	2.304(4)	2.429	2.428(7)
Ge2−O4	2.018	2.017(5)	1.914	1.948(3)	1.875	1.758(7)
O1−Ge1−Ge2−O3	−61.91	−60.79(17)	−12.70	−13.76(12)	−10.92	−10.54(13)
O1−Ge1−Ge2−O4	118.09	118.48(19)	168.34	167.51(12)	170.26	170.99(15)

[a]The structural parameters concerned with the Ge2 atom show those with the Ge2b atom.

Scheme 2. Interconversion of Digermanates 2a,b with Digermane 3 and Germylgermanates 4a−c

Figure 2. ORTEP drawing of digermane **3** (thermal ellipsoid plots with 50% probability). Selected bond lengths (Å) and angles (deg): Ge1−Ge2 2.4444(9), Ge1−O1 1.950(4), Ge1···O2 2.305(4), Ge1−C1 1.897(6), Ge1−C11 1.954(7), Ge2···O3 2.304(4), Ge2−O4 1.948(3), Ge2−C21 1.914(6), Ge2−C31 1.922(6), O1−Ge1−Ge2 98.06(12), O1−Ge1−C1 87.59(18), O1−Ge1−C11 100.4(2), O4−Ge2−Ge1 97.99(12), O4−Ge2−C21 100.73(19), O4−Ge2−C31 86.9(2).

O4 bonds are close to parallel, as is apparent from the O1−Ge1−Ge2−O4 torsion angle (167.51(12)°), showing an almost antiperiplanar conformation, which is different from the staggered conformation in **2b**. Nevertheless, the Ge−Ge bond length in **3** (2.4444(9) Å) is almost the same as that in **2b**, showing Ge−Ge single-bond character in both **2b** and **3**.

Such a parallel conformation was also found in the crystal structure of germylgermanate **4b**, which was obtained by the countercation exchange of **4a**. In **4b**, there is disorder of the Ge1 and Ge2 atoms along O−Ge−O axes and disorder of the H1 atom on four oxygen atoms (see the Supporting Information). A major component of the disorder is shown in Figure 3. In **4b**, the apical Ge1−O1 and Ge2b−O4 bonds are arranged almost parallel, as in **3**, and the Ge1−O2 bond eclipses the Ge2b−O4 bond. The left half of the germylgermanate has the TBP structure around the Ge1 atom as in **2b**, and the right half around the Ge2b atom has intramolecular Ge2b···O3 coordination (2.428(7) Å), as in **3**. The disorder of the Ge1 and the Ge2b atoms is considered to reflect the Ge1−O1 bond elongation and the Ge2b−O3 bond shortening by migration of the H1 atom from the O3 atom to the O1 atom, and the reverse reaction (Scheme 3). Such a migration is also reflected in the O1···H−O3 hydrogen bond (O1···O3, 2.601(4) Å) in the crystal structure of **4b**. The crystal structure of **4b** represents a snapshot of the structural changes
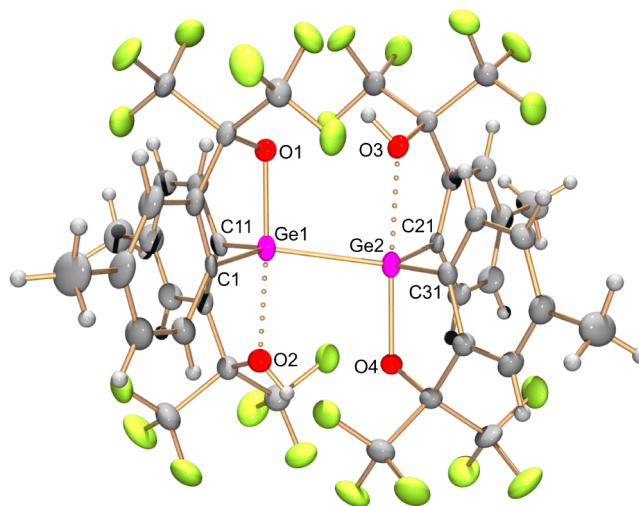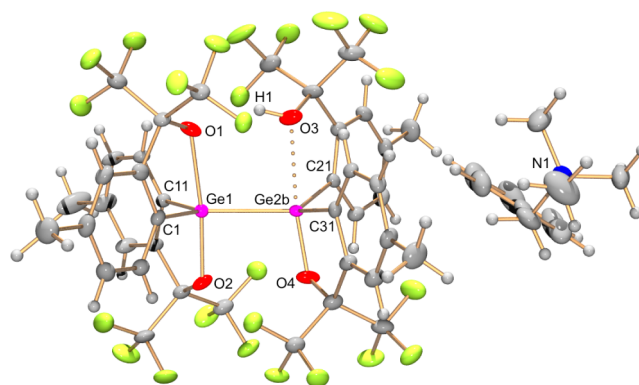

