



## Synthesis and structural characterization of selected silylated or germylated pyrazoleboronic acids



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### ABSTRACT

A series of 1-alkyl-1*H*-5-*M*-pyrazol-4-ylboronic acids (alkyl = Me or Et, M = SiMe<sub>3</sub>, SiMe<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, SiMe<sub>2</sub>OH, SiPh<sub>2</sub>OH, or GeMe<sub>3</sub>) has been obtained by the sequential lithiation/silylation (or germylation) and lithiation/boronation of the respective 1-alkyl-1*H*-4-bromopyrazoles. The boronic acids containing –SiMe<sub>2</sub>OH or –SiPh<sub>2</sub>OH groups were formed as a result of the Si–H bond activation initiated by the boron Lewis acid centre in the respective intermediates containing –SiMe<sub>2</sub>H or –SiPh<sub>2</sub>H groups. The activation process is facilitated by the presence of water, however, depending on the structure of the starting material, it can lead to the formation of products containing –Si–OH or –Si–O–Si– groups. The boronic acids obtained have been characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and by X-ray crystallography.

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Considerable efforts have been devoted to find new routes for the preparation of various bis-metallic derivatives and for their selective reactions with electrophiles.<sup>1</sup> Boron–*M* (M = Si, Ge) compounds are an interesting subclass of this group because they can serve as the starting materials in various cross-coupling reactions using B–C or Si(Ge)–C(H) reactivity.<sup>2</sup> It has been recently demonstrated that activation of the C–Ge or C–Si bond in rhodium-catalysed annulations of 2-silyl- and 2-germylphenylboronic esters and alkynes furnished benzogermoles and benzosiloles in excellent yields.<sup>3</sup> A possible application of these compounds requires the development of new reactants containing boron and silicon (or germanium) atoms bonded to various organic frameworks. The present work is the result of our interest in the preparation of heterocyclic boronic acids containing silyl or germyl groups. Here, we used pyrazole derivatives where we installed the –B(OH)<sub>2</sub> group at the 4-position and a silicon or germanium atom at the 5-position of pyrazole, respectively. During the reaction, we observed Si–H bond activation in compounds containing –SiMe<sub>2</sub>H or –SiPh<sub>2</sub>H groups 'ortho' to the boron atom. Interestingly, depending on the structure of the reactant, this process can result in hydroxylation of the silicon atom or in the formation of an Si–O–Si bridge.

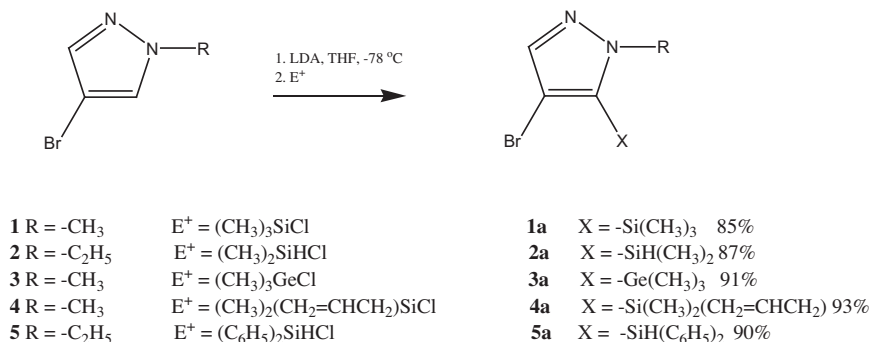
To develop a synthetic procedure for obtaining pyrazole-4-boronic acid derivatives containing a silyl or germyl group at the 5-position, we used a method based on our recent report.<sup>4</sup> We

found that lithiation of 4-bromopyrazole derivatives by LDA in THF at –78 °C gave stable 5-lithiopyrazoles, which could be later reacted with electrophiles affording products substituted at the 5-position. Using this protocol, we lithiated compounds **1** and **2**. The organolithium intermediates obtained were later treated with the respective chlorosilanes or chlorotrimethylgermanium to afford the desired products **1a–5a** in high yields (Scheme 1). In the next step the intermediates **1a–5a** obtained were subjected to Br–Li exchange using *t*-BuLi in diethyl ether at –78 °C. The organolithium derivatives obtained were treated with B(OEt)<sub>3</sub> at –78 °C. Subsequent hydrolytic work-up led to the respective boronic acids (Scheme 2). Reactions with **1a**, **3a** and **4a** furnished boronic acids **1b**, **3b** and **4b** cleanly, leaving the silicon or germanium substituents intact. These compounds are the first examples of pyrazoleboronic acids containing a silicon or germanium atom in the vicinity of the –B(OH)<sub>2</sub> group, and we attempted to determine their crystal structures by X-ray crystallography (Figs. 1–5). The structures of **1b** and **3b** feature a trigonal planar, three-coordinate boron centre with B–C bond lengths of 1.558(2) Å and 1.570(2) Å, respectively. The Si2–C8–C9 angle in **1b** is 129.9(8)° and it is similar to the corresponding Ge1–C1–C2 angle of 130.4(1)° in **3b**. The supramolecular structures of all the crystal structures presented in this work, involving the hydrogen bonding pattern, can be found in the Supporting information.

