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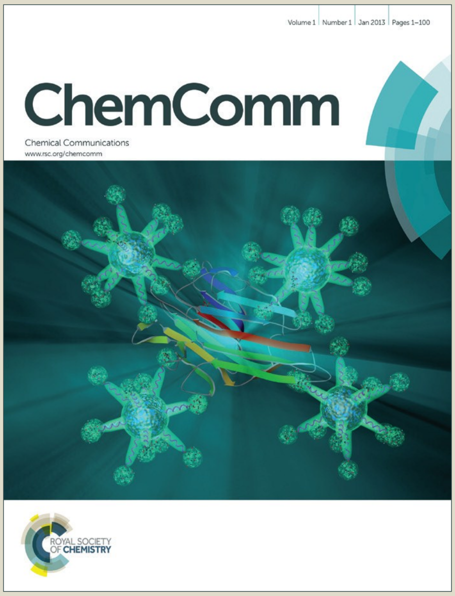

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Synthesis of Digermylene-Stabilized Linear Tetraboronate and Boroxine

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Two newly discovered linear tetraboronate and boroxine stabilized by digermylene are reported, which features a B_4O_5 chain and a B_3O_3 ring, respectively. DFT calculations reveal that not only can the digermylene stabilize the electron-deficient boron centers, but also increase the energies of the LUMOs of the boron moiety. Our results provide a hint for the development of boronate covalent organic frameworks.

Since Yaghi and co-workers reported the first crystalline boroxine covalent organic frameworks (COFs) in 2005,[1] boroxines (Fig. 1, **A**, B_3O_3) and boronate esters (Fig. 1, **B**, C_2O_2B) containing COFs have emerged as popular materials for gas adsorption and storage in the past decade.[2] The Lewis acidic boron atoms of COFs present unique adsorbent surface, which are ready to interact with Lewis basic substrates. For example, COF-10 showed the highest ammonia uptake capacity of any porous material.[3]

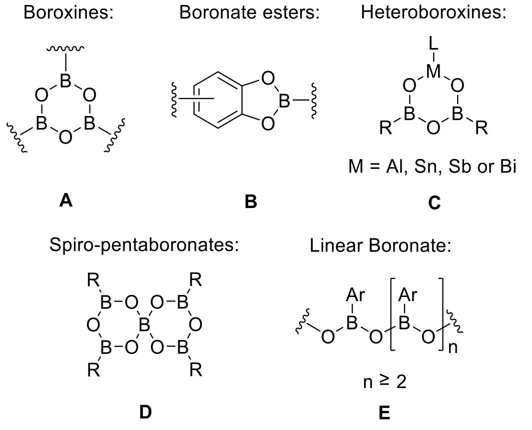
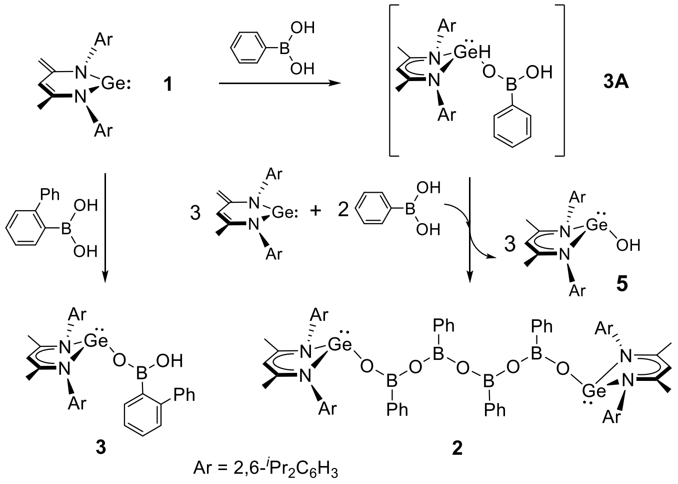


Fig. 1 The structure of (**A**) boroxines, (**B**) boronate esters, (**C**) heteroboroxines, (**D**) spiro-pentaboronates, and (**E**) linear boronate

Recently, intensive research efforts have explored the structural variety of the organic boron-oxygen linkage. Heteroboroxines (Fig. 1, **C**, MB_2O_3), are mainly prepared from arylboronic acids.[4] Roesky and co-workers showed that the reaction of aluminum(I) compound L^1Al (L^1 = $CH[(CMe)(2,6\text{-}^iPr_2C_6H_3N)]_2$) or aluminum(III) hydride L^1AlH_2 with arylboronic acids generated alumaboroxines $L^1Al[(OBAr)_2O]$.[5] Following this, main-group metals (Sn, Sb and Bi) containing heteroboroxines[6] and spiro-pentaborates[7] (Fig. 1, **D**, B_5O_6) were also reported by Dostál and co-workers. However, as pointed out by Korich and Iovine, heteroboroxines and other metal-containing boronates remain quite limited.[8] Further, linear boronates (Fig. 1, **E**) have not been reported.