Figure 3. ORTEP drawing of germylgermanate **4b** (thermal ellipsoid plots with 50% probability). Minor components of the disorder are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−Ge2b 2.445(8), Ge1−O1 2.189(4), Ge1−O2 1.934(4), Ge1−C1 1.960(4), Ge1−C11 1.936(5), Ge2b···O3 2.428(7), Ge2b−O4 1.758(7), Ge2b−C21 1.988(6), Ge2b−C31 1.968(8), O1−Ge1−Ge2b 96.8(2), O1−Ge1−C1 78.98(17), O1−Ge1−C11 90.64(19), O4−Ge2b−Ge1 100.0(3), O4−Ge2b−C21 98.6(2), O4−Ge2b−C31 90.7(3).

Scheme 3. Intramolecular Proton Transfer in Germylgermanates 4a−c

4a-c
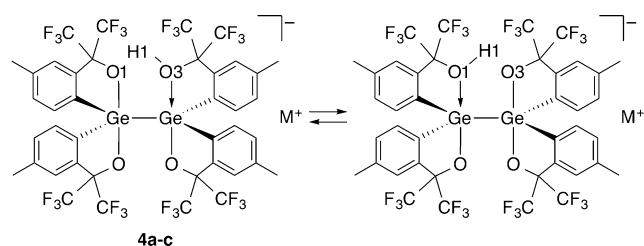
in the protonation/deprotonation processes between **2b** and **3**. The first deprotonation of **3** causes only structural changes around one germanium atom by shortening of the Ge1−O2 bond and elongation of the Ge1−O1 bond while keeping the Ge1−O1 and Ge2−O4 bonds in the antiperiplanar conformation. The second deprotonation caused not only similar structural changes around another germanium atom but also rotation around the Ge−Ge bond by disappearance of the hydrogen bond to achieve the staggered conformation in **2b**.

The structural differences between these molecules cause changes in behavior in solution. The ^{19}F NMR spectrum of **2b** showed two quartets (δ −75.4, −75.8 ppm) in acetone-d_6, as expected from the crystal structure. In contrast, only one singlet was observed at δ −76.1 ppm as signals arising from the trifluoromethyl groups in the ^{19}F NMR spectrum of **3** at room temperature, despite nonequivalence of the trifluoromethyl groups in the crystal structure. The peak neither broadened nor split, even at −90 °C. Both proton transfer from one oxygen to another and inversion of stereochemistry at the germanium atoms occurred so fast that the four trifluoromethyl groups were equivalently observed on the ^{19}F NMR time scale. Unlike the case for **2b** and **3**, germylgermanate **4b** showed three broad peaks at δ −74.3 (6F), −76.7 (6F), and −77.1 ppm (12F). The anion part of **4b** in the solution state is considered to form a C_2-symmetrical structure, which should show four sets of peaks in the ^{19}F NMR spectrum. Two of them overlapped by chance, resulting in observation of the above three signals. The variable-temperature (VT) ^{19}F NMR spectra of bis-(triphenylphosphino)iminium germylgermanate **4c**, which was prepared from **3**, showed a similar ^{19}F NMR spectrum (Figure 4). The three peaks became broadened as the temperature decreased and separated into six broad signals instead of the expected eight signals at −90 °C. These results suggest that the hydrogen atom, H1, in the anion moiety exchanges position rapidly from O3 to O1 atoms accompanying the Ge1−O1
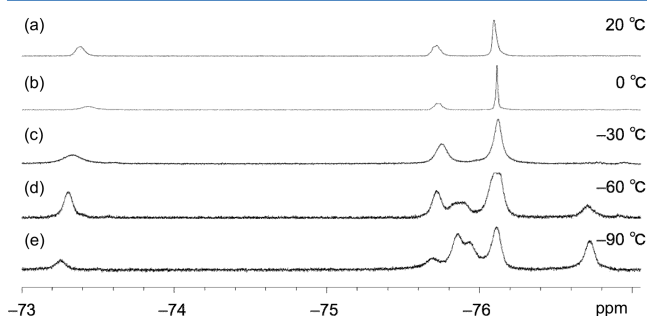

Figure 4. Variable-temperature ^{19}F NMR spectra of germylgermanate **4c** in acetone-d_6 at (a) +20 °C, (b) 0 °C, (c) −30 °C, (d) −60 °C, and (e) −90 °C in the same δ scale.

bond elongation by the protonation and the Ge2b−O3 bond shortening, and vice versa.

