Synthesis and Characterization of Organoboryl Germanium(II) Oxides Containing Ge–O–B and Ge–O–B–O–Ge Cores[①]

ZHANG De-Xiang[a]   LI Yao[a]   PENG Lan-Xin[a]

LI Hai-Pu[a, b]   YANG Ying[a②]

[a] (*School of Chemistry and Chemical Engineering, Central South University, Changsha* 410083, *China*)

[b] (*Key Laboratory of Hunan Province for Water Environment and*

Agriculture Product Safety, Changsha 410083, *China*)

ABSTRACT   Organoboryl germanium(II) oxides were synthesized from the 1,4-addition reaction of L′Ge (L′ = HC[C(CH$_2$)N(Ar)]C(Me)N(Ar), Ar = 2,6-iPr$_2$C$_6$H$_3$) with selected monosubstituted arylboronic acids RB(OH)$_2$ (R = 2,6-Me$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$, 1-Naph) at the molar ratios of 1:1 and 2:1. The mononuclear products RB(OH)OGeL (L = CH[C(Me)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$; R = 2,6-Me$_2$C$_6$H$_3$ (**1**), 2,4,6-Me$_3$C$_6$H$_2$ (**2**), 1-Naph (**3**)) containing the Ge–O–B core were obtained smoothly through the 1:1 reaction. However, the reaction of L′Ge with 2,6-Me$_2$C$_6$H$_3$B(OH)$_2$ in a 2:1 ratio gave only the mononuclear product (**1**) instead of the expected binuclear one. What's more, a new borate compound [(2,6-Me$_2$C$_6$H$_3$)$_4$B$_5$O$_6$]$^-$[H:C]$^+$ (**4**) (:C = C[N(iPr)C(Me)]$_2$) was concomitantly formed when the *in situ* prepared L′Ge was used as the precursor. In contrast, the use of 2,4,6-Me$_3$C$_6$H$_2$B(OH)$_2$ or 1-NaphB(OH)$_2$ as the organoboryl source in the similar reaction led to the formation and isolation of the binuclear products RB(OGeL)$_2$ (R = 2,4,6-Me$_3$C$_6$H$_2$ (**5**), 1-Naph (**6**)) containing the Ge–O–B–O–Ge core in a straight way. Compounds **1**～**6** were determined by single-crystal X-ray diffraction analysis.

Keywords: organic boronic acid, germylene, synthesis, crystal structure;

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1   INTRODUCTION

Organic boronic acids RB(OH)$_2$ are common organic reagents used in laboratories and industry and have found extensive application in the fields of medicine[1], biology[2, 3], materials[4, 5], and organic chemistry[6] for the preparation of organic intermediates or final products[7-9]. The complexes that contain the arylboronate ligand (RB(OH)O) from the reaction of arylboronic acid RB(OH)$_2$ with organometallic precursors can be employed to understand the crucial step in synthetic organic reactions such as the cross-coupling and 1,4-addition reactions catalyzed by those metals[10, 11]. In addition, arylboronic acids RB(OH)$_2$ were also utilized as a boron-oxygen ligand to construct the bimetallic zirconium heterocycles for the possible cocatalyst in olefin polymeri-zation[12] due to their latent Lewis acidity. Considering the availability of organic boronic acids for constructing B–O–M compounds and the convenience of germylenes for

constructing the interesting heterometallic systems[13-16], we propose to prepare the mono- and binuclear germylenes supported by organoboryl ligands.

Compared with the multi-step synthetic procedure for binuclear germylenes by the salt metathesis reaction or elimination reaction[17, 18], the route via the N-heterocyclic ylide-like germylene L′Ge (L′ = HC[C(CH$_2$)NAr]CMeNAr, Ar = 2,6-iPr$_2$C$_6$H$_3$)[19], which was capable of activating O–H[20, 21], COO–H[20], N–H[22, 23], and P–H[24, 25], seems more convenient and attractive. The construction of compounds containing the B–O–Ge(II) linkage is rarely reported[26-29] and their formation and factors are not well known. Wu et. al.[29] used phenylboronic acid PhB(OH)$_2$ to react with L′Ge to afford the unexpected digermylene [LGe(OBPh)$_2$]$_2$O (L = CH[C(Me)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) bearing the B$_4$O$_5$ chain core, which separated the two Ge(II) atoms too far, while the treatment of 2-Ph-C$_6$H$_4$B(OH)$_2$ with L′Ge only afforded the mononuclear 2-Ph-C$_6$H$_4$B(OH)OGeL of the 1:1 composition

as the sole product. However, the stoichiometric reaction of organic boronic acids $RB(OH)_2$ with L′Ge to produce mono- and binuclear germylenes neatly containing the G–O–B and Ge–O–B–O–Ge cores seems elusive. Thus, in this article, we report on the exploration of the reaction of arylboronic acids $RB(OH)_2$ (R = 4-Ph-C_6H_4, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, and 1-Naph) with L′Ge at the ratio of 1:1 or 2:1 for preparing the title compounds.

2 EXPERIMENTAL

2.1 General operation

All manipulations were carried out in a standard Schlenk technology in a dry argon atmosphere or in the glovebox with oxygen content less than 0.1 ppm. Solvents needed for synthetic reaction in the laboratory were pre-dried with 4A molecular sieve for 3 days, then added with appropriate Na/K alloy and benzophenone, heated and refluxed to make the solvents dark blue or purple. After evaporation, the solvents were stored in anhydrous and oxygen-free solvent bottles in the argon atmosphere for reserve. Compound L′Ge was prepared based on the literature procedure[19]. Other reagents involved in this article were purchased from Aladdin without special instructions.

The melting point of obtained compounds was measured on a digital display micro melting point meter (X-4B+). Infrared spectra were recorded by using KBr pellets with a NEXUS670 (Thermo Fisher Scientific) FT-IR spectrometer. The ^{1}H, ^{11}B, and ^{13}C NMR spectra were measured on a Bruker Advance II 400 MHz NMR instrument at ambient temperature. Elemental analyses for carbon, hydrogen, and nitrogen were performed with a Thermo Quest Italia SPA EA1110 instrument.

2.2 General procedure for the synthesis of B–O–Ge(II) compounds

A solution of the selected arylboronic acids (1 mol or 0.5 mol equiv in 5 mL toluene) was added to the toluene solution of L′Ge (20 mL) at –78 ℃ under vigorous stirring. After slowly warming to room temperature, the mixture was further stirred for 12 h, followed by filtration and evaporation for the product.