Owing to their unique ylide-like character, heavier carbene analogues, germylenes, show high reactivity in the activation of functional groups and small molecules.[9] N-heterocyclic ylide-like germylene **1**, first prepared by Driess and co-workers,[10] was capable of activating C-X (X = halogen),[10] C-H,[11] N-H,[12] O-H[13] and P-H[14] bonds and producing the corresponding 1,4-addition products. Herein we report a remarkably different reactivity of germylene **1** towards arylboronic acids, which results in a digermylene-stabilized linear tetraboronate (B_4O_5 chain) (Scheme 1, **2**) and a digermylene-stabilized boroxine **(**B_3O_3 ring) (Scheme 2, **4**). In addition, having a bulky substituent on arylboronic acids makes one of the B-OH group too sterically encumbered to react further and only produces monogermylene **3** (Scheme 1).



Scheme 1 The reaction of **1** with $PhB(OH)_2$ and $2\text{-}Ph\text{-}C_6H_4B(OH)_2$.

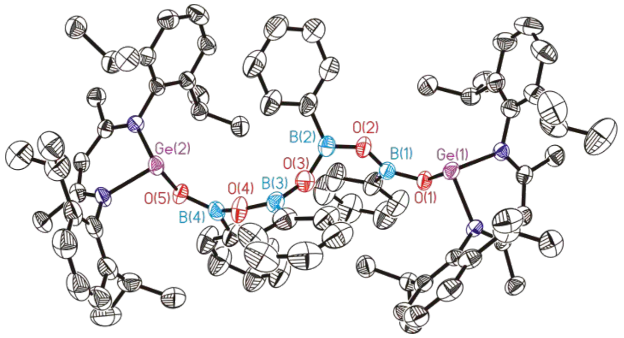
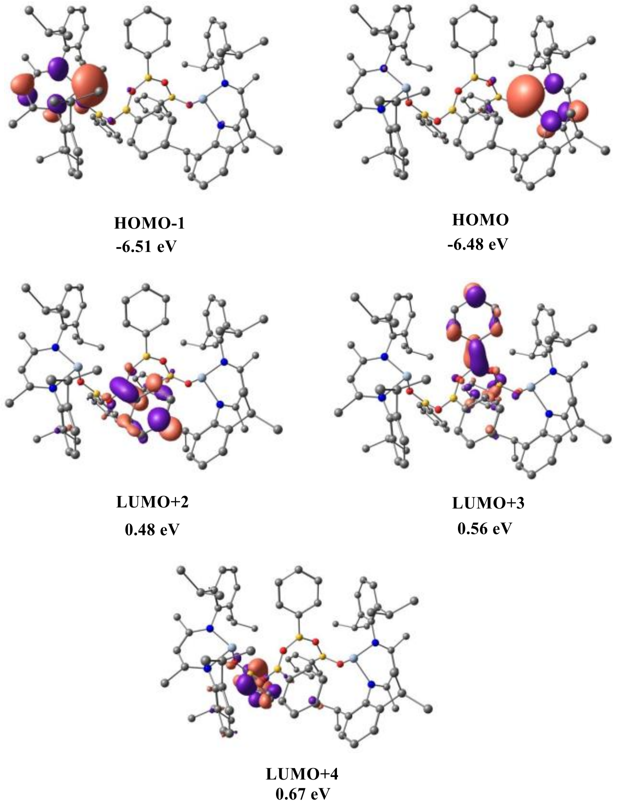


Fig. 2 Molecular structure of **2** with the anisotropic displacement parameters depicted at the 50% probability level. The hydrogen atoms and disorder on iso-propyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) 2.001(4), Ge(1)−N(2) 1.989(4), Ge(1)−O(1) 1.858(3), Ge(2)−N(3) 1.989(4), Ge(2)−N(4) 2.001(4), Ge(2)−O(5) 1.866(3), B(1)−O(1) 1.342(6), B(1)−O(2) 1.374(7); N(1)−Ge(1)−N(2) 90.06(15), N(3)−Ge(2)−N(4) 90.14(15), Ge(1)−O(1)−B(1) 127.9(4), Ge(2)−O(5)−B(4) 123.5(3).