To determine the bonding properties of the digermanates, DFT calculations of dianion 2^{2-}, digermane **3**, and monoanion 4^- were performed at the B3PW91/6-311+G(2d)[Ge]/6-31G(d)[others] level. Compounds 2^{2-} and 4^- correspond to the dianionic and monoanionic parts of **2b** and **4b**, respectively. All the optimized structures of 2^{2-}, **3**, and 4^- by the calculations reproduce very well the corresponding crystal structures of **2b**, **3**, and **4b**, respectively, except for the Ge2−O4 bond length of germylgermanate 4^-. For example, the Ge1−Ge2 bond lengths of the optimized structures (Ge1−Ge2 bond lengths: **2**, 2.464 Å; 4^-, 2.489 Å; **3**, 2.478 Å) match well with the corresponding values in the crystal structures. The O1−Ge1−Ge2−O4 torsion angles of the optimized structures (2^{2-}, 118.09°; 4^-, 170.26°; **3**, 168.34°) show good reproducibility of the staggered conformation of the Ge−O bonds in digermanate 2^{2-} and parallel conformation in both germylgermanate 4^- and digermane **3**. Natural population analysis of 2^{2-} revealed that the germanium atoms are positively charged (q_{Ge}, +1.30) and the oxygen and carbon atoms bound to the germanium atoms are negatively charged (q_O, −0.84; q_C, −0.38).[18] Localization of the negative charges at the electron-withdrawing ligands contributes to relieve the anticipated electrostatic repulsion of the anionic halves of the digermanates. The natural bond orbital analysis shows that the Ge−Ge bond of 2^{2-} consists of sp$^{2.31}$ hybridization, while that of **3** is in sp$^{2.51}$ hybridization. Each germanium atom in 4^- resembles hybridization states of 2^{2-} and **3**, being in sp$^{2.38}$ and sp$^{2.57}$ hybridization states. The Wiberg bond index of the Ge−Ge bond in 2^{2-} is 0.839, which is almost the same as 0.835 in **3** and 0.826 in 4^-. Therefore, as indicated by the X-ray crystallographic analysis, the Ge−Ge bond in the digermanate is a single bond, consisting of the quasi-sp^2-hybridized germanium atoms. The protonation of digermanate **2b** to digermane **3** only changes the hybridization of the germanium slightly, because **3** maintains the intramolecular Ge−O interactions in the trigonal-bipyramidal structure.