2.3 4-Ph-C_6H_4B(OH)OGeL (1′)

The 4-Ph-C_6H_4B(OH)$_2$ (0.198 g, 1 mmol) and L′Ge (0.489 g, 1 mmol) were used for the synthesis of 1′. Yield: 60%. m.p.: 237.5～241.3 ℃. FT-IR (cm^{-1}): ṽ = 3475 (w), 3020 (vw), 2961 (m), 2864 (vw), 1602 (m), 1552 (m), 1382 (vs), 1322 (s), 1263 (vs), 1178 (m), 1114 (m), 1008 (m), 928 (vw), 843 (w), 801

(w), 763 (m), 741 (m), 698 (m), 652 (vw), 579 (vw). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 5.41 (s, 1H, γ-C*H*), 4.25 (s, 1H, O*H*), 3.42～3.23 (sept, *J* = 13.6, 6.8, 2H, C*H*Me$_2$), 3.18～3.07 (sept, *J* = 13.6, 6.8, 2H, C*H*Me$_2$), 2.05 (s, 6H, C*Me*), 1.26 (d, *J* = 3.7, 6H, CH*Me$_2$*), 1.16 (d, *J* = 6.8, 6H, CH*Me$_2$*), 1.12 (d, *J* = 4.7, 6H, CH*Me$_2$*), 0.96 (d, *J* = 6.7, 6H, CH*Me$_2$*). ^{11}B NMR (128 MHz, C_6D_6, 298 K, ppm): δ = 1.33. ^{13}C NMR (101 MHz, C_6D_6, 298 K, ppm): δ = 166.66, 163.78, 161.90, 145.45, 142.34, 141.96, 140.91, 139.44, 137.80, 135.08, 134.84, 131.55, 127.87, 127.83, 127.70, 125.49, 125.29, 124.04, 123.00, 99.19 (γ-*C*), 28.20, 27.00, 25.92, 23.63, 23.39, 22.85 (C*Me*), 22.19, 20.85. Anal. Calcd. for $C_{41}H_{51}BGeN_2O_2$ (687.31): C, 71.65; H, 7.48; N, 4.08%. Found C, 71.49; H, 7.68; N, 4.26%.

2.4 2,6-$Me_2C_6H_3$B(OH)OGeL (1)

The 2,6-$Me_3C_6H_3$B(OH)$_2$ (0.153 g, 1 mmol) and L′Ge (0.489 g, 1 mmol) were used for the synthesis of 1. Yield: 66%. m.p.: 207.7～210.4 ℃. FT-IR (cm^{-1}): ṽ = 3540 (m), 3052 (vw), 2958 (s), 2869 (w), 1619 (vw), 1554 (w), 1519 (w), 1436 (m), 1372 (s), 1318 (m), 1251 (m), 1174 (vw), 1059 (vw), 1015 (w), 851 (vw), 788 (w), 762 (w), 722 (vw), 695 (vw), 669 (vw). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 6.81 (d, *J* = 7.5, 2H, Ph-*H*), 4.68 (s, 1H, γ-C*H*), 3.85 (sept, *J* = 13.6, 6.8, 2H, C*H*Me$_2$), 3.39 (s, 1H, O*H*), 3.19 (sept, *J* = 13.5, 6.8, 2H, C*H*Me$_2$), 1.67 (s, 6H, C*Me*), 1.54 (d, *J* = 6.7, 6H, C*Me*), 1.50 (s, 6H, CH*Me$_2$*), 1.16 (d, *J* = 6.8, 12H, CH*Me$_2$*), 1.07 (d, *J* = 6.8, 6H, CH*Me$_2$*). ^{11}B NMR (128 MHz, C_6D_6, 298 K, ppm): δ = 31.38. ^{13}C NMR (101 MHz, C_6D_6, 298 K, ppm): δ = 162.80, 160.35, 145.10, 143.17, 141.62, 138.09, 137.93, 128.14, 126.28, 124.73, 124.50, 123.67, 123.58, 122.42, 94.80 (γ-*C*), 27.68, 27.49, 27.47, 24.87, 23.87, 23.60, 23.54, 23.31 (C*Me*), 22.25, 21.59, 20.65, 19.60. Anal. Calcd. for $C_{37}H_{51}BGeN_2O_2$ (639.27): C, 69.52; H, 8.04; N, 4.38%. Found: C, 69.12; H, 8.04; N, 4.24%.

2.5 2,4,6-$Me_3C_6H_2$B(OH)OGeL (2)

The 2,4,6-$Me_3C_6H_2$B(OH)$_2$ (0.164 g, 1 mmol) and L′Ge (0.489 g, 1 mmol) were used for the synthesis of 2. Yield: 71%. m.p.: 214.7～215.9 ℃. FT-IR (cm^{-1}): ṽ = 3551 (w), 2961 (s), 2923 (w), 2863 (vw), 1607 (vw), 1564 (w), 1518 (w), 1463 (w), 1437 (m), 1378 (s), 1348 (m), 1319 (s), 1259 (w), 1174 (vw), 1098 (vw), 1055 (vw), 1017 (vw), 851 (vw), 801 (w). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 6.65 (s, 2H, Ph-*H*), 4.71 (s, 1H, γ-C*H*), 3.85 (sept, *J* = 13.6, 6.8, 2H, C*H*Me$_2$), 3.42 (s, 1H, O*H*), 3.21 (sept, *J* = 13.6, 6.8, 2H, C*H*Me$_2$), 2.10 (d, *J* = 5.3, 6H, C*Me*), 1.73 (s, 6H, C*Me*), 1.54 (s, 3H, C*Me*), 1.52 (s, 6H, CH*Me$_2$*), 1.23～1.15 (m, 12H, CH*Me$_2$*), 1.07 (d, *J* = 6.8, 6H,

CHMe_2). ^{11}B NMR (128MHz, C_6D_6, 298 K, ppm): δ = 31.61. ^{13}C NMR (101 MHz, C_6D_6, 298 K, ppm): δ = 162.80, 145.11, 143.17, 138.21, 135.46, 126.27, 125.79, 123.67, 123.52, 94.91 (γ-*C*), 27.70, 27.48, 24.90, 23.84, 23.70, 23.53, 21.63 (C*Me*), 20.67, 20.17. Anal. Calcd. for $C_{38}H_{53}BGeN_2O_2$ (653.29): C, 69.86; H, 8.18; N, 4.29%. Found: C, 69.93; H, 8.02; N, 4.15%.