Stirring a solution of a stoichiometric mixture of **1** and $PhB(OH)_2$ in toluene for 24 h resulted in an unprecedented formation of digermylene-stabilized linear tetraboronate $[L^1Ge(OBPh)_2]_2O$ (**2**), which was isolated as single crystals in 33% yield. Although the ^{11}B NMR spectrum of **2** showed one broad signal at 13.2 ppm, which is slightly different from the $PhB(OH)_2$ (9.3 ppm),[15] there is no terminal $C{=}CH_2$ signal (ligand backbone)[10] but 6 β-CH_3 was detected in the ^1H NMR spectrum, indicating the occurrence of 1,4-addition reaction of $PhB(OH)_2$ toward **1**. Additionally, the IR spectrum of **2** confirmed no ν_{OH} band around 3600 cm^{-1}. Indeed, crystals of **2** suitable for single-crystal XRD analysis were obtained from a mixed solution of toluene and ^{n}hexane. Compound **2** represents a new type of linear tetraboronate compound that consists of a B_4O_5 chain as the backbone and Ge^{II} atom at the terminal position (Fig. 2). The molecular structure of **2** features nearly right angles at N−Ge−N [90.06(15) and 90.14(15)°]. The average B−O bond length [1.352 Å] in **2** is distinctly longer than the B=O bond length [1.304(2) Å] in $L^2BOAlCl_3$ ($L^2 = HC(CMe)_2(NC_6F_5)_2$)[16] and the B≡O bond length [1.210(3) Å] in $[(Cy_3P)_2(PhS)Pt(BO)]$.[17] Also, the average Ge−O bond length [1.862 Å] in **2** is longer than that of Ge−OH bond [1.828(1) Å] in L^1GeOH.[17]

For a better understanding of the bonding situation and stability of the B_4O_5 chain in **2**, density functional theory (DFT) calculations were carried out at the M06-2X/6-31G(d) level of theory. Fig. 3 depicts the selected frontier molecular orbitals of **2**. The highest occupied molecular orbital (HOMO) and HOMO-1 are mainly localized at the p orbitals of the germanium atoms. The lowest unoccupied molecular orbital (LUMO) and LUMO+1 are the C-N π antibonding orbitals of germylene rings (See ESI for details). The Lewis acidic ability of the B_4O_5 chain are shown by the vacant orbitals of boron atoms in LUMO+2 (0.48 eV), LUMO+3 (0.56 eV) and LUMO+4 (0.67 eV). To be comparable, frontier molecular orbitals of $HO[B(Ph)O]_4H$ (**2B**, H atoms instead digermylene) were analyzed at the same level of theory, showing that the LUMO (-0.28 eV), LUMO+1 (0.21 eV) and LUMO+2 (0.29 eV) are mainly the empty orbitals of boron atoms, which are significantly lower in energy than those of **2**. Therefore, the digermylene groups of **2** can decrease the Lewis acidic character of the B_4O_5 chain, making boron atoms of **2** less susceptible to Lewis bases.

Indeed, the computed free energy of complexation of **2A** with ammonia is 8.8 kcal mol^{-1} (Fig. 4, top), which is higher than that (5.5 kcal mol^{-1}) of **2B** with ammonia. Moreover, the second-order perturbation theory of the natural bond orbital (NBO) method at the M06-2X/TZVP//M06-2X/6-31G(d) level of theory performed on a model compound **2A** (methyl groups instead 2,6-diisopropylphenyl groups) gives relatively high stabilization energies (36.6 and 15.0 kcal mol^{-1}) by two-electron donor–acceptor interactions from the lone pairs of germanium atoms into the central boron vacant orbitals (Fig. 4, bottom).


HOMO-1
-6.51 eV

HOMO
-6.48 eV

LUMO+2
0.48 eV

LUMO+3
0.56 eV

LUMO+4
0.67 eV

Fig. 3 Selected frontier molecular orbitals of **2** (isovalue = 0.05). The hydrogen atoms have been omitted for clarity.