The DFT calculations of **2b** and **4b**, including benzyl-trimethylammonium ions, were performed to compare the energy levels of HOMO of the Ge−Ge-bonded compounds. Selected molecular orbitals of the dianionic part of **2b** and **3** and the monoanionic part of **4b** are shown in Figure 5. In digermanate **2b**, the bonding σ orbital of the Ge−Ge bond and the n orbital of the oxygen atoms contribute greatly to the highest occupied molecular orbital (HOMO) (energy level, −4.65 eV). The lowest unoccupied molecular orbital (LUMO) of the dianion moiety in **2b** is LUMO+4 (0.25 eV), which is contributed by the π^* orbital of the benzene rings of the bidentate ligands. The HOMO−LUMO energy gap (4.90 eV) of the dianion moiety is slightly larger than that in hexaphenyldigermane (4.79 eV).[19] Nevertheless, the cyclic voltammetry and differential pulse voltammetry of **2b** in THF showed the oxidation potential at ca. 0.7 V vs ferrocene/ferrocenium lower than that of hexaphenyldigermane (1.96(2) V).[20] This can be ascribed to the high HOMO level of digermanate **2b**. Actually, the energy level of the HOMO (−4.65 eV) of **2b** is higher than those of **3** (−6.62 eV) and **4b** (−5.69 eV). This is a reasonable result because the HOMO level decreases in the order dianion, monoanion, and neutral species. Contribution of the π orbital of the benzene ring to the HOMO seems to increase in this order. Changing the charge of the Ge−Ge-bonded compound to dianionic is important to
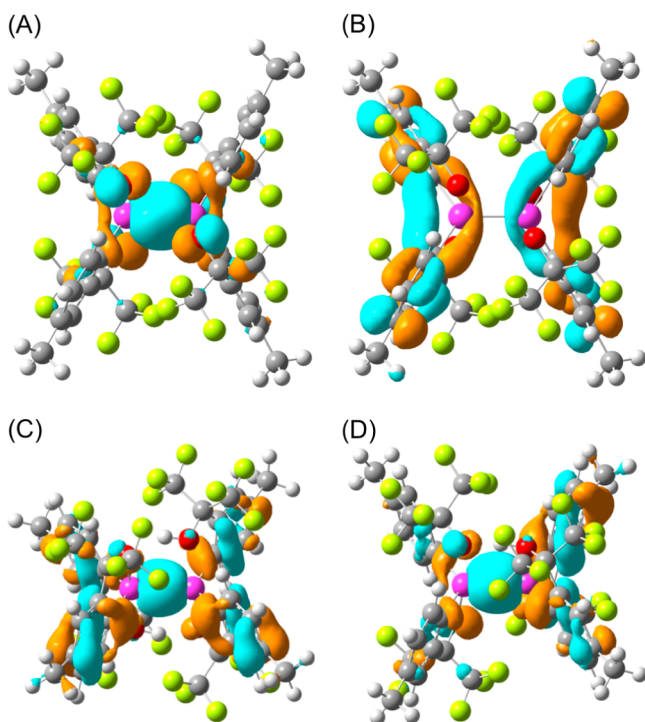
Figure 5. (A) Dianionic moiety of HOMO of **2b**. (B) Dianionic moiety of LUMO+4 of **2b**. (C) HOMO of **3**. (D) Monoanionic moiety of HOMO of **4b** (isovalue 0.03).

raise the HOMO level and to increase relatively the contribution of the σ orbital of the Ge–Ge bond and the n orbital of the oxygen atoms to the HOMO of the Ge–Ge-bonded compounds.

■ CONCLUSION

In summary, the first dianionic compounds bearing a bond between two pentacoordinated germanium atoms have been synthesized as a stable form. They were reversibly converted to the anionic and neutral Ge–Ge-bonded compounds while maintaining the coordination number of the germanium atoms. The interconversion features changes in electronic properties and structures around the germanium atoms. These new structures composed of such Ge–Ge bonds will be useful for the construction of functional materials that respond to acid–base reactions.

■ EXPERIMENTAL SECTION

General Procedures. Solvents were purified before use by reported methods. Reactions using lithium, butyllithium, and lithium hydride were carried out under an argon atmosphere. The ^{1}H NMR (300, 400, or 500 MHz) and ^{13}C{^{1}H} NMR (100 and 126 MHz) spectra were measured using tetramethylsilane as an external standard. The ^{7}Li NMR (155 MHz) and ^{19}F NMR (376 MHz) spectra were measured using lithium chloride and Freon as external standards, respectively. All melting points are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Synthesis of Spirogermane 1. To a diethyl ether solution (20 mL) of 1-(2-bromo-5-methylphenyl)-2,2,2-trifluoro-1-(trifluoromethyl)ethanol[21] (15.0 g, 44.4 mmol) was added an ice-cold diethyl ether solution of isopropylmagnesium chloride (2.0 M, 30 mL, 60 mmol) over 20 min at room temperature. The suspension was added to magnesium (1.10 g, 45.2 mmol) in diethyl ether (20 mL) at room temperature, and the mixture was stirred at reflux temperature

for 2 h. After the suspension was cooled to room temperature, germanium tetrachloride (2.5 mL, 22 mmol) in diethyl ether (10 mL) was added and the mixture was stirred for 16 h. After quenching with diluted hydrochloric acid, the organic phase was extracted with diethyl ether and dried with anhydrous magnesium sulfate. After filtration and evaporation, recrystallization of the crude solid from hexane gave spirogermane **1** (6.54 g, 51%). **1**: colorless solid; mp 167.6−168.2 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.53 (s, 6H), 7.49 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.69 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 21.95, 82.13 (septet, $^2J_{CF}$ = 31 Hz), 122.38 (q, $^1J_{CF}$ = 284 Hz), 122.58 (q, $^1J_{CF}$ = 284 Hz), 123.41, 127.02, 132.08, 132.70, 140.62, 144.14; ^{19}F NMR (376 Hz, CDCl$_3$) δ −78.32 (q, $^4J_{FF}$ = 8.4 Hz, 6F), −77.51 (q, $^4J_{FF}$ = 8.4 Hz, 6F); MS (EI, 70 eV) m/z 586 (M$^+$). Anal. Calcd for C$_{20}$H$_{12}$F$_{12}$GeO$_2$: C, 41.07; H, 2.07. Found: C, 40.97; H, 2.21.