2. 6 1-NaphB(OH)OGeL (3)

The 1-NaphB(OH)$_2$ (0.172 g, 1 mmol) and L′Ge (0.489 g, 1 mmol) were used for the synthesis of **3**. Yield: 77%. m.p.: 223.1～225.6 ℃. FT-IR (cm^{-1}): $\tilde{\nu}$ = 3437 (w), 2961 (s), 2668 (m), 1624 (m), 1552 (s), 1454 (m), 1437 (m), 1378 (s), 1319 (m), 1267 (s), 1093 (vs), 1021 (s), 932 (vw), 847 (vw), 796 (s), 754 (w), 699 (w), 554 (vw). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 9.68 (d, J = 8.6, 1H, Naph-*H*), 8.42 (d, J = 6.8, 1H, Naph-*H*), 7.75 (dd, J = 13.0, 8.2, 2H, Naph-*H*), 7.48 (t, J = 7.5, 1H, Naph-*H*), 7.42～7.31 (m, 2H, Naph-*H*), 5.22 (s, 1H, γ-C*H*), 4.38 (s, 1H, -O*H*), 3.70～3.51 (sept, J = 13.6, 6.8 2H, C*H*Me$_2$), 3.28 (sept, J = 13.6, 6.8, 2H, C*H*Me$_2$), 1.62 (s, 6H, C*Me*), 1.31 (d, J = 6.8, 6H, CH*Me$_2$*), 1.09 (dd, J = 9.8, 6.9, 12H, CH*Me$_2$*), 0.92 (d, J = 6.8, 6H, CH*Me$_2$*). ^{11}B NMR (128MHz, C_6D_6, 298 K, ppm): δ = 29.60. ^{13}C NMR (101 MHz, C_6D_6, 298 K, ppm): δ = 160.35, 142.34, 141.63, 140.10, 139.40, 127.10, 126.86, 126.74, 126.62, 124.68, 122.42, 93.12 (γ-*C*), 27.47, 23.31, 22.25, 19.60 (C*Me*). Anal. Calcd. for $C_{39}H_{49}BGeN_2O_2$ (661.27): C, 70.84; H, 7.47; N, 4.24%. Found: C, 70.65; H, 7.34; N, 4.43%.

2. 7 2,4,6-Me$_3$C$_6$H$_2$B(OGeL)$_2$ (5)

The 2,4,6-Me$_3$C$_6$H$_2$B(OH)$_2$ (0.172 g, 1 mmol) and L′Ge (0.987 g, 2 mmol) were used for the synthesis of **5**. Yield: 65%. m.p.: 262.7～264.8 ℃. FT-IR (cm^{-1}): $\tilde{\nu}$ = 3059 (w), 2957 (vs), 2859 (m), 1526 (vs), 1437 (s), 1390 (vs), 1276 (s), 1225 (s), 1166 (m), 1098 (m), 1055 (m), 1021 (m), 940 (w), 847 (m), 784 (s), 754 (m), 724 (w), 677 (w), 613 (vw), 563 (w). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 5.52 (s, 1H, Ph-*H*), 5.14 (s, 1H, Ph-H), 4.79 (s, 2H, γ-C*H*), 3.46 (sept, J = 13.1, 6.4, 2H, C*H*Me$_2$), 3.36-3.29 (sept, J = 13.1, 6.4 2H, C*H*Me$_2$), 3.18 (sept, J = 13.4, 6.7, 2H, C*H*Me$_2$), 3.07 (sept, J = 13.7, 6.8, 2H, C*H*Me$_2$), 2.11 (s, 12H, C*Me*), 1.60 (s, 6H, C*Me*), 1.50 (s, 15H, CH*Me*), 1.09 (dd, J = 6.7, 3.7, 16H, CH*Me*), 1.03 (d, J = 6.8,

5H, CH*Me*), 0.89 (s, 16H, C*Me*), 0.61 (s, 8H, C*Me*). ^{11}B NMR (128 MHz, C_6D_6, 298 K, ppm): δ = 34.28. ^{13}C NMR (101 MHz, C_6D_6, 298 K, ppm): δ = 163.99, 160.78, 145.44, 144.51, 142.11, 142.06, 135.64, 128.57, 126.31, 125.11, 124.93, 124.38, 123.09, 122.88, 95.90 (γ-*C*), 31.19, 28.31, 27.90, 27.13, 24.71, 24.51, 24.11, 24.02, 23.73 (C*Me*), 23.62, 22.68, 22.28, 20.67, 20.03. Anal. Calcd. for $C_{67}H_{93}BGe_2N_4O_2$ (1142.58): C, 70.43; H, 8.20; N, 4.90%. Found: C, 70.23; H, 8.13; N, 4.87%.

2. 8 1-NaphB(OGeL)$_2$ (6)

The 1-NaphB(OH)$_2$ (0.172 g, 1 mmol) and L′Ge (0.987 g, 2 mmol) were used for the synthesis of **6**. Yield: 58%. m.p.: 270.4～272.1 ℃. FT-IR (cm^{-1}): $\tilde{\nu}$ = 2961 (s), 2919 (w), 2868 (w), 1556 (m), 1462 (m), 1433 (w), 1385 (s), 1317 (m), 1282 (m), 1255 (w), 1107 (s), 1046 (w), 1017 (w), 932 (vw), 851 (w), 787 (w), 626 (vw). ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 9.82 (d, J = 8.6, 1H, Naph-*H*), 8.51 (d, J = 6.8, 1H, Naph-*H*), 7.81 (t, J = 9.0, 2H, Naph-*H*), 7.58～7.52 (m, 1H, Naph-*H*), 7.42 (dt, J = 19.9, 7.6, 2H, Naph-*H*), 4.91 (s, 2H, γ-C*H*), 3.57 (sept, J = 13.6, 6.7 4H, C*H*Me$_2$), 3.16 (sept, J = 13.6, 6.7, 4H, C*H*Me$_2$), 1.50 (s, 12H, C*Me*), 1.16 (d, J = 6.0, 12H, CH*Me$_2$*), 1.10 (d, J = 6.8, 12H, CH*Me$_2$*), 0.93 (d, J = 14.6, 12H, CH*Me$_2$*), 0.52 (d, J = 14.6, 12H, CH*Me$_2$*). ^{11}B NMR (128 MHz, C_6D_6, 298 K, ppm): δ = 31.60. ^{13}C NMR (101 MHz, C_6D_6, 298 K, ppm) δ = 163.69, 144.90, 142.16, 140.93, 138.08, 135.60, 133.10, 130.25, 128.14, 125.97, 124.50, 124.27, 123.76, 123.56, 123.27, 122.82, 95.78 (γ-*C*), 27.83, 26.83, 24.36, 24.19, 23.55 (C*Me*), 23.27, 22.93. Anal. Calcd. for $C_{68}H_{89}BGe_2N_4O_2$ (1150.56): C, 70.99; H, 7.80; N, 4.87%. Found: C, 70.66; H, 7.72; N, 4.68%.