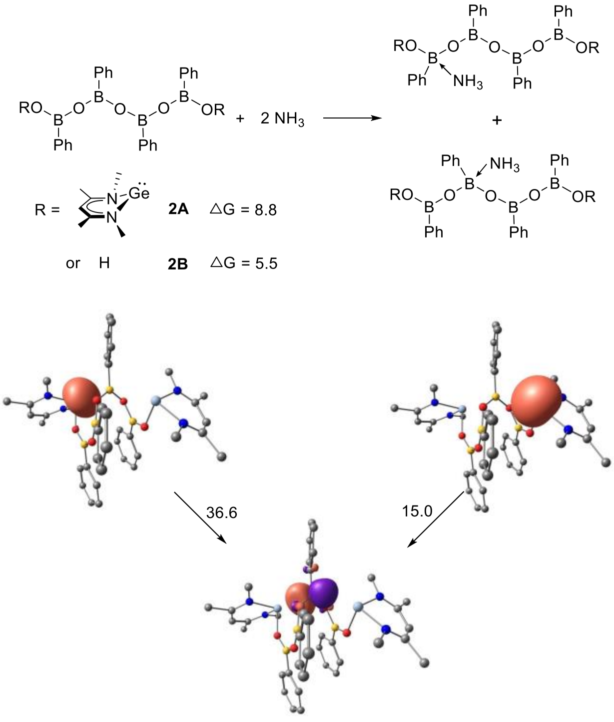


Fig. 4 (Top) Modeled reactions performed at M06-2X/6-311++G(2d,p)//B3LYP/6-31G(d) level of theory in the gas phase.

(Bottom) Selected NBOs for the second-order perturbation theory analysis. Energies are given in kcal mol^{-1}.

Here we propose a mechanism via intermediate [L^{1}GeOB(Ph)OH] (**3A**) to illustrate the aforementioned formation reaction of **2** (Scheme 1). Firstly, the reaction of N-heterocyclic ylide-like germylene **1** with PhB(OH)$_2$ produces an intermediate **3A**. Then **3A** undergoes a dehydration-condensation process with PhB(OH)$_2$ under the promotion of **1**. To verify our assumption, we treated one equivalent of **1** with one equivalent 2-Ph-C$_6$H$_4$B(OH)$_2$. Colourless crystals of **3** were obtained in high yield. The ^{1}H NMR analysis of **3** revealed two singlets at 5.06 ppm and at 3.87 ppm, which were the characteristic peak of the ligand backbone γ-C*H* and BO*H*, respectively. The IR spractrum of **3** showed a strong absorption band at 3603.6 cm^{-1}, confirming the existence of OH group. As expected, the molecular structure of **3** indicated that it is a mono 1,4-addition product L^{1}GeOB(2-Ph-C$_6$H$_4$)OH (Fig. 5). In the structure of **3**, one of the two B−OH groups remains intact due to the steric hindrance. The formation of **3** strongly supports the mechanism postulated above. Further, the two B−O bond lengths in **3** [1.370(3) and 1.347(3) Å] are close to those in **2**. The three angles on the Ge^{II} center of **3**, the N−Ge−N angle [90.08(8) °] and the N−Ge−O [92.07(7) and 90.68(7) °], are nearly right angles as well.

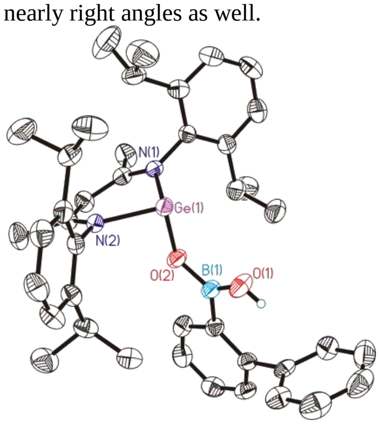
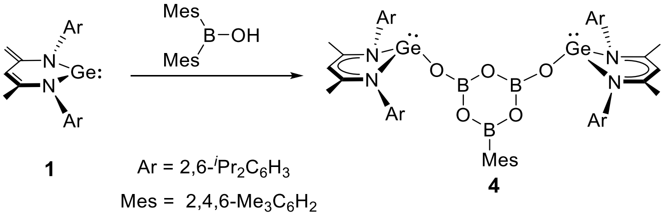


Fig. 5 Molecular structure of **3** with the anisotropic displacement parameters depicted at the 50% probability level. The hydrogen atoms except that for the OH group have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) 1.9873(19), Ge(1)−N(2) 2.0103(19), Ge(1)−O(2) 1.8601(15), B(1)−O(1) 1.370(3), B(1)−O(2) 1.347(3); N(1)−Ge(1)−N(2) 90.08(8), Ge(1)−O(2)−B(1) 126.01(15), O(1)−B(1)−O(2) 118.5(2).