Synthesis of Digermanate 2a. A 30 wt % oil dispersion of lithium (16 mg, 2.3 mmol as Li) was washed with dry hexane and then treated with a DME solution (ca. 1.5 mL) of spirogermane **1** (1.2 g, 2.0 mmol) at −78 °C. The reaction mixture was stirred at −78 °C overnight and then at room temperature for 1 day. After evaporation of the solvent, the solid was washed with DME and then water. Drying the solid gave digermanate **2a**, which was isolated as hexahydrate **2a·**6H$_2$O (0.46 g, 36%). The water content in the solid was estimated by subtraction of integrals of the peak of water in acetone-d_6 before and after dissolution of the solid that was used for the elemental analysis. The solid sublimed at 259 °C. **2a·**6H$_2$O: white solid; mp 259 °C sublim; ^{1}H NMR (500 MHz, acetone-d_6) δ 2.25 (s, 12H), 2.98 (s, 12H), 7.13−7.15 (m, 8H), 7.96 (d, $^3J_{HH}$ = 7.5 Hz, 4H).; ^{7}Li NMR (155 MHz, acetone-d_6) δ 2.34 (s); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6) δ 21.35 (s), 83.35 (sept, $^2J_{CF}$ = 28 Hz), 125.01 (q, $^1J_{CF}$ = 290 Hz), 125.44 (s), 125.49 (q, $^1J_{CF}$ = 290 Hz), 129.74 (s), 135.46 (s), 138.07 (s), 139.08 (s), 139.36 (s); ^{19}F NMR (376 MHz, acetone-d_6) δ −75.54 (d, J = 8.3 Hz, 12F), −76.19 (d, J = 8.3 Hz, 12F); LRMS (FAB, negative) m/z 1177 [M(**2a**) − Li]$^-$. Anal. Calcd for C$_{40}$H$_{24}$F$_{24}$Ge$_2$Li$_2$O$_4$·6H$_2$O: C, 37.19; H, 2.81. Found: C, 37.02; H, 2.57.

Synthesis of Digermanate 2b. Digermanate **2a·**6H$_2$O (58 mg, 45 μmol) in acetone/water (3 mL/2 mL) was treated with benzyltrimethylammonium chloride (0.19 g, 1.0 mmol) at room temperature, and the mixture was stirred overnight. After evaporation of acetone under reduced pressure, precipitates in the water were collected by filtration and dried to give digermanate **2b** (51 mg, 77%). Digermanate **2b**: white solid; ^{1}H NMR (400 MHz, acetone-d_6) δ 2.19 (s, 12H), 3.41 (s, 18H), 4.81 (s, 4H), 6.94 (d, $^3J_{HH}$ = 7.6 Hz, 4H), 7.03 (s, 4H), 7.59 (t, $^3J_{HH}$ = 7.2 Hz, 4H), 7.60 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 7.70 (d, $^3J_{HH}$ = 7.6 Hz, 4H), 8.31 (d, $^3J_{HH}$ = 7.2 Hz, 4H); ^{19}F NMR (376 MHz, acetone-d_6) δ −75.39 (d, J = 7.5 Hz, 12F), −75.75 (d, J = 7.9 Hz, 12F).

Synthesis of Digermane 3. Digermanate **2a·**6H$_2$O (51 mg, 39 μmol) in THF (3 mL) was treated with hydrochloric acid (0.1 M, 2.0 mL, 2.0 mmol) at room temperature, and the mixture was stirred for 1 h. After evaporation of THF, precipitates were collected by filtration and dried to give digermane **3** (45 mg, 97%). **3**: white solid; mp 286.0−286.8 °C dec; ^{1}H NMR (500 MHz, acetone-d_6) δ 2.35 (s, 12H), 4.96 (br, 2H), 7.32 (s, 4H), 7.39 (d, $^3J_{HH}$ = 7.5 Hz, 4H), 8.08 (d, $^3J_{HH}$ = 7.5 Hz, 4H); ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6) δ 21.34 (s), 82.40 (sept, $^2J_{CF}$ = 28 Hz), 123.57 (q, $^4J_{FF}$ = 289 Hz), 124.03 (q, $^4J_{CF}$ = 289 Hz) 126.44 (s), 131.60 (s), 134.19 (s), 135.28 (s), 135.94 (s), 140.99 (s); ^{19}F NMR (376 MHz, acetone-d_6) δ −76.10 (s); LRMS (FAB, negative) m/z 1171 [M − H]$^-$. Anal. Calcd for C$_{40}$H$_{26}$F$_{24}$Ge$_2$O$_4$: C, 41.00; H, 2.24. Found: C, 40.88; H, 2.48.