2. 9 Structure determination and refinement

Crystals of **1**～**6** suitable for X-ray diffraction were obtained from the concentrated toluene solutions at –20 ℃. The crystallographic data were measured on a Bruker SMART APEX II CCD single crystal diffractometer and were refined by SHELXL[30], and all non-proton coordinate values and anisotropic temperature factors were refined by the full-matrix least-squares method. All proton positions in the structure were determined by theoretical calculation.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) of Complexes 1～3 and 5

Compounds	1	2	3	5
Bond	Dist.	Dist.	Dist.	Dist.
Ge(1)–N(1)	2.015(1)	1.999(6)	1.987(1)	2.020(6)
Ge(1)–N(2)	2.011(1)	2.041(6)	1.975(1)	2.056(5)
Ge(1)–O(1)	1.848(1)	1.853(5)	1.852(2)	1.849(5)

To be continued

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B(1)–O(1)	1.339(2)	1.34(1)	1.345(3)	1.336(3)
B(1)–O(2)	1.380(2)	1.38(1)	1.366(3)	1.336(3)
Angle	(°)	(°)	(°)	(°)
O(1)–B(1)–O(2)	115.6(2)	116.2(8)	125.3(2)	129.0
N(1)–Ge(1)–O(1)	94.31(5)	94.1(1)	92.03(6)	97.2(2)
N(2)–Ge(1)–O(1)	93.47(5)	95.5(2)	93.42(6)	94.1(2)
Ge(1)–O(1)–B(1)	125.5(1)	124.2(5)	135.9(1)	130.5

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) of 4

Bond	Dist.	Angle	(°)
B(1)–O(1)	1.475	O(1)–B(1)–O(2)	111.1
B(2)–O(1)	1.320(5)	O(1)–B(2)–O(3)	120.7(3)
B(3)–O(2)	1.333(4)	O(2)–B(3)–O(3)	119.6(3)

3 RESULTS AND DISCUSSION

The previous report[29] that produced the digermylene [LGe(OBPh)$_2$]$_2$O and mononuclear 2-Ph-C$_6$H$_4$B(OH)OGeL through the reaction of the respective RB(OH)$_2$ (R = Ph, 2-Ph-C$_6$H$_4$) with L′Ge provided us a hint for better understanding the ligand effect by simply varying the substituents (carbon numbers) of R group ranging from Ph to Ph-C$_6$H$_4$. The first attempt was to react 4-Ph-C$_6$H$_4$B(OH)$_2$ with L′Ge at ratios of 1:1 and 2:1. The ^{1}H NMR analysis of the separated product indicated a 1:1 composition of 4-Ph-C$_6$H$_4$B(OH)OGeL (1′), similar to the finding in the case of 2-Ph-C$_6$H$_4$B(OH)$_2$[29]. It is therefore suggested that the six-carbon substituent (2/4-Ph), either at the ortho- or para-position affiliated to the starting phenyl group of PhB(OH)$_2$, might be too bulky to realize the formation of digermylene. Accordingly, we focused on the fewer carbon substituents in the further detailed exploration, including the two-carbon (2,6-Me$_2$C$_6$H$_3$), three-carbon (2,4,6-Me$_3$C$_6$H$_2$), and four carbon (1-Naph) ones (Scheme 1).

The 1:1 reaction of 2,6-Me$_2$C$_6$H$_3$B(OH)$_2$ with L′Ge was carried out straightforward to afford the white solids as the product (**1**, Scheme 1) in moderate yield (66%). The melting point of **1** is 207.7～210.4 ℃, showing good thermal stability. In the FT-IR spectrum, the stretching vibration of O–H bonds appeared at 3540.55 cm^{-1}, due to the single unreacted hydroxyl group of the organic boronic acid in the product.

Ar=2,6-*i*Pr$_2$C$_6$H$_3$

R = (1) (2) (3)
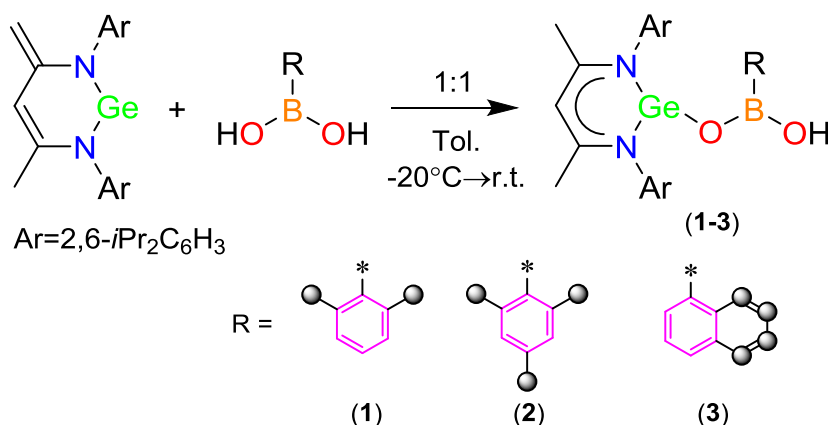
Scheme 1. Syntheses of 1～3

In the ^{1}H NMR spectrum of **1**, the signal of this unreacted hydroxyl proton was observed at δ 3.39 ppm. The singlet at δ 4.68 ppm (γ-C*H*) and the two septets at 3.81～3.88 ppm (methine protons of the isopropyl groups) revealed the typical framework of the β-diketiminate ligand. The comparison of the integration areas of methyl groups between 2,6-Me$_2$C$_6$H$_3$ substituents with those on the backbone of diketiminate ligand confirmed the 1:1 composition of the product **1**. The ^{11}B NMR spectrum of **1** exhibited a broad resonance at δ 31.612 ppm. The recrystallization of **1** in *n*-hexane at room temperature

afforded colorless crystals, which were subjected to single-crystal diffraction X-ray characterization. Compound **1** crystallizes in monoclinic $P2_1/n$ space group. The selected bond lengths and bond angles are listed in Table 1. The molecular structure of 2,6-Me$_2$C$_6$H$_4$B(OH)OGeL (**1**) is depicted in Fig. 1.
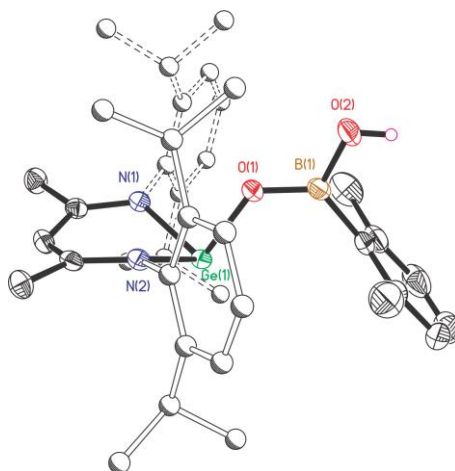

Fig. 1.   Molecular structure of 1. Thermal ellipsoids are drawn at 30% level.
Hydrogen atoms except for the OH group are omitted for clarity