To probe the reaction mechanism further, we treated one equivalent of **1** with two equivalents PhB(OH)$_2$ under the same conditions. However, no desired product **2** was isolated from this reaction mixture, indicating that the presence of excess amount of germylene **1** promoted the elimination of water under B$_4$O$_5$ chain formation. To further validate our assumption, we mixed one equivalent of **1** with one equivalent PhB(OH)$_2$. The resulting mixture was kept at -20 ^{o}C for 5 days to make sure that most of the desired product **2** crystallized out. Then the mother liquor was stored at -20 ^{o}C for another 2 weeks. A small amount of colorless crystals of L^{1}GeOH **5** was obtained and fully characterized.[18]



Scheme 2 The reaction of **1** with Mes$_2$B(OH).

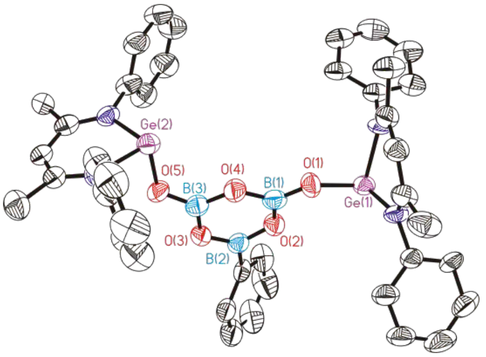


Fig. 6 Molecular structure of **4** with the anisotropic displacement parameters depicted at the 50% probability level. The hydrogen atoms isopropyl groups and methyl groups (at the aryl group at boron) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−N(1) 2.008(6), Ge(1)−N(2) 1.995(7), Ge(1)−O(1) 1.882(5), Ge(2)−N(3) 2.012(7), Ge(2)−N(4) 2.027(7), Ge(2)−O(5) 1.880(6), B(1)−O(1) 1.317(13), B(1)−O(2) 1.386(12), B(1)−O(4) 1.373(12); N(1)−Ge(1)−N(2) 89.9(3), N(3)−Ge(2)−N(4) 91.2(3), Ge(1)−O(1)−B(1) 124.8(6), Ge(2)−O(5)−B(3) 123.0(6), .

These results inspired us to investigate other precursors containing the B-OH moiety. Reacting **1** with hydroxydimesitylborane Mes$_2$BOH afforded white crystalline solid **4**. Unexpectedly, X-ray diffraction analysis showed that **4** was a novel digermylene-stabilized boroxine [(L^{1}GeOBO)$_2$O]BMes (Fig. 6). In the molecular structure of **4**, two Ge^{II} atoms are linked through a B$_3$O$_3$ six-membered ring, which is different from that seen in **2**. The average bond lengths of B−O [1.363 Å] and Ge−O [1.881 Å] are slightly longer than those in **2**. In the ^{1}H and ^{13}C NMR spectra, only one set of signals was observed, providing that the two capped Ge(II) moieties were equivalent. The ligand backbone γ-C*H* of **4** displayed a singlet at 4.86 ppm in the ^{1}H NMR spectrum, while in the ^{11}B NMR spectrum, it showed a broad peak at 18.4 ppm, which is close to other boroxine compounds.[4-7,19] Compound **4**, which features two Ge^{II} atoms linked by a boroxine ring, represents a new type of digermylene. Similarly, the digermylene groups of **4** can decrease the Lewis acidic property of the B$_3$O$_3$ ring (See ESI for details).

Conclusions

In summary, we report the unprecedented reactivity of the N-heterocyclic ylide-like germylene **1** towards B-OH compounds. The reaction of **1** with PhB(OH)$_2$ leads to the unexpected digermylene-stablized linear tetraboronate (B$_4$O$_5$ chain), which represents a new class of boronate chain tetramer that has not yet been reported. The reaction of **1** and Mes$_2$BOH produced another unexpected digermylene-stablized boroxine (B$_3$O$_3$ ring), which is the first example of boroxine-linked heavier carbene analogue. Furthermore, the formation of a mono 1,4-addition product **3** indicates that the steric hindrance of the substituent group changes the self-assembly behavior of boronic acids. The Ge^{II} center as well as the active OH group may make compound **3** a promising precursor of Ge^{II} ligands in catalysis.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental procedure, Crystallographic tables, characterization and computational details, CIF files. See DOI: 10.1039/c000000x/

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