Synthesis of Germylgermanate 4a. Digermanate **2a·**6H$_2$O (0.26 g, 0.20 mmol) in THF (3 mL) was treated with hydrochloric acid (0.1 M, 2.0 mL, 0.20 mmol) at room temperature, and the mixture was stirred for 1 h. After evaporation of THF, precipitates were collected by filtration and dried to give germylgermanate **4a**, and it was isolated as the monohydrate **4a·**H$_2$O (0.25 g, quantitative). The water content in the solid was estimated by subtraction of integrals of the peak of water in acetone-d_6 before and after dissolution of the solid that was used for the elemental analysis. The solid sublimed at 281.3

°C. **4a·H₂O**: white solid; mp 281.3 °C sublim; ¹H NMR (500 MHz, acetone-d_6) δ 2.25 (s, 12H), 3.53 (br, 3H), 7.09–7.12 (m, 4H), 7.30 (s, 4H), 7.92 (br, 2H), 8.04 (d, $^3J_{HH}$ = 7.0 Hz, 2H); ⁷Li NMR (155 MHz, acetone-d_6) δ 2.31 (s); ¹³C{¹H} NMR (126 MHz, acetone-d_6) δ 21.17 (s), 21.20 (s), 80.49 (sept, $^2J_{CF}$ = 29 Hz), 84.20 (sept, $^2J_{CF}$ = 28 Hz), 124.39 (q, $^1J_{CF}$ = 290 Hz), 124.52 (q, $^1J_{CF}$ = 289 Hz), 124.79 (q, $^1J_{CF}$ = 290 Hz), 125.25 (q, $^1J_{CF}$ = 289 Hz), 125.66 (s), 126.10 (s), 129.97 (s), 130.38 (s), 135.66 (s), 136.08 (s), 137.02 (s), 137.93 (s), 138.39 (s), 139.05 (s), 139.21 (s), 140.36 (s); ¹⁹F NMR (376 MHz, acetone-d_6) δ −73.37 (br, 6F), −75.68 (br, 6F), −76.07 (br, 12F); LRMS (FAB, negative) m/z 1171 [M − Li]⁻; HRMS (ESI, negative) m/z calcd for $C_{40}H_{27}F_{24}Ge_2O_5$ 1172.9793 [M − Li]⁻, found 1172.9791. Anal. Calcd for $C_{40}H_{27}F_{24}Ge_2O_5Li$: C, 40.18; H, 2.28. Found: C, 40.54; H, 2.63.

Conversion of Digermane 3 to Germylgermanate 4b. A THF solution (5 mL) of digermane **3** (252 mg, 0.215 mmol) was treated with a hexane solution of butyllithium (0.16 mol/L, 0.1 mL, 0.16 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. After the solvents were evaporated, the crude solids of germylgermanate **4a** and (PhCH₂)Me₃NCl (40 mg, 0.23 mmol) were stirred in acetone (3 mL)/water (2 mL) for 1 h. After addition of more water, white precipitates formed. The precipitates were filtrated, washed with water, and dried to give germylgermanate **4b** (122 mg, 43%). Recrystallization from THF/hexane gave the single crystals suitable for X-ray crystallographic analysis. **4b**: white solid; mp 223.6–225.1 °C; ¹H NMR (300 MHz, acetone-d_6) δ 2.26 (s, 12H), 3.35 (s, 9H), 4.79 (s, 2H), 7.11 (t, J = 7.2 Hz, 4H), 7.31 (s, 4H), 7.52–7.69 (m, 5H), 7.93 (d, J = 6.0 Hz, 2H), 8.05 (d, J = 7.9 Hz, 2H). ¹³C NMR (75 MHz, acetone-d_6) δ 21.30 (s), 21.32 (s), 53.25 (t, J_{CN} = 3.8 Hz), 70.28 (t, J_{CN} = 2.7 Hz), 80.31 (q, $^2J_{CF}$ = 27 Hz), 84.39 (q, $^2J_{CF}$ = 29 Hz), 124.52 (q, $^1J_{CF}$ = 286 Hz), 124.63 (q, $^1J_{CF}$ = 286 Hz), 124.92 (q, $^1J_{CF}$ = 288 Hz), 125.38 (q, $^1J_{CF}$ = 287 Hz), 125.77 (s), 126.21 (s), 128.86 (s), 130.09 (s), 130.52 (s), 131.67 (s), 133.82 (s), 135.78 (s), 136.21(s), 137.15 (s), 138.10 (s), 138.55 (s), 139.14 (s), 139.29 (s), 140.51 (s). ¹⁹F NMR (376 MHz, acetone-d_6) δ −74.34 (br, 6F), −76.66 (br, 6F), −77.05 (s, 12F). Anal. Calcd for $C_{50}H_{41}F_{24}Ge_2NO_4$: C, 45.46; H, 3.13; N, 1.06. Found: C, 45.34; H, 3.39; N, 1.07.