The unit cell contained two molecules of **1**, which shared similar structural parameters and were connected by the single intermolecular hydrogen bond (O–H ··O 2.159 Å) to deliver a formal dimer. Fig. 1 presents one of them. The formation of Ge–O–B linkage was firmly confirmed, where the central Ge atom was coordinated by two N and one O atoms in a distorted tetrahedral environment when considering the lone pairs on it. The six-membered C$_3$N$_2$Ge ring took a twist boat conformation with an angle of 38.86 ° between C$_3$ and N$_2$Ge planes. Interestingly, the lone pairs and the 2,6-Me$_2$C$_6$H$_4$ plane may take the parallel orientation, and the latter played a window awning to partially shade the Ge(II) center. In addition, the 2,6-Me$_2$C$_6$H$_4$ plane is almost perpendicular (88.63 °) to the quasi mirror-symmetric plane (represented by

γ-C–Ge(1)–O(1) plane) of the backbone of the *β*-diketiminate ligand. The bond length of Ge(1)–O(1) (1.848(1) Å) falls in a reasonable range (1.827(2)～1.952(1) Å)[20, 31, 32], and the bond angle of Ge(1)–O(1)–B(1) (125.5(1) °) is close to those in the literature (124.8(6)～127.9(4) °)[29].

The reaction of 2,4,6-Me$_3$C$_6$H$_2$B(OH)$_2$ with L′Ge in the molar ratio of 1:1 led to the isolation of yellow crystalline solids (**2**). The melting point (214.7～215.9 ℃) of **2** is slightly higher than that of **1** (207.7～210.4 ℃). By comparing with those for **1**, the FT-IR and NMR spectra confirmed the successful formation of 2,4,6-Me$_3$C$_6$H$_2$B(OH)OGeL (**2**). Compound **2** crystallizes in monoclinic space group $P2_1/c$, and its molecular structure (Fig. 2) is remarkably similar to that of **1**.
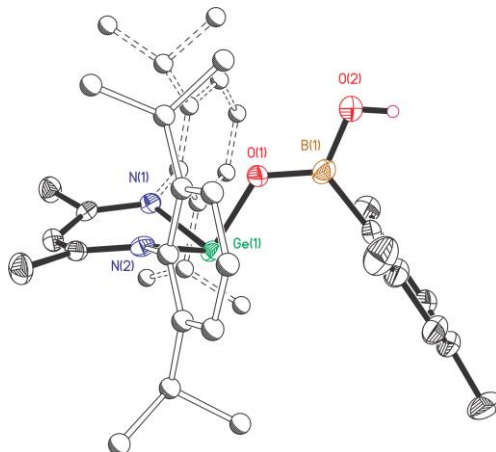

Fig. 2.   Molecular structure of 2. Thermal ellipsoids are drawn at 30% level.
Hydrogen atoms except for the OH group are omitted for clarity

The angle between the C_3 and N_2Ge planes (43.61°) within the six-membered ring C_3N_2Ge is found slightly wider than that of **1** (38.86°), while that between the $2,6-Me_2C_6H_4$ and γ-C–Ge(1)–O(1) planes (87.57°) is a little smaller. This observation is possibly brought by the increased bulky hindrance from $2,6-Me_2C_6H_3$ to $2,4,6-Me_3C_6H_2$ substituents. The bond angle of B–O–Ge (124.2(5)°) of **2** is comparable to that of **1** (125.5(1)°). There was no intermolecular hydrogen bonding formed in **2**, which might be related to the presence of solvent molecules in the unit cell.

The treatment of $1-NaphB(OH)_2$ with one equivalent of L′Ge in toluene gave a solid product (**3**) with relatively high melting point (223.1～225.6 ℃) when compared with those of **1** (207.7～210.4 ℃) and **2** (214.7～215.9 ℃). The formation of $1-NaphB(OH)OGeL$ (**3**) in a 1:1 composition was further justified by FT-IR and NMR characterizations. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ (Fig. 3). The neighboring two molecules were fused via the intermolecular hydrogen bond (O–H···O, 2.059 Å), similar to the case in **1**.
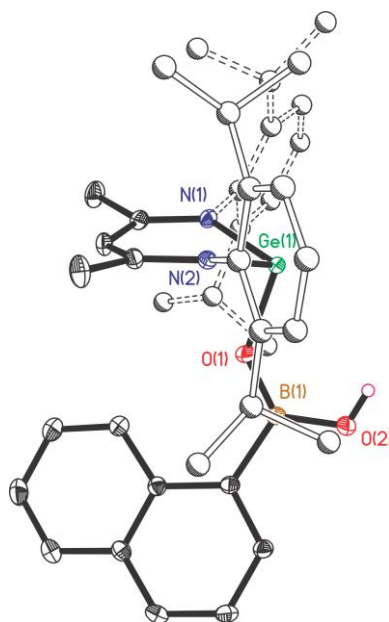

Fig. 3.   Molecular structure of 3. Thermal ellipsoids are drawn at 30% level.
Other hydrogen atoms except for the OH group are omitted for clarity

One striking structural feature in **3** is the nearly opposite orientation of the R group (1-Naph) relative to the lone pair direction. The angle between the 1-Naph and γ-C–Ge(1)–O(1) planes is as narrow as 30.27°, that is to say, the R group does not play as a window awning shielding the lone pair in this case; instead, it looks more like a fore-and-aft sail mounted on the upturned C_3N_2Ge boat. In this view, the structure of **3** resembles much more to that of $2-Ph-C_6H_4B(OH)OGeL$[29], except for the difference that the 1-Naph group is directed to the boat stern and the $2-Ph-C_6H_4$ group to the bow. The angle between the C_3 and N_2Ge planes (31.67°) is much sharper, while the bond angle of Ge(1)–O(1)–B(1) is greatly wider (135.9(1)°) than those of **1** (124.2(5)°), **2** (125.5(1)°), and $2-Ph-C_6H_4B(OH)OGe$ (126.0(1)°)[29]. Apart from the steric factors, the electronic factor that the naphthyl group can disperse the lone pairs on hydroxyl oxygen through the induction effect may also contribute to the weaker bond

repulsive force and larger bond angle[33].

It can be seen from the above that the R groups of phenyl based $RB(OH)_2$ varying from the two-carbon ($2,6-Me_2C_6H_3$) to three-carbon ($2,4,6-Me_3C_6H_2$) and four-carbon (1-Naph) substituents (Scheme 1), all helping to smoothly realize the formation of organoboryl germanium(II) oxides containing Ge–O–B core (**1**～**3**). Subsequently, these monosubstituted arylboronic acids were used to prepare the digermylene.