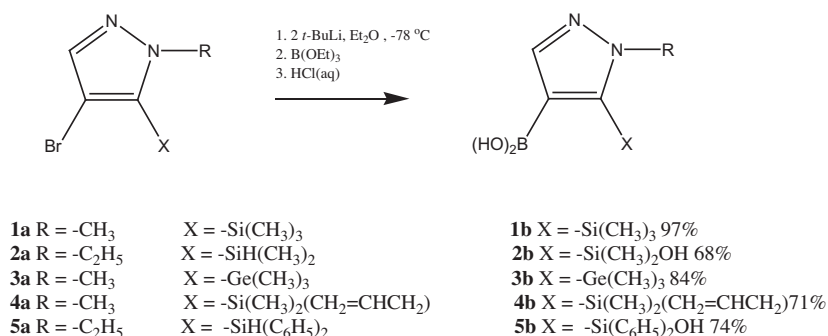
In the cases of **2a** and **5a**, the Si–H bond was cleaved to afford the respective boronic acids **2b** and **5b** containing an Si–OH moiety. The oxidation of silanes to silanols has been studied

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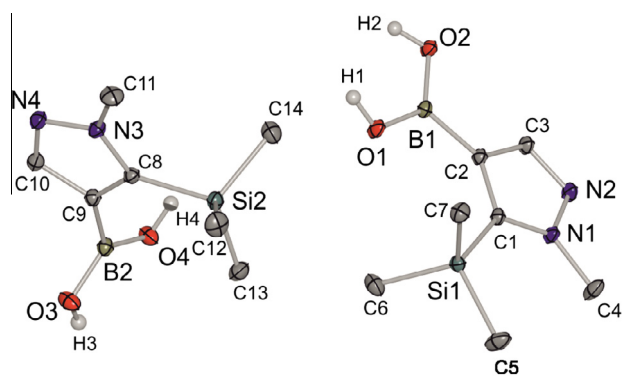
E-mail address: [ktom@ch.pw.edu.pl](mailto:ktom@ch.pw.edu.pl) (T. Kliś).



Scheme 1. Synthesis of the starting materials.



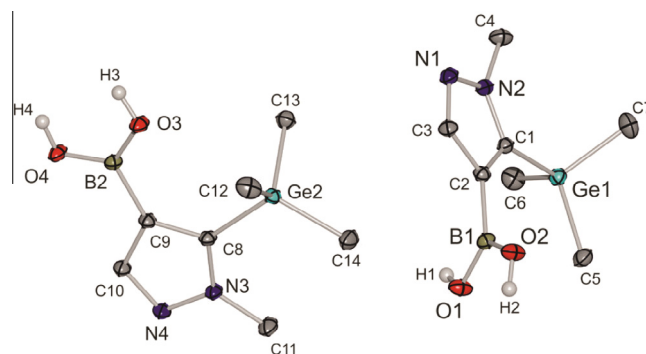
Scheme 2. Synthesis of boronic acids from pyrazole derivatives.



**Figure 1.** Labelling of atoms and estimation of their atomic thermal motion as anisotropy displacement parameters (50% probability level) for **1b** (two independent molecules in the asymmetric part of the unit cell). Selected bond lengths (Å) and angles (°): C2–B 1.558(2), B1–O1 1.356(1), B1–O2 1.378(2), C1–Si1 1.899(1), N1–N2 1.362(1), C9–B2 1.558(2), B2–O3 1.356(1), B2–O4 1.371(1), C8–Si2 1.885(1), N3–N4 1.355(1), C1–C2–B1 131.6(9), C2–C1–Si1 128.6(8), C9–C8–B2 131.9(9), C9–C8–Si2 129.9(8), C1–C2–B1–O1 14.4(2), C8–C9–B2–O3 117.2(1). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number 1025401.

extensively and several methods based on transition metal catalysts and organocatalytic reactions have been developed.<sup>5</sup> However, some new methods involving the use of strong Lewis acids have been described.<sup>6</sup> A general feature of such reactions is the activation of the Si–H bond via formation of a silane-borane adduct  $R_3Si^{\delta+}HB^{\delta-}$  (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Abstraction of the hydrogen atom from silicon and formation of a new Si–O bond has also been observed in the reaction of *o*-(dimesitylboryl)(dimethylsilyl)benzene with alcohols or water.<sup>7</sup> The reaction presented in this work is the first example of Si–H bond activation by organoalkoxyboranes. During the synthesis of **2b** and **5b**, we observed that hydrolysis of the

reaction mixture after addition of B(OEt)<sub>3</sub> resulted in vigorous hydrogen evolution. This fact can be attributed to decomposition of the B–H bond which was previously formed as the result of the hydrogen transfer. The presence of the boron and silicon atoms in the mutual 'ortho' positions suggests that the Si–H bond in **2a** and **5a** undergoes the intramolecular activation. This hypothesis is supported by the fact that the Si–H bond in 4-dimethylsilylphenylboronic acid is stable.<sup>8</sup> In order to gain a deeper insight into the B–H bond formation process we performed the lithiation–boronation of **2a** without hydrolytic work-up. The colourless suspension obtained after addition of B(OEt)<sub>3</sub> to the reaction mixture was filtered off, rinsed with hexane and dried. The dry solid was dissolved in CD<sub>3</sub>CN and the solution obtained was investigated by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectrum recorded at room



**Figure 2.** Labelling of atoms and estimation of their atomic thermal motion as anisotropy displacement parameters (50% probability level) for **3b** (two independent molecules in the asymmetric part of the unit cell). Selected bond lengths (Å) and angles (°): B1–C2 1.570(2), B1–O1 1.372(2), Ge1–C1 1.954(1), B1–C2–C1 131.1(1), Ge1–C1–C2 130.4(1), O1–B1–C2–C1 65.2(2), Ge1–C1–C2–B1 4.4(2). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number 1025403.

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