Conversion of Digermane 3 to Germylgermanate 4c. A THF solution (2 mL) of digermane **3** (138 mg, 0.12 mmol) was treated with a hexane solution of butyllithium (0.16 mol/L, 0.6 mL, 0.1 mmol) at 0 °C, and the mixture was stirred at room temperature for 3 h. After solvents were evaporated, the crude solids and (Ph₃P)₂NCl (582 mg) were stirred in acetone (3 mL)/water (12 mL) for 5 min to form white precipitates. The precipitates were filtered, washed with water, and dried to give germylgermanate **4c·PNP** (131 mg, 65%). Germylgermanate **4c·PNP** was used for VT-NMR measurements without further purification. **4c**: white solid; mp 218.5–221.3 °C; ¹H NMR (500 MHz, acetone-d_6) δ 2.25 (s, 12H), 2.79 (s, 1H), 7.08 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.10 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.30 (s, 4H), 7.55–7.58 (m, 10H), 7.69–7.73 (m, 20H), 7.91 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 8.03 (d, $^3J_{HH}$ = 7.7 Hz, 2H); ¹³C{¹H} NMR (126 MHz, acetone-d_6) δ 21.35 (s), 21.38 (s), 80.62 (sept, $^2J_{CF}$ = 29 Hz), 84.29 (sept, $^2J_{CF}$ = 29 Hz), 124.44 (q, $^1J_{CF}$ = 287 Hz), 124.55 (q, $^1J_{CF}$ = 287 Hz), 124.84 (q, $^1J_{CF}$ = 289 Hz), 125.30 (q, $^1J_{CF}$ = 287 Hz), 125.71 (s), 126.12 (s), 128.14 (dd, J_{CP} = 128 Hz, 2 Hz), 134.42 (d, J_{CP}= 2 Hz), 130.13–130.33 (m), 132.99–133.17 (m), 135.66 (s), 136.10 (s), 137.03 (s), 137.98 (s), 138.50 (s), 139.03 (s), 139.20 (s), 140.41 (s); ¹⁹F NMR (376 MHz, acetone-d_6) δ −73.35 (br, 6F), −75.73 (br, 6F), −76.11 (br, 12F).

Conversion of Germylgermanate 4a·H₂O to Digermane 3. Hydrochloric acid (1 M, 1.0 mL, 1.0 mmol) was added to a THF solution (3 mL) of germylgemanate **4a·H₂O** (59 mg, 49 μmol) at room temperature. After the mixture was stirred for 1 h and THF was evaporated, the precipitates in water were collected by filtration and dried to give digermane **3** (36 mg, 62%).

Conversion of Digermane 3 to Digermanate 2a·6H₂O. A THF solution (2 mL) of digermane **3** (12 mg, 10 μmol) was added to a THF suspension (5 mL) of lithium hydride (8.0 mg, 1.0 mmol) at room temperature, and the mixture was stirred for 4 days. After quenching with methanol, solvents were evaporated to give crude

solids. The solids were washed with water and dried to give digermanate **2a·6H₂O** (6 μg, 45%).

Conversion of Germylgermanate 4 to Digermanate 2a·6H₂O. A THF solution (2 mL) of germylgermanate **4a·H₂O** (25 mg, 21 μmol) was added to a hexane solution of butyllithium (1.53 M, 40 μL, 61 μmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. After evaporation of solvents, crude solids were washed with water and dried to give digermanate **2a·6H₂O** (10 mg, 37%).