The reaction time of L′Ge with $2,6-Me_2C_6H_3B(OH)_2$ at the molar ratio of 2:1 (Scheme 2) was extended to 24 h to ensure the completion. The spectroscopic characterization of the obtained solids showed that it turned out to be the 1:1 product (**1**) instead of the digermylene $2,6-Me_3C_6H_3B(OGeL)_2$ (Scheme 2). Interestingly, in several repeated experiments using the *in situ* generated L′Ge, yellow-green crystals (**4**) slowly grew from the mother liquor during concentration.
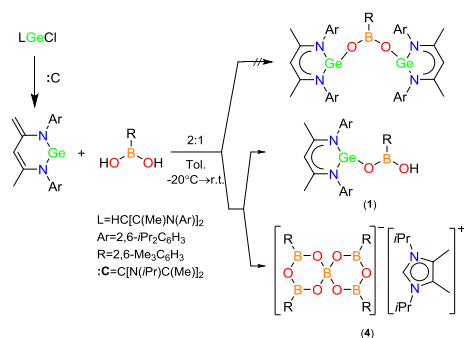
Scheme 2.　Reaction of L′Ge with 2,6-Me$_2$C$_6$H$_3$B(OH)$_2$ at the molar ratio of 2:1

The single-crystal X-ray diffraction analysis revealed that it was a novel borate [(2,6-Me$_2$C$_6$H$_3$)$_4$B$_5$O$_6$]$^-$[H:C]$^+$ (**4**, Scheme 2) (:C = C[N(*i*Pr)C(Me)]$_2$). Compound **4** crystallizes in the orthorhombic space group *P*4$_3$2$_1$2. As shown in Fig. 4, in the anionic part, the central B atom shared by two B$_3$O$_3$ six-membered rings was situated in a tetrahedral environment completed by four O atoms, while other B atoms were all three-coordinated. The two B$_3$O$_3$ rings were almost perpendicular to each other (88.85°, estimated by the angle between two O(1)–B(1)–O(2) planes), and each B$_3$O$_3$ ring took a slightly twisted boat conformation.
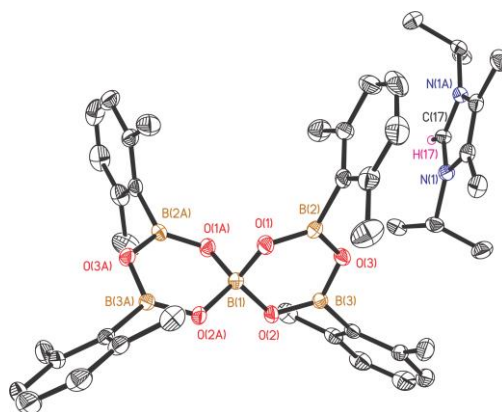

Fig. 4.　Molecular structure of 4. Thermal ellipsoids are drawn at 30% level.
Hydrogen atoms except for [H:C]$^+$ are omitted for clarity

The bond lengths of B(1)–O(1) (1.475 Å) and B(1)–O(2) (1.459 Å) of **4** were comparable to those in other borates [R$_4$B$_5$O$_6$]$^-$[ArMR]$^+$ (R = Ph, 4-CF$_3$C$_6$H$_4$, 4-BrC$_6$H$_4$; Ar = CH-2,6-(CHNMe); M = Sb, Bi) (typically 1.474(9) Å)[34] and [Ar$_4$B$_5$O$_6$]$^-$[Rh(PMe$_3$)$_4$]$^+$ (Ar = 2,6-Me$_2$C$_6$H$_3$)[35]. The formation of **4** might be initiated by the self-polymerization[35] of the arylboronic acid 2,6-Me$_2$C$_6$H$_3$B(OH)$_2$ in the presence of [H:C]$^+$Cl$^-$ or the residual :C during the *in situ* formation of L′Ge. Compound **4** represented a rare borate example of such to contain a metal-free cationic part.

The parallel 2:1 reaction of L′Ge with 2,4,6-Me$_3$C$_6$H$_2$-B(OH)$_2$ led to the separation of **5** (Scheme 3). The melting point of **5** is about 50 ℃ higher than that of **2**.
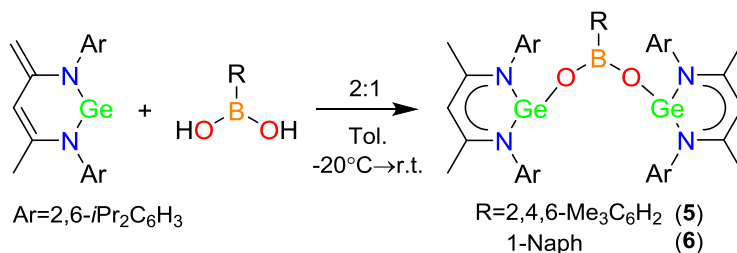
Scheme 3.　Syntheses of 5 and 6

In the FT-IR spectrum of **5**, the absence of O–H vibration absorption band suggested the complete reaction of both hydroxyl groups with L′Ge. This point is further confirmed by ^{1}H NMR characterization, together with the correct integral ratio of protons of naphthyl group and the *β*-diketiminate ligand for the 2:1 composition of organoboryl binuclear

germanium(II) oxide 2,4,6-Me$_3$C$_6$H$_2$B(OGeL)$_2$ (**5**). The ^{11}B NMR spectrum of **5** showed a broad signal at *δ* 34.282 ppm.

Compound **5** crystallizes in the monoclinic space group *C*2/*c*. As depicted in Fig. 5, the two LGe fragments were bridged by the deprotonated 2,4,6-Me$_3$C$_6$H$_2$BO$_2$ ligand.
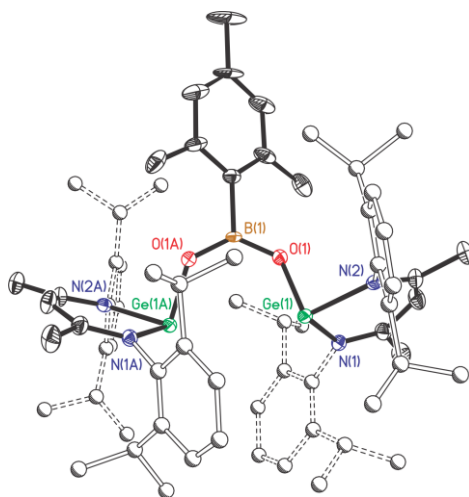

Fig. 5.   Molecular structure of 5. Thermal ellipsoids are drawn at 30% level with the hydrogen atoms omitted for clarity

The length of Ge–O (1.849(5) Å) bond is close to those of **1**～**3** (1.848(1)～1.853(5) Å). The bent Ge–O–B–O–Ge chain took a configuration of letter "n", allowing for the short distance between two Ge(II) atoms (3.682 Å). This is much shorter than those for the reported digermylenes[29] [LGe(OBPh)$_2$]$_2$O (9.555 Å) separated by nine atoms or [(LGeOBO)$_2$O]BMes (6.962 Å) separated by five atoms. The short Ge(II)···Ge(II) separation in **5** may be of benefit to the chelate or synergetic effect in the future assembly of the heterometallic system by germylene donors[36].

The six-membered C$_3$N$_2$Ge ring of the *β*-diketiminate ligand backbone of **5** also took a twisted boat conformation, with an angle between C$_3$ and N$_2$Ge planes of as narrow as 17.79°. However, when compared with that of **2**, the C$_3$N$_2$Ge boat conformation experienced an inversion from **2** to **5**, suggesting a flexible adaption of the *β*-diketiminate ligand by complying with the situation in reaction and crystallization.

The 2:1 reaction of L′Ge with 1-NaphB(OH)$_2$ led to the crop of yellow crystalline solids (**6**). The melting point of **6** is 270.4～272.1 ℃, which is also almost 50 ℃ higher than that of **3**. Spectroscopic characterizations confirmed the formation of digermylene 1-NaphB(OGeL)$_2$ (**6**). The single crystals of **6** were subjected to X-ray structural analysis. Compound **6** crystallizes in monoclinic *I*2/*m* space group (*a* = 13.93, *b* =

18.03, *c* = 14.42 Å; *β* = 103.35°, *V* = 3522.06 Å^3). Although the severe disorder of bridging ligand impeded the further refinement, the expected structural feature can be surely perceived.

4   CONCLUSION

In summary, three monosubstituted arylboronic acids RB(OH)$_2$ (R = 2,6-Me$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$, 1-Naph) were used as the protonation reagent to react with the N-heterocyclic ylide-like germylene L′Ge (L′ = HC[C(CH$_2$)NAr]CMeNAr, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) for the preparation of organoboryl germanium(II) oxides containing Ge–O–B and Ge–O–B–O–Ge cores. The mononuclear product RB(OH)OGeL (L = CH[C(Me)N(Ar)]$_2$; R = 2,6-Me$_2$C$_6$H$_3$ (**1**), 2,4,6-Me$_3$C$_6$H$_2$ (**2**), 1-Naph (**3**)) and the binuclear product RB(OGeL)$_2$ (R = 2,4,6-Me$_3$C$_6$H$_2$ (**5**), 1-Naph (**6**)) were obtained in a straight way. When taking R = Ph as the starting point (zero-carbon modification) and R = 2/4-PhC$_6$H$_4$ (six-carbon modification) as the ending point by combining the literature work, it was suggested that the window for both formation Ge–O–B and Ge–O–B–O–Ge products is relatively narrow, possibly affected by the self-polymerization degree of the arylboronic acids as well as

the steric hindrance of their R groups. The obtained digermylenes can be further employed as donors to construct the heterometallic B–O–Ge→M (M = metal) system for the screen of the promising candidate in catalysis

REFERENCES

(1)   Du, J.; He, M.; Wang, X.; Fan, H.; Wei, Y. Facile preparation of boronic acid-functionalized magnetic nanoparticles with a high capacity and their use in the enrichment of cis-diol-containing compounds from plasma. *Biomed. Chromatogr.* **2015**, 29, 312–320.

(2)   Li, M.; Xu, S. Y.; Gross, A. J.; Hammond, J. L.; Estrela, P.; Weber, J.; Lacina, K.; James, T. D.; Marken, F. Ferrocene-boronic acid-fructose binding based on dual-plate generator-collector voltammetry and square-wave voltammetry. *ChemElectroChem.* **2015**, 2, 867–871.

(3)   Bartelmess, J.; De Luca, E.; Signorelli, A.; Baldrighi, M.; Becce, M.; Brescia, R.; Nardone, V.; Parisini, E.; Echegoyen, L.; Pompa, P. P.; Giordani, S. Boron dipyrromethene (BODIPY) functionalized carbon nano-onions for high resolution cellular imaging. *Nanoscale* **2014**, 6, 13761–13769.

(4)   Sneddon, G.; Greenaway, A.; Yiu, H. H. P. The potential applications of nanoporous materials for the adsorption, separation, and catalytic conversion of carbon dioxide. *Adv. Energy Mater.* **2014**, 4, 1301873.

(5)   Franks, A. T.; Franz, K. J. A prochelator with a modular masking group featuring hydrogen peroxide activation with concurrent fluorescent reporting. *Chem. Commun.* **2014**, 50, 11317–11320.

(6)   Bull, S. D.; Davidson, M. G.; van den Elsen, J. M. H.; Fossey, J. S.; Jenkins, A. T. A.; Jiang, Y. B.; Kubo, Y.; Marken, F.; Sakurai, K.; Zhao, J.; James, T. D. Exploiting the reversible covalent bonding of boronic acids: recognition, sensing, and assembly. *Acc. Chem. Res.* **2013**, 46, 312–326.

(7)   Rodríguez-Cuamatzi, P.; Vargas-Díaz, G.; Höpfl, H. Modification of 2D water that contains hexameric units in chair and boat conformations—a contribution to the structural elucidation of bulk water. *Angew. Chem. Int. Ed.* **2004**, 43, 3041–3044.

(8)   Rodríguez-Cuamatzi, P.; Arillo-Flores, O. I.; Bernal-Uruchurtu, M. I.; Höpfl, H. Theoretical and experimental evaluation of homo- and heterodimeric hydrogen-bonded motifs containing boronic acids, carboxylic acids, and carboxylate anions: application for the generation of highly stable hydrogen-bonded supramolecular systems. *Cryst. Growth Des.* **2005**, 5, 167–175.

(9)   Rodríguez-Cuamatzi, P.; Luna-García, R.; Torres-Huerta, A.; Bernal-Uruchurtu, M. I.; Barba, V.; Höpfl, H. On the organizing role of water molecules in the assembly of boronic acids and 4,4´-bipyridine: 1D, 2D and 3D hydrogen-bonded architectures containing cyclophane-type motifs. *Cryst. Growth Des.* **2009**, 9, 1575–1583.

(10) Pantcheva, I.; Nishihara, Y.; Osakada, K. Arylplatinum complexes with arylboronate ligands. Their preparation, structure, and relevance to transmetalation. *Organometallics* **2005**, 24, 3815–3817.

(11) Zhao, P.; Incarvito, C. D.; Hartwig, J. F. Directly observed transmetalation from boron to rhodium. β-Aryl elimination from Rh(I) arylboronates and diarylborinates. *J. Am. Chem. Soc.* **2007**, 129, 1876–1877.

(12) Balkwill, J. E.; Cole, S. C.; Coles, M. P.; Hitchcock, P. B. Bimetallic zirconium heterocycles supported by boron-oxygen ligands. *Inorg. Chem.* **2002**, 41, 3548–3552.