Electrochemical Measurement of Digermanate 2a. The electrochemical experiment was carried out using a glassy-carbon rod as a working electrode, a platinum wire counter electrode, and an Ag⁺/Ag reference electrode. A standard one-compartment cell was used. The measurement was carried out in a 0.5 mmol L⁻¹ THF solution of **2a·6H₂O** containing 0.1 mol L⁻¹ tetrabutylammonium perchlorate as a supporting electrolyte under a nitrogen atmosphere at 25 °C. Scan rates of the cyclic voltammetry and differential pulse voltammetry measurements were 0.1 and 0.02 V s⁻¹, respectively.

X-ray Crystallographic Analysis of 2b·acetone·3H₂O, 3, and 4b. The X-ray diffraction data were collected on a charge-coupled device diffractometer with graphite-monochromated Mo Kα radiation. Data were processed using CrystalClear (Rigaku). The intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-97) and expanded using Fourier techniques.[22] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules in **2b·acetone·3H₂O** were not assigned. Other hydrogen atoms were placed at calculated positions and refined isotropically. A refinement procedure for the disordered structure of **4b** is described in the Supporting Information. Crystallographic data of **2b·acetone·3H₂O**: $C_{63}H_{62}F_{24}Ge_2N_2O_8$, mol wt 1576.33, monoclinic, Cc, a = 19.519(17) Å, b = 15.046(12) Å, c = 24.98(2) Å, β = 110.579(5)°, V = 6868(10) Å³, Z = 4, μ(Mo Kα) = 0.994 mm⁻¹, D_c = 1.525 g cm⁻³, T = 120 K, 18301 measured and 9818 independent reflections, 904 parameters, R1 ($I > 2\sigma(I)$) = 0.0502, wR2 (all data) = 0.1280, GOF = 1.135, absolute structure (Flack) parameter x = −0.052(11). Hydrogen atoms of water molecules were not located. Crystallographic data of **3**: $C_{40}H_{26}F_{24}Ge_2O_4$, mol wt 1171.83, monoclinic, $P2_1$, a = 11.4038(4) Å, b = 11.2214(3) Å, c = 17.0504(4) Å, β = 96.072(7)°, V = 2169.64(11) Å³, Z = 2, μ(Mo Kα) = 1.529 mm⁻¹, D_c = 1.794 g cm⁻³, T = 120 K, 9171 measured and 9171 independent reflections, 638 parameters, R1 ($I > 2\sigma(I)$) = 0.0439, wR2 (all data) = 0.1343, GOF = 1.044, absolute structure (Flack) parameter x = 0.3(2). Crystallographic data of **4b**: $C_{50}H_{41}F_{24}Ge_2NO_4$, mol wt 1321.02, monoclinic, $P2_1/n$, a = 16.9831(8) Å, b = 15.8709(7) Å, c = 20.2743(10) Å, β = 107.969(2)°, V = 5198.1(4) Å³, Z = 4, μ(Mo Kα) = 1.288 mm⁻¹, D_c = 1.688 g cm⁻³, T = 120 K, 52902 measured and 9663 independent reflections, 786 parameters, R1 ($I > 2\sigma(I)$) = 0.0568, wR2 (all data) = 0.1064, GOF = 1.316. Crystal data are available from the Cambridge Crystallographic Database Centre, deposition nos. CCDC 1016493 (**2b·acetone·3H₂O**), 1016505 (**3**) and 1016494 (**4b**).

Density Functional Theory Calculations. The geometries of dianion **2²⁻**, digermane **3**, monoanion **4⁻**, digermanate **2b**, and germylgermanate **4b** were fully optimized with density functional theory at the B3PW91/6-311+G(2d)[Ge]/6-31G(d)[others][23−25] level using the GAUSSIAN 09 program.[26] Cartesian coordinates in optimized geometries of **2²⁻**, **3**, **4⁻**, **2b**, and **4b** are shown in the Supporting Information.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Figures, tables, and CIF and xyz files giving crystallographic data for **2b·acetone·3H₂O**, **3**, and **4b**, NMR spectral charts of **1**, **2a,b**, **3a**, and **4a−c**, a cyclic voltammogram of **2a**, a differential pulse voltammogram of **2a**, details of refinement of the crystal structure of **4b**, Cartesian coordinates of optimized geometries of **2²⁻**, **3**, **4⁻**, **2b**, and **4b**, selected molecular orbitals, and comparison of the crystal structures and optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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