(13) Yang, Y.; Zhao, N.; Zhu, H.; Roesky, H. Syntheses and reactions of derivatives of (pyrrolylaldiminato)germanium(II) and -aluminum(III). *Organometallics* **2012**, 31, 1958–1964.

(14) Yang, Y.; Zhao, N.; Wu, Y.; Zhu, H.; Roesky, H. Synthesis and characterization of beta-diketiminate germanium(II) compounds. *Inorg. Chem.* **2012**, 51, 2425–2431.

(15) Yang, Y.; Roesky, H. W.; Jones, P. G.; So, C. W.; Zhang, Z. S.; Herbst-Irmer, R.; Ye, H. Q. Synthesis and structural characterization of monomeric heterobimetallic oxides with a Ge(II)–O–M skeleton (M = Yb, Y). *Inorg. Chem.* **2007**, 46, 10860–10863.

(16) Yadav, D.; Kumar Siwatch, R.; Sinhababu, S.; Karwasara, S.; Singh, D.; Rajaraman, G.; Nagendran, S. Digermylene oxide stabilized group 11 metal iodide complexes. *Inorg. Chem.* **2015**, 54, 11067–11076.

(17) Zabula, A. V.; Hahn, F. E.; Pape, T.; Hepp, A. Preparation and coordination chemistry of bidentate benzimidazoline-2-germylenes. *Organometallics* **2007**, 26, 1972–1980.

(18) Dickschat, J. V.; Heitmann, D.; Pape, T.; Hahn, F. E. Synthesis of stable diphenyl-di(germylene) and diphenyl-di(plumbylene). *J. Organomet. Chem.* **2013**, 744, 160–164.

(19) Driess, M.; Yao, S.; Brym, M.; van Wullen, C. A heterofulvene-like germylene with a betain reactivity. *Angew. Chem. Int. Ed.* **2006**, 45, 4349–4352.

(20) Jana, A.; Nekoueishahraki, B.; Roesky, H. W.; Schulzke, C. Stable compounds of composition LGe(II)R (R = OH, PhO, C_6F_5O, $PhCO_2$) prepared by nucleophilic addition reactions. *Organometallics* **2009**, 28, 3763–3766.

ZHANG D. X. *et al.*: Synthesis and Characterization of Organoboryl
Germanium(II) Oxides Containing Ge–O–B and Ge–O–B–O–Ge Cores

No. 6

(21) Wang, W.; Yao, S.; van Wüllen, C.; Driess, M. A cyclopentadienide analogue containing divalent germanium and a heavy cyclobutadiene-like dianion with an unusual Ge_4 core. *J. Am. Chem. Soc.* **2008**, 130, 9640–9641.

(22) Jana, A.; Objartel, I.; Roesky, H. W.; Stalke, D. Cleavage of a N–H bond of ammonia at room temperature by a germylene. *Inorg. Chem.* **2009**, 48, 798–800.

(23) Yao, S.; Zhang, X.; Xiong, Y.; Schwarz, H.; Driess, M. Isomerization of an N-heterocyclic germylene to an azagermabenzen-1-ylidene and its coupling to a unique bis(germylene). *Organometallics* **2010**, 29, 5353–5357.

(24) Harris, L. M.; Tam, E. C. Y.; Cummins, S. J. W.; Coles, M. P.; Fulton, J. R. The reactivity of germanium phosphanides with chalcogens. *Inorg. Chem.* **2017**, 56, 3087–3094.

(25) Wu, Y.; Liu, L.; Su, J.; Yan, K.; Wang, T.; Zhu, J.; Gao, X.; Gao, Y.; Zhao, Y. Reactivity of germylene toward phosphorus-containing compounds: nucleophilic addition and tautomerism. *Inorg. Chem.* **2015**, 54, 4423–4430.

(26) Wu, Y.; Shan, C.; Sun, Y.; Chen, P.; Ying, J.; Zhu, J.; Liu, L.; Zhao, Y. Main group metal-ligand cooperation of N-heterocyclic germylene: an efficient catalyst for hydroboration of carbonyl compounds. *Chem. Commun.* **2016**, 52, 13799–13802.

(27) Loh, Y. K.; Ying, L.; Ángeles Fuentes, M.; Do, D. C. H.; Aldridge, S. An N-heterocyclic boryloxy ligand isoelectronic with N-heterocyclic imines: access to an acyclic dioxysilylene and its heavier congeners. *Angew. Chem. Int. Ed.* **2019**, 58, 4847–4851.

(28) Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. Efficient reduction of carbon dioxide to methanol equivalents catalyzed by two-coordinate amido-germanium(II) and -tin(II) hydride complexes. *ACS Catal.* **2017**, 7, 1853–1859.

(29) Wu, Y.; Liu, L.; Su, J.; Yan, K.; Zhu, J.; Zhao, Y. Synthesis of digermylene-stabilized linear tetraboronate and boroxine. *Chem. Commun.* **2016**, 52, 1582–1585.

(30) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, 71, 3-8.

(31) Ferro, L.; Hitchcock, P. B.; Coles, M. P.; Fulton, J. R. Reactivity of divalent germanium alkoxide complexes is in sharp contrast to the heavier tin and lead analogues. *Inorg. Chem.* **2012**, 51, 1544–1551.

(32) Li, B.; Li, Y.; Zhao, N.; Chen, Y.; Chen, Y.; Fu, G.; Zhu, H.; Ding, Y. Synthesis, structure and a nucleophilic coordination reaction of germanetellurones. *Dalton Trans.* **2014**, 43, 12100–12108.

(33) Xiao, Q.; Tian, L.; Tan, R.; Xia, Y.; Qiu, D.; Zhang, Y.; Wang, J. Transition-metal-free electrophilic amination of arylboroxines. *Org. Lett.* **2012**, 14, 4230–4233.

(34) Dostál, L.; Jambor, R.; Růžička, A.; Jirásko, R.; Lyčka, A.; Beckmann, J.; Ketkov, S. From stiba- and bismaheteroboroxines to N,C,N-chelated diorganoantimony(III) and bismuth(III) cations—an unexpected case of aryl group migration. *Inorg. Chem.* **2015**, 54, 6010–6019.

(35) Nishihara, Y.; Nara, K.; Osakada, K. Tetraarylpentaborates, $[B_5O_6Ar_4]^-$ (Ar = C_6H_4OMe-4, $C_6H_3Me_2$-2,6): their formation from the reaction of arylboronic acids with an aryloxorhodium complex, structure, and chemical properties. *Inorg. Chem.* **2002**, 41, 4090–4092.

(36) Anulewicz-Ostrowska, R.; Luliński, S.; Pindelska, E.; Serwatowski, J. Reactions of hydroxymesitylboranes with metal alkyls: an approach to new sterically hindered (metaloxy)mesitylboranes. *Inorg. Chem.* **2002**, 41, 2525–2528.